

Functional Anti-Icing and Anti-Corrosive Composites

by

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To My Mother

*A strong gentle soul who taught me to believe
in hard work and that so much could be done with little*



Abstract

Functional composite coatings consisting of nano- and micro- filler particles are suitable candidates to meet the property and performance requirements in applications ranging from aerospace to biomedical implants. In this thesis work, several novel composites having anti-icing or anti-corrosion functions have been designed and realized. In all composites, silica based porous nano- and/or micro-filler particles were used due to their chemical stability, biocompatibility, easy surface functionalization and easy-to-tailor morphologies. Porous silica based fillers loaded with anti-icing agent or corrosion inhibitor were incorporated either in SBS matrix or in Fe-P electrodeposited films to obtain composite coatings with unique anti-icing or anti-corrosion properties based on either the release of the agents filled into porous silica-based fillers in the SBS matrix or the ability of silica based fillers to anodically polarize the metallic Fe-P matrix.

Mesoporous silica assemblies having different pore structures and morphologies were synthesized by sol-gel method using different types of non-ionic surfactants (polyethylene oxide-based block copolymers) and tetra ethyl orthosilicate (TEOS) precursor in highly acidic region and at room temperature. High specific surface area of 200-600 m²/g was achieved without any heat treatment or aging of the samples at elevated temperature. The morphology of the mesoporous silica assemblies was successfully controlled between spherical particles and monoliths by surfactant/TEOS ratio and acid catalyzer concentration. The spherical silica particles (800-4300 nm in diameter) were composed of primary particles (20-30 nm in diameter) within which cylindrical mesopores were aligned, but the alignment direction of each primary particle was random.

Diatomaceous earth (DE) or mesoporous silica loaded SBS based composites were developed as novel anti-icing agent releasing coatings. 30% by weight silica (DE or mesoporous silica) loaded SBS composites were post filled by keeping the composites in anti-icing agent (EG or PEG) solutions in diethyl ether/acetone binary mixtures. The dissolved anti-icing agents penetrated into the swollen SBS matrix in the binary mixture. Porous silica particles served as the anti-icing agent carrier in the hydrophobic SBS matrix. The amount of anti-icing agent retained in the composite

was increased by increasing the concentration of the anti-icing agent in the binary mixture, which resulted in longer freezing times of water droplets on the composite. The effective anti-icing mechanism was shown to be the release of the anti-icing agent upon contact with water and subsequent decrease of the water freezing temperature. The release of PEG in the inner DE pores was achieved by cutting the composite films into smaller pieces and increasing the water/composite interfacial area. This shows that the developed composites maintain their anti-icing activity for longer times in the presence of scratches and wear. Scratches and wear allow the anti-icing agent filled pores of silica particles buried in the SBS matrix to be exposed to the top surface with the possibility of new anti-icing agents being released when in contact with water.

The similar release mechanism was shown to work for anti-corrosive coatings on metals. Environmentally friendly corrosion inhibitor (Chitosan or PEG) loaded silica-based fillers (DE, mesoporous silica or halloysite nanotubes) embedded in SBS matrix were applied to copper substrates by dip coating method. The anti-corrosion properties of the coatings were electrochemically measured in 0.5 M NaCl solution. Unloaded SBS coating acted as passive barrier by protecting the metal from dissolution. The Tafel plots and cyclic voltammograms clearly showed that the corrosion current density and passive current density of copper coated by the composite were ~63% lower compared to unloaded SBS. The passive current density, the corrosion current density and the extent of pitting corrosion decreased with increasing amount of inhibitor loaded silica-based containers in the composite coatings.

The incorporation of corrosion inhibitor loaded or unloaded silica-based fillers (mesoporous silica particles or halloysite nanotubes) into electrodeposited Fe-P layers was shown to enhance the corrosion resistance of the films. The corrosion rate of Fe-P layers decreased by as much as a factor of 14 from 0.56 mm/year to 0.04 mm/year by incorporating silica-based fillers in the Fe-P matrix.

Özet

Nano ve mikro büyüklükte dolgu parçacıkları içeren işlevsel kompozit kaplamalar, uzay alanından biyomedikal implantlara kadar çok çeşitli uygulamalarda, özellik ve performans gerekliliklerini karşılayabilen uygun aday malzemelerdir. Bu tez çalışmasında, buzlanmayı ve korozyonu önleme işlevine sahip birkaç özgün kompozit malzeme tasarlandı ve gerçekleştirildi. Bütün bu kompozit malzemelerde, kimyasal kararlılığı, biyouyumluluğu, yüzeylerinin kolaylıkla işlevselleştirilebilmesi ve morfolojilerinin kolaylıkla değiştirilebilmesi nedenleriyle silika bazlı gözenekli nano- ve/veya mikro- dolgu parçacıkları kullanıldı. Buzlanmayı önleyici madde veya korozyon inhibitörü ile yüklenmiş gözenekli silika bazlı dolgu malzemeleri, SBS matrisi veya elektrokaplanmış Fe-P filmlerin içine katılarak buzlanmayı veya korozyonu önleme işlevine sahip özgün kompozit kaplamalar elde edildi. Bu işlevler, SBS matrisi içinde gözenekli silika bazlı dolgu malzemelerine doldurulmuş ajanların salımıyla, Fe-P matrisi içinde ise silika bazlı dolgu malzemelerinin Fe-P matrisini anodik olarak polarize etmesiyle sağlandı.

Farklı gözenek yapılarına ve morfolojilerine sahip mezogözenekli silika yapılar, farklı tiplerde iyonik olmayan yüzey aktif maddeler (polietilen oksit bazlı blok kopolimerler) ve tetra etil ortosilikat (TEOS) kullanılarak, yüksek asidik bölgede ve oda sıcaklığında sol-jel yöntemi ile sentezlendi. 200-600 m²/g aralığında yüksek özgül yüzey alanı, herhangi bir ısıtma işlemi veya yüksek sıcaklıkta yaşlandırma olmaksızın elde edildi. Mezogözenekli silika yapıların morfolojileri küresel parçacık ve monolit morfolojileri arasında yüzey aktif madde/TEOS oranı ve asit katalizör konsantrasyonu ayarlanarak başarılı bir şekilde kontrol edildi. Küresel silika parçacıkları (çapları ~ 800-4300 nm), silindirik mezogözeneklerin bir yönde hizalandığı birincil parçacıklardan (çapları ~ 20-30 nm) oluştu, ancak küresel parçacık içindeki her bir birincil parçacığın hizalanma yönü rastgeleydi.

Diatomlu toprak (DE) veya mezogözenekli silika doldurulmuş SBS bazlı kompozitler buzlanma önleyici madde salınımı yapan özgün kaplamalar olarak geliştirildi. Ağırlıkça %30 oranında silika (DE veya mezogözenekli silika) dolgu malzemesi içeren SBS kompozitlerin içine buzlanma önleyici ajanlar, kompozitin

hazırlanması sonrasında dietil eter/aseton ikili karışımı içindeki buzlanma önleyici ajan (EG veya PEG) çözeltisine daldırılması suretiyle dolduruldu. Çözünmüş buzlanma önleyici ajan malzemeler, bu ikili karışım içinde şişmiş halde bulunan SBS matrisi içine nüfuz etti. Gözenekli silika parçacıkları, hidrofobik SBS matrisinde buzlanma önleyici madde taşıyıcısı olarak görev yaptı. Kompozit içinde bulunan buzlanma önleyici madde miktarı, ikili karışımdaki buzlanma önleyici madde konsantrasyonu ile arttırıldı ve bu kompozit üzerindeki su damlacıklarının daha uzun sürede donmasını sağladı. Etki eden buzlanma önleyici mekanizmanın buzlanma önleyici ajanın su ile temasıyla beraber kompozitten salımı ve bunun sonucunda suyun donma sıcaklığının düşmesi olduğu gösterildi. Matris içindeki DE gözeneklerinde yer alan PEG'in salımı, kompozit filmlerin daha küçük parçalara kesilmesi ve su/kompozit arayüzey alanının arttırılmasıyla gerçekleştirildi. Bu aynı zamanda, geliştirilmiş olan kompozitlerin, buzlanma önleyici işlevlerini çizilme ve aşınma durumlarında bile uzun süreler koruyabileceğini göstermektedir. Çizikler ve aşınmalar, gözenekleri buzlanma önleyici madde ile dolu ve SBS matrisi içinde gömülü olan silika parçacıklarının üst yüzeye çıkmasına ve suyla temas etmesine, böylelikle buzlanma önleyici ajanların salımına olanak verir.

Benzer salınım mekanizmasının, metaller üzerindeki korozyon önleyici kaplamalar için de çalıştığı gösterildi. SBS matrisine gömülmüş, çevre dostu korozyon önleyici (Kitosan veya PEG) yüklü silika bazlı dolgu maddeleri (DE, mezogözenekli silika veya haloysit nanotüpler) bakır alt tabakalarına daldırma yöntemiyle uygulandı. Kaplamaların korozyon önleyici özellikleri, 0.5M NaCl çözeltisi içinde elektrokimyasal yöntemlerle ölçüldü. Dolgu malzemesi yüklenmemiş SBS kaplamalar, metali çözünmekten koruyarak pasif bir bariyer görevi görmektedir. Tafel eğrileri ve döngüsel voltamogramlar, kompozitle kaplanan bakırın, korozyon akım yoğunluğunun ve pasif akım yoğunluğunun, dolgu malzemesiyle yüklenmemiş SBS'e kıyasla ~63% daha düşük olduğu netlikle gösterdi. Pasif akım yoğunluğu, korozyon akım yoğunluğu ve çukur oluşturma (pitting) korozyonunun derecesi kompozit kaplamalardaki inhibitör yüklü silika bazlı gözenekli parçacıkların miktarının artmasıyla azaldı.

Elektrokaplanmış Fe-P tabakalarına korozyon inhibitörü yüklenmiş veya yüklenmemiş silika bazlı dolgu maddelerinin (mezogözenekli silika parçacıklar veya

halosit nanot pler) katılmasının, filmlerin korozyona karşı olan diren lerini arttırdığı g zlendi. Fe-P tabakalarında silika bazlı dolgu maddeleri kullanılarak, bu tabakalardaki korozyon hızı, ~14 kat azalarak, 0.56 mm/yıl'dan 0.04 mm/yıl'a kadar d şt .



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Chapter 1: Design of Functional Composites

1.1 Motivation and Objectives

Functional composites are a new generation of materials that exhibit unique physical and functional properties. These are multiphase solid materials where a structural phase is embedded into a continuous phase, with structural phase showing the dimensions in nanometer and micrometer range. The structural phase consists of inorganic particles, fibers, tubes etc. Functional composites provide synergistic properties which can never be obtained by constituent phases alone. The aim of the structural phase is to provide strength and functionality to the composites. The continuous phase binds the inorganic species and improves elasticity and ductility of composites. Depending on the type of continuous phase, functional composites can be classified in three types: (i) polymer matrix composites, (ii) ceramic matrix composites, and (iii) metal matrix composites [1, 2]. Polymer composites are the most used class of composites. The development of ceramic and metal matrix composites is at its earlier stages due to the issues related to the optimization of nano- and micro- filler dispersions in these matrices [3]. Functional composites have potential applications in various fields ranging from aerospace to electronics. Despite their excellent properties, bulk composites have certain issues related to production cost and preservation of nano or micro structures in integrated products.

Functional composite coatings can be used as an alternative to provide the excellent properties of bulk nano/micro composites at relatively low production costs. Functional composite coatings can cover larger surface area with lesser quantity of nano- and micro- materials due to their lower thickness as compared to bulk composites. The composite coatings have thickness values ranging from micrometer to millimeter scale [4]. Functional composite coatings show excellent optical, thermal, mechanical and tribological properties. Depending upon the applications, cost, thickness, purity, desired properties and substrate limitations, composite coatings can be manufactured by various methods. These methods include electroplating, self-assembly, spin coating, chemical vapor deposition, sputtering, dip

coating and spray coating [2, 5]. Due to their lightweight and ease of production, polymeric composite coatings can be coated easily than their ceramic and metallic counterparts.

Polymer composites coatings are composed of a continuous polymeric matrix which is incorporating nanometer and micrometer sized inorganic filler particles. As filler dimensions reach nanometer scale, the interfacial interactions between the phases are enhanced and this results in improved material properties. The effectiveness of nanofillers depends on their shape and surface area to volume ratio. The addition of filler materials to the polymeric matrix imparts them biodegradability, improved mechanical properties, impact resistance, flame retardancy, thermal stability and barrier properties [6]. The common methods used for the synthesis of polymeric composites are solution casting, melt mixing, sol-gel processing, template synthesis and in-situ polymerization methods [7]. Polymer composites are widely used in applications ranging from aerospace engineering applications to biomedical devices, from civil commercial applications to microelectronic and optoelectronic applications [8]. Carbon nanotubes have been most widely used as filler materials to enhance the physical properties of polymeric composites. The high production costs and toxicity of carbon nanotubes have limited their applications [9]. Current research activities on polymer composites aim at enhancing the performance of nanocomposites by controlling the nano- and micro- filler ratio, the molecular interactions between nano/micro fillers and polymeric matrices. The main aim of this work is to synthesize functional polymeric composite coatings for various applications by incorporating low cost, non-toxic and biocompatible nano- and micro- fillers in polymeric matrix. For that purpose, silica-based porous nano- and micro- fillers were incorporated into Poly(styrene-butadiene-styrene) (SBS) polymer matrix. These composite coatings can be easily synthesized at various thicknesses. The possible applications of these polymeric composites as anti-icing and anti-corrosive coatings were investigated. A novel method was introduced to post fill the pores of silica-based fillers in polymeric composite coatings. The composite coatings synthesized in this work can retain their respective functionality even if the coatings are damaged by wear.

Anti-icing coatings have been in great demand in applications such as transmission, shipping, aviation and power generation [10-12]. While superhydrophobic surfaces

with micro/nanometer roughness have been proven to prevent ice nucleation under certain conditions [13, 14], the same roughness is detrimental under pressure [15] and upon physical damage [16]. The drawbacks of textured superhydrophobic surfaces have been eliminated by the slippery liquid-infused surfaces [17-19]. Regardless of all this frosting [20] and longevity [21] are still problems in slippery liquid-infused surfaces. However, to date, there is no systematic study on composite coatings having porous micro- and nano- particles in polymer matrices which can be filled with anti-icing agents. In chapter 3, these polymeric composite coatings for anti-icing applications will be presented and different material systems for preventing ice nucleation will be investigated. We showed that the release of the anti-icing agent from the porous particles upon contact with water decreased the freezing temperature of the water. The approach has the advantage of maintaining the anti-icing agent at the top surface even if the coating is damaged by scratches.

The development of corrosion protection systems for metallic substrates remain an important challenge. There are variety of methods used for corrosion prevention of materials. The most common approaches used for corrosion prevention are active and passive approach. The aim of active corrosion protection system is to influence the corrosion reactions in a manner that corrosion is avoided. It is done by the addition of corrosion inhibitor or developing corrosion resistant alloys etc. Inhibitors are commonly used to prevent the corrosive attack by suppressing the chemical reactions [22-24]. The passive corrosion protection is achieved by depositing anti-corrosion coatings that protect metal surfaces and act as a barrier to inhibit the contact between chemical compounds or corrosive materials [22]. The passive corrosion protection methods include cathodic protection [25, 26], anodic protection [27], coating [28] and alloying. The combination of both approaches can provide long-term corrosion protection to the metallic surfaces [23, 24]. In chapter 4, the corrosion resistant coatings having silica-based nano- and micro- containers filled with inhibitors in polymeric matrix will be discussed. Similar to the anti-icing coating, the protection mechanism of these coatings having porous nano- and micro-particles filled with corrosion inhibitors is based on diffusion of the inhibitor upon contact with the corrosive media to the metal surface. Our results showed that polymer composite coatings prevented or slowed down the corrosion rate of the investigated metal substrates.

Metal matrix composites are composed of a metal or alloy continuous matrix incorporating nano- and micro- sized inorganic particles. These composites possess the properties of both metals and ceramic materials. The addition of inorganic fillers into metallic matrix imparts them excellent toughness, ductility, high shear strength and high service temperature. The common methods used for synthesis of metal matrix composites are vapour deposition, rapid solidification, powder metallurgy, thermal spraying, sputtering and electrochemical deposition. Metal matrix composites have an excellent potential to be used in automotive and aerospace industries. The development of metal matrix composites is still hindered by the issues related to the homogeneous distribution of nano- and micro- particles in metallic matrix. In chapter 4, metal matrix composites synthesized by incorporating porous silica-based particles in iron-phosphorous alloy matrix will be presented. The ability of these metal matrix composites as corrosion resistant coatings was investigated.

Iron plating is preferred for various applications due to its captivating physical properties, abundance and lower cost. The properties of iron can be improved by alloying it with various elements. The addition of phosphorous changes the structure of the deposited alloy. Depending upon the concentration of phosphorus, the alloy can be crystalline or amorphous. The amorphous alloys show better mechanical properties and corrosion resistance than their crystalline counterparts of same concentration [29-31]. The insertion of nano- and micro- particles in iron-phosphorous alloy coating will significantly broaden the usage of these coatings. The inserted nanoparticles will endow these alloy coatings superior wear and corrosion resistance. The addition of inhibitor loaded silica nano- and micro- particles in alloy coatings can further enhance their corrosion resistance [32]. In chapter 4, the corrosion resistant coatings having silica-based fillers loaded with inhibitors in Fe-P alloy matrix will be discussed. The corrosion prevention mechanism of these composites is based on the release of corrosion inhibitor from silica particles upon contact with corrosive media. We showed that the addition of inhibitor loaded silica-based particles prevented or slowed down the corrosion of Fe-P alloy composite films.

The solid nano- and micro- filler materials used in composite materials differ in structure and properties from the matrix material. These fillers are usually inorganic

materials. The nano- and micro- fillers show properties different than the bulk material due to their higher surface area to volume ratio. The most commonly used nanofillers are classified according to their geometry as nanoparticles, nanotubes, nanowires etc. The porous silica-based filler materials were used in this study. Mesoporous silica nanoparticles have great potential in fields of catalysis, sensing and drug delivery due to their unique properties such as biocompatibility, higher surface area, chemical stability, easy surface functionalization, tailor made morphologies and pore sizes [33]. The surface properties of mesoporous silica particles can be altered depending on the reactants used in synthesis. The mesoporous silica nanoparticles can be synthesized by micro emulsion, flame spray pyrolysis, chemical vapor deposition and sol gel methods. However, the low cost, simplicity and ability to control reaction parameters have made sol-gel process as a preferred method for silica synthesis [34]. Sol-gel process has been modified by changing the types of silica precursors, reaction conditions, surfactant templates and drying methods. Many types of ionic (e.g., hexadecyltrimethylammonium bromide (CTAB)) and non-ionic surfactants (e.g., amphiphilic triblock copolymers) have been used for obtaining mesoporous silica with different pore structure and morphological characteristics [35]. However, to date, there is no systematic study on synthesis of mesoporous silica assemblies by combining poloxamer as non-ionic surfactants with tetra orthosilicate (TEOS) precursor in highly acidic region. The mesoporous silica synthesis by mixing poloxamer with TEOS in highly acidic region has several advantages that includes solubility of surfactant enhances due to the presence of polyethylene oxide block, addition of co-solvent is not required to increase the solubility or pore size, and higher concentration of hydrogen ions enhances the reaction kinetics which reduces reaction completion time. In Chapter 2, the synthesis of mesoporous silica particles having spherical to monolith morphology prepared by mixing TEOS and Pluronic F127 in acidic solution will be presented. We showed that the morphology of mesoporous silica particles can be controlled by Pluronic F127 and acid catalyst concentrations. The synthesized mesoporous silica particles were used as nano- and micro- containers in polymeric/metallic matrices.

Following the introduction (Chapter 1), the thesis is further divided into 4 more chapters. In chapter 2, the synthesis of mesoporous silica particles by combining Pluronic F127 with TEOS in acidic solution and the detailed analysis of the factors

affecting the morphology and pore size distribution of mesoporous silica particles are given. In Chapter 3, the preparation of anti-icing composites by incorporating silica-based porous fillers in SBS matrix, the characterization of anti-icing ability of these coatings, and the details of the novel method used for post filling of anti-icing agent in composites are discussed. In chapter 4, the synthesis of both polymeric and metallic matrix based anti-corrosive composite coatings and the characterization of corrosion protection ability of these coatings are given. In chapter 5, this thesis work is comprehensively concluded by emphasizing the novelty of the obtained results and their importance for the future research on and applications of the composite coatings.



Chapter 2: Synthesis of Mesoporous Silica Particles and controlling their Morphologies

2.1 Motivation

Mesoporous silica nanoparticles have great application potential in fields of catalysis, sensing and drug delivery due to their unique properties such as biocompatibility, higher surface area, chemical stability, easy surface functionalization, tailor made morphologies and pore sizes [33]. The properties such as pore size, specific surface area and surface properties can be altered depending on the reactants used in synthesis of mesoporous silica nanoparticles. Mesoporous silica nanoparticles are stable against mechanical stress and chemical degradation due to strong Si-O bond. Mesoporous silica nanoparticles possess better biocompatibility than other inorganic oxides such as titanium oxide and iron oxide [36]. The mesoporous silica nanoparticles can be synthesized with various techniques which includes micro emulsion, flame spray pyrolysis, sol-gel method and chemical vapor deposition. However, the low cost, simplicity and ability to control reaction parameters have made sol-gel process as a preferred method for silica synthesis [34]. Sol-gel process has been modified by changing the types of silica precursors, reaction conditions, surfactant templates and drying methods. Many types of ionic (e.g., hexadecyltrimethylammonium bromide (CTAB)) and non-ionic surfactants (e.g., amphiphilic triblock copolymers) have been used for obtaining mesoporous silica with different pore structure and morphological characteristics [35]. However, to date, the synthesis of mesoporous silica assemblies by combining polyethylene oxide-based block copolymers as non-ionic surfactants with tetra orthosilicate (TEOS) precursor in highly acidic region have not been studied. Exploring the room temperature synthesis of silica from TEOS and non-ionic surfactant mixture at acidic pH can help to design silica structures and gain control over morphology of mesoporous silica. This proposed method has several advantages over ionic surfactant synthesis method in base catalyzed conditions that includes solubility of surfactant enhances due to the presence of polyethylene oxide block, addition of co-solvent is not required to increase the solubility or pore size, and higher concentration of hydrogen ions enhances the reaction kinetics which reduces reaction

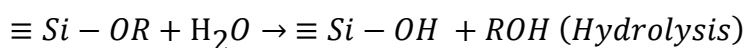
completion time. The mesoporous particles synthesized here will be used as nano- and micro-containers for anti-icing agents and corrosion inhibitors for anti-icing and anti-corrosive composite coatings respectively. The details of anti-icing coatings containing silica particles as anti-icing agent carrier will be discussed in Chapter 3 and the details of anti-corrosive coatings containing silica particles as inhibitor loaded carriers will be explained in Chapter 4.

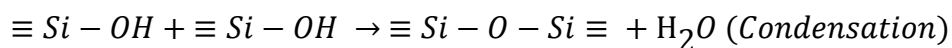
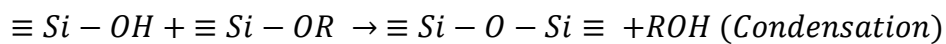
In this work, we intended

- To synthesize mesoporous silica particles and investigate
- To investigate the parameters affecting the morphology and pore size of the mesoporous silica assemblies which includes,
 - The effect of acid concentration at constant surfactant/precursor ratio.
 - The effect of surfactant amount at constant acid and precursor concentration.
 - The effect of various surfactants on the size and specific surface area of pores.
- To investigate the structural stability of mesoporous silica particles.
- To investigate adsorption and release properties of mesoporous silica particles.

2.2 Sol-gel mechanism

Sol gel process is a widely-applied procedure to produce silica assemblies. Sol is a stable solution of colloidal particles and gel is an integrated three-dimensional network of particles surrounding a liquid phase. Sol-gel is a name given to a process in which a solution turns into a three-dimensional gel. Sol-gel mechanism consists of two reactions namely hydrolysis and condensation. Hydrolysis is a reaction in which the addition of water molecule to a chemical substance splits it in two molecules adding -H to one part and -OH to other part. Colloidal particles are produced in hydrolysis reaction. Condensation is a reaction in which two small molecules combine to form a large complex molecule and water or alcohol as by products. The crosslinking through siloxane bond during condensation reaction results in three dimensional gels. Condensation reactions must follow hydrolysis reactions because condensation reaction occurs by releasing alcohol or water molecules.





Sol gel reaction under acidic and basic condition is different. During acidic reaction conditions, the oxygen atom of a $\equiv Si-O$, $\equiv Si-OH$, or $\equiv Si-OR$ group is easily protonated in hydrolysis reaction. Moreover, electron density is withdrawn from the silicon atom. The withdrawal of electron density makes silicon atom electrophilic in nature. This electrophilic silicon can be attacked by water molecules during hydrolysis reaction or by $\equiv Si-OH$ groups during condensation reaction. The rate of hydrolysis and condensation reaction increases with increase in the same order as electron density. During the base catalyzed reaction conditions, the deprotonation of water or a $\equiv Si-OH$ group results in formation of OH^- or $\equiv SiO^-$ group. The nucleophilic attack to silicon either by OH^- during hydrolysis reaction or by $\equiv SiO^-$ during condensation reaction results in reaction process. The rate of hydrolysis and condensation reaction increases in the reverse order as electron density [37]. Fig. 2.2.1 shows the effect of pH on hydrolysis and condensation reactions.

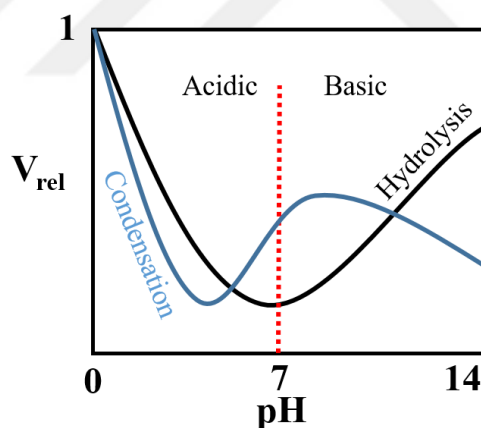


Fig. 2.1 Effect of pH on relative rate of reactions of hydrolysis and condensation [37].

The hydrolysis and condensation reactions are followed by growth and aggregation steps in sol-gel methods. In case of acidic reaction conditions, the reactions at central silicon atoms results in chain like structures. The reactions at terminal silicon atoms result in branched structures under basic reaction conditions.

In strongly acid catalyzed reactions, hydrolysis of silica precursor is very fast, and it forms silanol ($Si(OH)_4$). Similarly, condensation reaction is also very fast and any

two hydroxylated species interact to form siloxane (Si-O-Si) with either water or alcohol as by products. The hydrolysis and polycondensation reactions are started at numerous sites. When sufficient number of siloxanes are present, they interact and form colloidal particles. These clusters linearly linked together due to less solubility of silicon oxide in acidic solution. Amphiphilic block copolymer was used as surface templating agent and as grain growth suppressant. The microphase separation of an amphiphilic block copolymer in water into hydrophilic and hydrophobic domains is the basis of supramolecular templating. The formation of silica particles involves the interaction of silica with amphiphilic block copolymers that facilitates the assembly of silicate micelles. Under strongly acidic conditions, both silica and surfactants carry positive charge. The interaction between silica and surfactant is a double layer hydrogen bonding interaction. They interact through a counter ion which carries negative charge. The presence of this amphiphilic block copolymer micelles covering the nanoparticles also suppress their growth [34, 38]. Removal of templating agent with heat treatment leaves behind mesopores.

2.3 Morphogenesis of mesoporous assemblies

Mesoporous silica nanoparticles have attracted a lot of interest due to their enlarged surface area, uniform porosity and better thermal properties. These properties made mesoporous silica particles potential candidates for a number of applications such as, heterogeneous catalysis, separation process, host guest chemistry, adsorbents for quantum structures, separation of large biological molecules, environmental pollution control, drug delivery [39]. The synthesis of mesoporous silica particles is based upon the combination of inorganic chemistry and self-assembly process, to control the texture of these particles on the nanometer scale [40]. The template-directed synthesis method is the most widely used method for synthesis of mesoporous silica particles [41]. The templates used for mesoporous silica synthesis can be ionic or non-ionic surfactants. The self-assembling ability of these surfactants results in ordered micelles. The pore size of silica structures can be controlled by the size of the surfactants applied during the synthesis process [42]. There is a weak interaction between silica species and surface templating agents. The interaction between non-ionic surfactant and silica species are weak hydrogen bonding interactions but the interaction between ionic surfactant and silica species are electrostatic interactions. These interactions result in nucleation and growth of silica

structures. The surfactants can be removed by heat treatment or etching techniques [43]. Cetyl trimethylammonium chloride or bromide (CTAC or CTAB) are the most widely used ionic surfactants in literature. The isoelectric point of aqueous silica solutions is at pH 2 [44]. The silica particles carry a positive charge below pH 2, so the interactions between surfactant and silica needs a negative counterion. The effect of negative counterions like Cl^- , Br^- on the silica morphology was investigated. This effect is also limited to only CTAB and CTAC [45]. The synthesis using ionic surfactants were carried out under extreme acidic or alkaline conditions. The pore size yielded was around 10-100 Å. The thin walls and smaller pore size are the biggest limitations for the use of ionic surfactants. The only way to enhance the pore size beyond 0.5 nm is by using swelling agents. The use of swelling agents made the synthesis procedure complicated and irreproducible. These limitations were vanquished by using self-assembly characteristics of block copolymer surfactants. The properties of block co-polymers can be tuned by adjusting solvent composition and polymeric architecture [46].

2.3.1 Non-ionic surfactant templates

Non-ionic surfactants are neutral molecules consisting of hydrophilic water soluble and hydrophobic water insoluble parts. The most common non-ionic surfactants are polyethylene oxide-based co-polymers and poloxamers. The hydrophilic parts of these surfactants mostly consist of polyethylene oxide groups. The hydrophilic polyethylene oxide chains result in self-assembled micelles which interact with silica species [47]. These non-ionic surfactants are mostly used because of their low cost, biodegradability and low toxicity.

Pinnavaia et al synthesized mesoporous silica structures under neutral conditions by polyethylene oxide based triblock copolymers and oligomeric surfactants [48, 49]. The worm like silica structures were formed. The pore diameters were 2.4 to 5.8 nm. They used ethanol as cosolvent to improve the thermal stability of silica structures.

Attard et al. have used $\text{C}_{12}\text{EO}_{18}$ and C_{16}EO_8 as non-ionic structure directing agents [50]. They prepared ordered mesoporous structures by using these non-ionic surfactants. The pore size obtained was around 3 nm.

Templin et al. synthesized two mesoporous ceramics by using polyisoprene-polyethylene oxide block copolymers as templates [51]. They used both acidic and

non-aqueous solutions for synthesis. They concluded that the use of high molecular weight copolymers helps in the synthesis of large pore meso-structures.

Fan et al. synthesized cubic mesoporous silica by using Pluronic F127 as templating agent in 2M HCl solution [52]. Potassium chloride and 1,3,5-trimethylbenzene (TMB) were used as additives. The as-synthesized silica particles were calcined at 550 °C for 6 h. The nitrogen adsorption isotherms confirmed that the pores size of those cubic structures was in the range of 4-9 nm.

Chen et al. prepared four different mesoporous structures in Pluronic F127 assembly system in an acidic solution [53]. The structural transformations were induced by adding an anionic co-templating agent and swelling agent in the system. The structural transformations from cubic to hexagonal and then to cubic bi-continuous were achieved by merely adjusting the amount of anionic surfactant in Pluronic F127 system. The pores of 5-12 nm size were obtained. The use of swelling agent enhanced the pores size to 16 nm. The mesoporous synthesis was carried out at 100 °C. They suggested that the use of mixed surfactants would help in synthesis of diverse mesoporous structures.

Kleitz et al. synthesized cage like mesoporous silica structures. The cubic silica structures were obtained by using Pluronic F127 as templating agent [54]. They carried out this synthesis at low acidic concentrations (0.4-0.5 M HCl). They claimed that the use of low acidic concentrations allowed the thermodynamic control of silica-Pluronic F127 self-assembly. The hydrothermal treatment enabled the tailoring of pore diameters at temperatures ranging from 45 °C to 150 °C. The maximum pore diameters were obtained after 130 °C as 9.3 nm.

Han et al. synthesized mesoporous silica particles with various pore structures. Pluronic F127 was used as templating agent and a cationic surfactant was used as growth suppressant [55]. The swelling agent was used to tune the size of the pores. The reaction was carried at pH 1.6-1.8. The weak acidic conditions resulted in slower reaction kinetics. They suggested that the double hydrogen bonding interaction of cationic surfactant with silica species suppressed the growth of silica particles. They obtained 300-500 nm sized particles with pore size between 5-20 nm.

Wang et al. synthesized the mesoporous silica structures with ultrathick walls. The mesoporous silica structures were synthesized by using Brij 700 as structure

templating agents [56]. The effect of hydrothermal treatment was investigated. The results showed that the pore size can be enhanced from 2 to 4 nm by changing the synthesis temperature from 5 °C to 40 °C. They suggested that the specific surface area can be tailored by changing the calcination and hydrothermal treatment temperatures.

Yu et al. synthesized mesoporous silica single crystals by using Pluronic F 108 templating agent [57]. The synthesis was carried out under acidic conditions. The inorganic salts were used to enhance the interaction between silica specie and templating agents. The strong interaction resulted in long range order of silica-Pluronic domains. The pore size obtained was 7.4 nm. The mesoporous silica single crystals have rhombdodecahedron shapes with size of approximately 1 μm . They observed that increasing the synthesis temperature resulted in spherical particles. These spherical particles resulted because the rate of hydrolysis and condensation reactions enhanced due to change in temperature.

Ballem et al. investigated the effect of temperature on the morphology of mesoporous silica particles [58]. The mesoporous silica particles with cubic structures were prepared by using Pluronic F127 as structure directing agent at low acidic concentration (0.2 M). The size of mesoporous silica particles can be tailored between 0.5 – 8 μm by changing the synthesis temperature. They observed the sharp change in particles morphology from larger to smaller ones at 20 °C with increase in synthesis temperature. The change in morphology was attributed to the change in reaction kinetics. The pore size was increased from 3.8 to 4.1 nm by increasing the synthesis temperature.

Cao et al. investigated the effect of synthesis temperature and inorganic salts on the morphology of mesoporous silica structures [59]. The mesoporous silica structures were prepared in acidic solution by using Pluronic F127 as templating agent. The spherical particles were obtained at 25 – 30 °C synthesis temperature. The morphology changed from spherical to decahedral and dodecahedral at 45 °C and to prism like structure at 50 °C. They attributed these morphological changes to condensation reaction. The condensation reaction is controlled thermodynamically or kinetically. They concluded that at low synthesis temperature the condensation reaction is thermodynamically controlled. But in case of higher synthesis temperature, the condensation reaction is kinetically controlled.

Polaxomers are commonly used as structure directing agents for silica synthesis. The addition of salts or co-surfactants influence the mesophase structure by altering the critical micelle concentration. The combination of ionic and non-ionic surfactant can be used to suppress the grain growth of silica species. The morphology and porosity of mesoporous assemblies synthesized by using non-ionic surfactants can be altered by changing the synthesis temperature. However, the room temperature synthesis of mesoporous silica particles under strong acidic condition using only Pluronic F127 as structure directing agent have not been reported in literature yet.

2.3.2 Acid catalyzed synthesis of mesoporous silica structures

Mesoporous silica nanoparticles are usually synthesized in water with the help of hydrolysis and condensation reaction of silicon alkoxide or silicate salts. The rate of hydrolysis and condensation reaction is very slow at room temperature. The reaction rate can be enhanced with the help of catalysts. These catalysts can be acid or base. The hydrolysis and condensation reactions result in silica clusters. These clusters grow and form particles. Metal alkoxides are more soluble in basic medium than acidic medium. The acid catalyzed reactions result in linear clusters while the base catalyzed forms branched clusters [34]. The structure formation under extreme acidic conditions is still not well explored. Moreover, the effect of non-ionic surfactant on the structure formation under highly acidic conditions also needs to be understood.

Boissière et al. synthesized spherical mesoporous silica particles by a newly introduced double step method [60]. The condensation and aggregation steps were separated. The pH of the reaction mixture was between 2-4. The hydrolysis reaction was induced by adding sodium fluoride in the reaction mixture. The mesoporous silica particles of 3-8 μm size were obtained. The nitrogen adsorption isotherms showed the large specific surface area of $910 \text{ m}^2 \text{ g}^{-1}$ and pore size of 2.4 nm.

Zhao et al. prepared mesoporous silica structures with various shapes such as spheres, discoidlike, rope, fiber, gyroid and doughnuts by using cosolvents, cosurfactants and electrolyte solutions [61]. All these morphologies were synthesized in acidic solutions (2-4 M HCl) by using Pluronic P123 as surfactant. Dimethylformamide (DMF) and CTAB were used as cosolvent and cosurfactants respectively. The mean pore size of 8 nm and BET surface area of $710 \text{ m}^2 \text{ g}^{-1}$ was observed for spherical mesoporous silica particles. They concluded that the shape of

mesoporous silica particles depends on the surface energy at the interface of surfactant and inorganic silica species.

Mesa et al. investigated the effect of synthesis temperature and duration, dilution and acidity on the morphology of mesoporous silica [62]. The synthesis of mesoporous silica was carried out with two different methods. The synthesis method depends on one heating cycle and two heating cycle systems. The mesoporous silica particles with spherical structures were synthesized under one heating cycle, low acidity, elevated temperature and low dilution conditions. The spherical particles have mean pore size of 6.5 nm and specific surface area of 947 m² g⁻¹.

Suzuki et al. synthesized hexagonally ordered mesoporous silica nanoparticles by using CTAB as surface templating agent and Pluronic F127 as grain growth suppressant [63]. The hydrolysis reaction was carried out under acidic conditions, but the assembly process was carried out at basic pH. The pH of the synthesis solution was changed by adding ammonia in the reaction mixture. The nanoparticles have size ranging from 20-50 nm and mean pore size of 2 nm. They concluded that the grain growth was suppressed by the presence of Pluronic F127.

Kosuge et al. synthesized rodlike and fiberlike mesoporous silica structures by changing experimental conditions such as shearing force, acid source, reactant ratios and temperature [64]. They used sodium silicate as silica precursor, Pluronic P123 as surface templating agent and various acids solutions were used as solvents. The rodlike structures were synthesized without stirring of the reactant mixtures, while the stirring of reaction mixture with a speed of 400-1000 rpm resulted in fiberlike structures. These fiberlike structures were formed by the coupling of the rods of same length scales. The rodlike structures prepared had the width of 0.5 μm and length of 1-2 μm. The lengths of fiberlike structures were between 130-225 μm. The mean pore size obtained was 4-5 nm.

Haskouri et al. synthesized mesoporous silica structures by modulating reaction time and temperature [65]. They used CTAB as templating agent and TEOS as silica precursor. Nitrilotriethanol was used as hydrolytic agent. The synthesis of mesoporous silica structures was carried out at equalized hydrolysis and condensation reaction rates. The particles synthesized with this method have the pore size of 3.3 nm.

Boonamnuyvitaya et al. synthesized mesoporous silica materials by using CTAB, Brij56 and SDS as surface directing agents [66]. The synthesis was carried out at acidic and basic conditions. The reaction mixtures were aged for 5-7 days at 90 °C. The highest pore size and pore volume was achieved for mesoporous silica particles synthesized at basic pH. They observed that the pore size and volume increased with the amount of surfactants. They attributed this effect to the effect of surfactant on the size and morphology of mesoporous silica materials.

Baute et al. investigated the effect of salts on the morphology of mesoporous silica materials. Sodium nitrate was used as an additive in the reaction mixture and Pluronic P123 as surface templating agent [67]. The addition of salt decreased the solubility of PEO chains of Pluronic which resulted in decreased critical micelle concentration value. They observed that the interrelation between acid concentration and salt quantity had an impact on the final structure of mesoporous silica materials. The particle synthesized by the addition of inorganic salt in the sol-gel system had specific surface area of $565 \text{ m}^2 \text{ g}^{-1}$ and pore size of 10 nm.

Liu et al. synthesized the mesoporous silica from the mixtures of sodium silicate and TEOS in a buffer solution of pH 4.4 [68]. The effect of molar ratio of TEOS and sodium silicate on the pore size was investigated. They observed that TEOS behaved both as swelling agent and silica precursor. The molar ratio of silica precursors successfully tuned the pore size of silicas from 10-16 nm. The maximum pore size was attributed to the slow hydrolysis and condensation reactions. They suggested that ethanol produced during the synthesis process has an effect on the pore size and structure.

Kim et al. synthesized nano-porous silicas by acid decomposition of silicate salts. Sodium silicate was decomposed in 4.76 M sulfuric acid [69]. The decomposed products were washed and aged at pH 4 and pH 9. The particles synthesized by acid decomposition have pores size ranging between 1-15 nm.

Zhou et al. synthesized macroscopic 3D hierarchal mesoporous silica structures. These mesoporous silica structures have intricate pottery like shapes [70]. The synthesis of sodium silicate was carried out in concentrated acid. The helical self-assemblies assisted by nitrate ions in acid solutions resulted in these micro pottery

vessel morphologies. The synthesized mesoporous silicas have ordered pores of 2.6 nm. The specific surface area of these vessels was observed to be 1295 m² g⁻¹.

Yang et al. synthesized mesoporous silica structures with earthworm like morphologies [71]. These silicas were synthesized in strong acidic medium with CTAB as surface templating agent and sodium fluoride as an additive. The fluoride ion played the key role in structure formation of silica. These fluoride ions adsorbed on polar head of CTAB and joined by hydrogen bonding with silica species. They investigated the effect of fluoride to silica ratio, pH and shear rate on the morphology of silica structures. The fluoride to silica ratio of 0.25 molar, shear rate of 550 rpm and pH of 0.06 induced the earthworm like morphology.

In conclusion, the acid catalyzed silica assemblies were synthesized by using non-ionic and ionic surfactants as templating agents. The effect of salt addition, reaction temperature, stirring rate and aging on the morphologies of mesoporous silica assemblies were investigated. The room temperature synthesis of mesoporous silica particles under acidic conditions by using non-ionic surfactant templates have not been reported in literature yet. The room temperature synthesis of silica particles can help to realize a more cost-effective method for synthesis of mesoporous silica.

2.4 Materials, Methods and Techniques

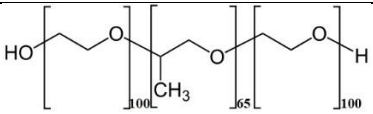
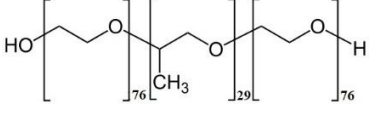
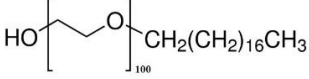
In this section, the materials and methods that were used in synthesis of silica particles will be introduced.

2.4.1 Synthesis of silica structures

2.4.1.1 Materials

The synthesis of silica structures was performed by three different routes. The acidic and basic conditions were used for silica synthesis. Tetraethyl orthosilicate (TEOS) (Mw. 208.33 g/mol) was used as silica precursor, because of its relatively low cost, easy handling and relatively fast hydrolysis. TEOS was purchased from Merck. The amphiphilic block copolymers were used as structure directing agent. The chemical structure and molecular weight of these amphiphilic block copolymers were given in Table 2.1. Pluronic F127 and F68 were used as structure directing medium, because of their good solubility in water, commercial availability and biodegradability. For acidic synthesis, hydrochloric acid of different molarities was used as solvent and purchased from Sigma Aldrich. Ammonia used for basic synthesis conditions was bought from Merck.

Table 2.1 Properties of structure directing agents used in this study with their specifications.

Inhibitor	Molecular weight (g/mol)	Chemical structure	Company
Pluronic F127	12600		Sigma Aldrich
Pluronic F68	8350		Sigma Aldrich
Brij 700	4670		Sigma Aldrich

2.4.1.2 Preparation of silica structures

Sol-gel synthesis of mesoporous and non-porous silica nano- and micro- structures in the presence of non-ionic surfactants was performed under acidic pH and basic pH respectively.

2.4.1.2.1 Synthesis of mesoporous silica structures

Typically, 0.01-0.3 g of Pluronic F127 was dissolved in 1 mL of 10^{-4} - 8 M HCl solution. These solutions were mixed with 200 to 1000 μ L of TEOS. The samples were shaken vigorously for 30 seconds. The resulting viscous mixtures were casted in teflon plates to evaporate solvent and reaction by products for 24 h. The coarse silica monoliths or powders were calcined for 8 h at 450 °C. An array of samples was synthesized with this method by just changing type of surfactant, pH of the solution, the concentration of Pluronic and amount of TEOS.

2.4.1.2.2 Non-porous silica synthesis

The synthesis of non-porous silica was carried under basic conditions. The ethanol-water mixture was prepared by mixing 200 μ L water with 800 μ L of ethanol. 0.01 g of Pluronic F127 was added in 1 mL of ethanol-water mixture. Then 50 μ L each of ammonia (25 wt% in water) and TEOS was added to the solution at once. This reaction mixture was kept on shaker for 2 h. The milk-white as-synthesized material was collected by centrifugation. This material was dried in open air and then calcined at 450 °C for removal of Pluronic F127.

2.4.2 Characterization

2.4.2.1 Scanning Electron Microscope

Field emission scanning electron microscope (ZEISS Ultra Plus SEM) was used to analyze the surface morphology and porosity of silica structures. The secondary electron detector was used to produce the topographic images. The images of silica samples were taken at different magnifications by using accelerating voltage in the range of 3 to 5 kV.

2.4.2.2 Transmission Electron Microscope (TEM)

Transmission electron microscope (JEOL JEM-1400) was used to investigate topographical, compositional and morphological information about ultrathin samples.

We used TEM for investigating the porosity and morphology of the silica structures.

2.4.2.3 Surface Area measurement

Micromeritics ASAP 2020 physisorption instrument was used to measure nitrogen adsorption isotherms of various porous and non-porous silica samples and Brunauer, Emmett and Teller (BET) surface area of these silica structures was calculated. The experimental adsorption data is given in the form of adsorption isotherms with amount of gas adsorbed is plotted against relative pressure. The adsorption isotherms of many gas-solid systems have characteristic shapes and provide valuable preliminary information about the pore structures of the solids. According to IUPAC, the adsorption isotherms can be divided into six types [72]. These six types of adsorption isotherms are shown in Fig. 2.2.

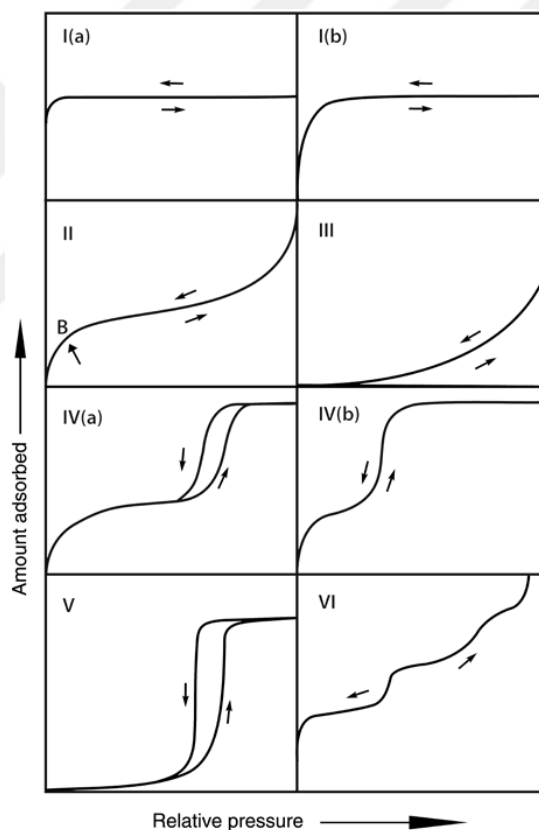


Fig. 2.2 IUPAC classification of adsorption isotherms [72].

Type I isotherms are shown by microporous solids. These isotherms are concave to relative pressure axis. The sharp rise in adsorption values at low pressure is due to the strong solid-gas interactions in narrow micropores. The adsorption amount reaches a limiting value due to the limited amount of accessible micropores. Type Ia is shown by the solids having narrow range of micropores of ~ 1 nm size and Type Ib

is shown by the solids having broader range of micropores and mesopores of $\sim 2.5\text{nm}$ size. Type II isotherm is shown by non-porous or macroporous materials. The adsorption isotherm is concave at lower pressure, linear at middle pressure and convex at higher pressure values. This adsorption isotherm is due to the monolayer and multilayer adsorption of gases on solid materials. Type III isotherm is convex to the pressure axis. There is no clear indication of monolayer formation. This isotherm indicates the weak interaction between gas and solid materials. Type IV isotherms are shown by mesoporous materials. The initial region of Type IV isotherms is same as Type II except these isotherms saturates at higher relative pressure values due to capillary condensation. Type IVa isotherms are more common than Type IVb. Type IVa isotherms exhibit hysteresis loops, the lower branch of isotherms is obtained by adsorption of gas and the upper branch is obtained by the desorption of gas. The hysteresis is resulted due to filling and emptying of mesopores due to capillary condensation phenomenon. Type V isotherms are rarely shown by macroporous materials. The initial region of Type V isotherms is same as Type III except these isotherms saturates at higher relative pressure values due to capillary condensation. Type VI isotherms are shown due to the layer by layer adsorption of gases on highly smooth nonporous surfaces. The step height indicates the adsorption capacity of each layer [72].

It is already known that almost every mesoporous material gives reproducible and distinctive hysteresis loops. These hysteresis loops occur as both adsorption and desorption branches of isotherms cannot satisfy the conditions of thermodynamic reversibility due to the existence of certain metastable states. According to IUPAC hysteresis loops are divided into six distinct types. These six types are shown in Fig. 2.3.

Type H1 is shown by materials having narrow range of uniformly distributed mesoporous. This is a narrow hysteresis loop with steep and nearly parallel adsorption and desorption branches. Type H2 loops are shown by materials with complex interconnected porous structure. This loop is broad with a flat area and steep desorption branch. Type H3 hysteresis loop is shown by particles having plate-like structures. Type H4 hysteresis loop is shown by materials having micro-mesoporous structures. Both Type H3 and H4 do not have any distinctive desorption

boundary curve. Type H5 is shown by materials having both open and partially blocked porous structures.

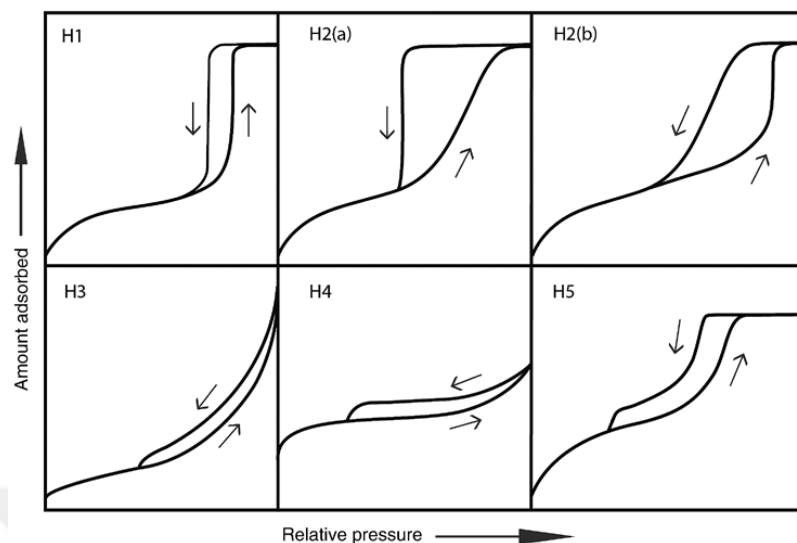


Fig. 2.3 IUPAC classification of hysteresis loops [72].

2.4.2.4 Ultraviolet-visible spectrophotometer

Ultraviolet-visible spectrophotometer (UV/VIS) is used to determine the concentration of different analytes. We evaluated the loading efficiency and release kinetics of mesoporous silica particles loaded with Rhodamine 6G by using UV/VIS spectrophotometer (PG T80). The loading and release of Rhodamine 6G was measured between 600 nm and 400 nm. Rhodamine 6G gives maximum absorbance at 530 nm.

2.5 Synthesis of mesoporous silica assemblies

We synthesized and investigated mesoporous silica assemblies with different shapes and sizes that can be used in various applications. The mesoporous silica assemblies were synthesized by block copolymer templating method, where non-ionic block copolymers were mixed with silica precursor in highly acidic region. Pluronic F127, F68 and Brij 700 were used as non-ionic surfactants because of their good solubility in water, commercial availability and biodegradability. Tetraorthosilicate (TEOS) was used as silica precursor because of its relatively low cost, easy handling and relatively fast hydrolysis. The method used for silica synthesis in this study is unique as TEOS have never been combined with non-ionic surfactants in highly acidic region. This synthesis method helped to design silica structures with controlled morphology at room temperature. The reaction parameters such as stirring speed, type of surfactant and concentration of acid catalyzer were changed to tune the shape and size of mesoporous silicas. The stability of as-synthesized mesoporous silica structures was determined in water. The mesoporous silica assemblies were characterized by scanning electron microscope, nitrogen adsorption isotherms, transmission electron microscope and zeta potential. The adsorption and release properties of mesoporous silica particles were successfully investigated by UV-VIS spectroscopy. The results showed that the morphology of mesoporous silica samples can be effectively controlled between spherical particles and monoliths by adjusting the amount of non-ionic surfactant and acid catalyzer. These variable morphologies resulted in ordered and disordered pores with BET surface area ranging between 200-600 m²/g.

2.5.1 Selection of better structure directing agent

The synthesized mesoporous silica structures were used as fillers for anti-icing and anti-corrosive composite coatings as discussed in Chapter 3 and 4, respectively. For such applications where the fillers are loaded with various anti-icing agents and corrosion inhibitors, the specific surface area of the mesoporous silica structures is required to be high enough to carry maximum corrosion inhibitor/anti-icing agent in the composite coatings. The mesoporous silica assemblies were synthesized by using Pluronic F68 and F127 as structure directing agents because of their good solubility in water, commercial availability and biodegradability. The effect of Pluronic F127 and F68 on the specific surface area of the mesoporous silica assemblies was investigated. For that purpose, 0.1 g of F127 or F68 was dissolved in 1 mL of 7M

HCl solution. 1 mL of this solution was mixed with 2 mL of TEOS. The resulting mixture was casted in Teflon plate for evaporating water and reaction by product ethanol. The microphase separation of Pluronic in water into hydrophilic and hydrophobic domains is the basis of this block copolymer templating method. The formation of silica particles involves the interaction of silica precursor with Pluronic that facilitates the assembly of silicate micelles. Pluronic acts as a porogen and stabilize the interfacial area of a nanoscopic structure. The removal of Pluronic leaves behind the nano sized pores. Pluronic was removed from the silica system by calcination process. The decomposition of mesoporous silica was determined by thermogravimetric analysis (TGA). The TGA result of as synthesized silica is shown in Fig. 2.4. The first mass loss at 100 °C is attributed to the loss of hydroxyl group present in as synthesized silica assemblies. The mass loss at 363 °C is due to Pluronic F127. Pluronic decomposes and leaves the silica system at this temperature. This result is in line with the literature data for similar Pluronic containing systems [73]. This decomposition temperature of Pluronic was considered for calcination of all samples containing Pluronic as structure directing agents.

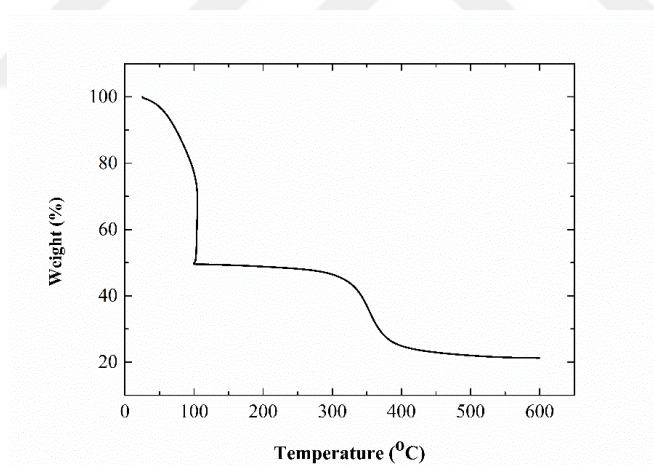


Fig. 2.4 Thermal gravimetric analysis of as synthesized silica with Pluronic F127. The amount of silica precursor was 2 mL in 1mL solution of surfactant and HCl concentration was kept at 7M.

The samples synthesized with Pluronic F127 and F68 were calcined at 450 °C for 8 h. The morphology of the calcined mesoporous silica structures is shown in Fig. 2.5. The SEM images showed that the morphology of these structures is almost same. These images also showed that these structures are porous. The calcined samples were analyzed with physisorption instrument. Their Brunauer–Emmett–Teller (BET)

surface area was measured. The adsorption isotherm of these two samples are shown in the Fig. 2.6. These isotherms are saturating at high pressure values. The increase in adsorbed quantity of nitrogen at high pressure for all the isotherms is due to the adsorption of more layers on top of the first adsorbed mono layer which is shown by the concave part of the isotherms. The BET surface area for Pluronic F127 and F68 is 462 m²/g and 433 m²/g respectively. The difference in the specific surface area could be due to the molecular weight of these two Pluronic systems. Hydrophilic part of copolymer also acts as a porogen. After the removal of hydrophobic part, hydrophilic part of Pluronic also leave behind microporosity. This additional porosity resulted in increased BET surface area [74]. The size of PEO block in F127 is 106 and in F68 it is 80. The additional porosity due to PEO removal also enhanced the specific surface area of silica assemblies synthesized by using Pluronic F127 as structure directing agent. To synthesize mesoporous structures with higher specific surface area, we used Pluronic F127 as structure directing agent.

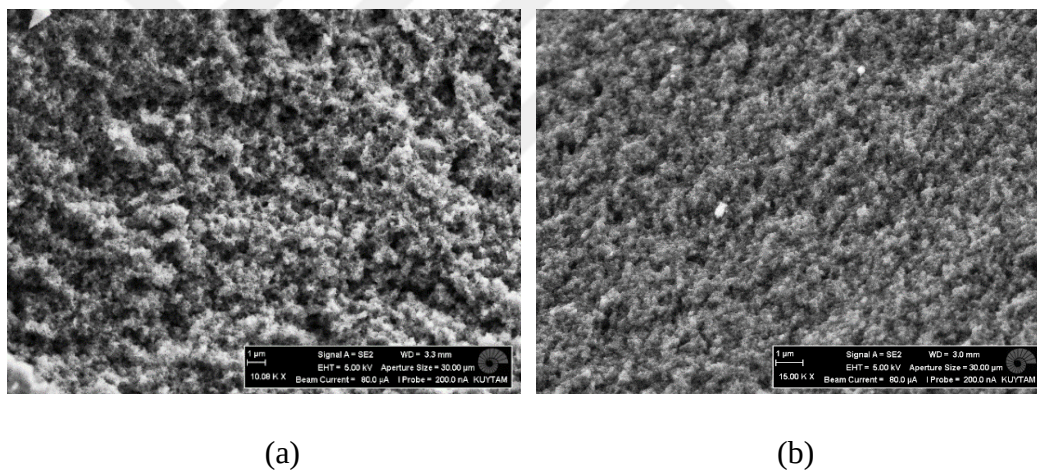


Fig. 2.5 Scanning microscope images of mesoporous silica, (a) synthesized with Pluronic F127, (b) synthesized with Pluronic F68 (scale bar 1 μm). The amount of silica precursor was 2 in 1mL solution of surfactant and HCl concentration was kept at 7M.

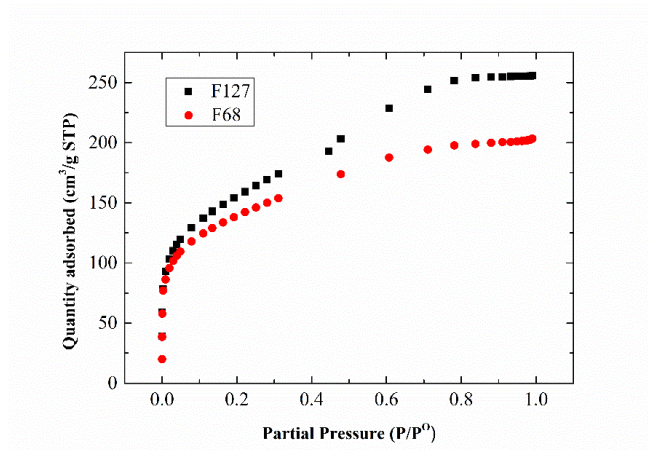


Fig. 2.6 Comparison of adsorption isotherms of mesoporous silica with different Pluronic types (F127, F68). The amount of silica precursor was 2 mL in 1 mL surfactant solution and HCl concentration was kept at 7M.

2.5.2 The effect of surfactant concentration on silica morphology

Sol-gel synthesis of the mesoporous silica in the presence of the block copolymer was performed. The mesoporous silica particles were obtained through acid-catalyzed synthesis using Pluronic F127 as structure directing agent and tetraorthosilicate (TEOS) as Si source. The synthesis was carried out by changing the amount of Pluronic F127 in reaction mixture. Typically, 0.01-0.05 g of Pluronic F127 was dissolved in 1 mL of 7M HCl solution. The amount of TEOS used for this synthesis was 200 μ L. The morphologies of all the samples synthesized by changing Pluronic concentration are shown in Fig. 2.7. These images showed that the morphologies of all these samples consisted of aggregated spherical particles. This spherical mesoporous silica particle formation can be attributed to the fast reaction rates which resulted in the formation of many silica nuclei during gelation process. Large particles are energetically more favorable than small ones. The molecules on the surface are less stable than the molecules well-ordered or packed in interior. As time goes on smaller unstable particles condense on the large particles. The presence of charged species in reaction mixture results in cancellation of the surface charge of silica particles and the particles aggregate to form dense 3D networks.

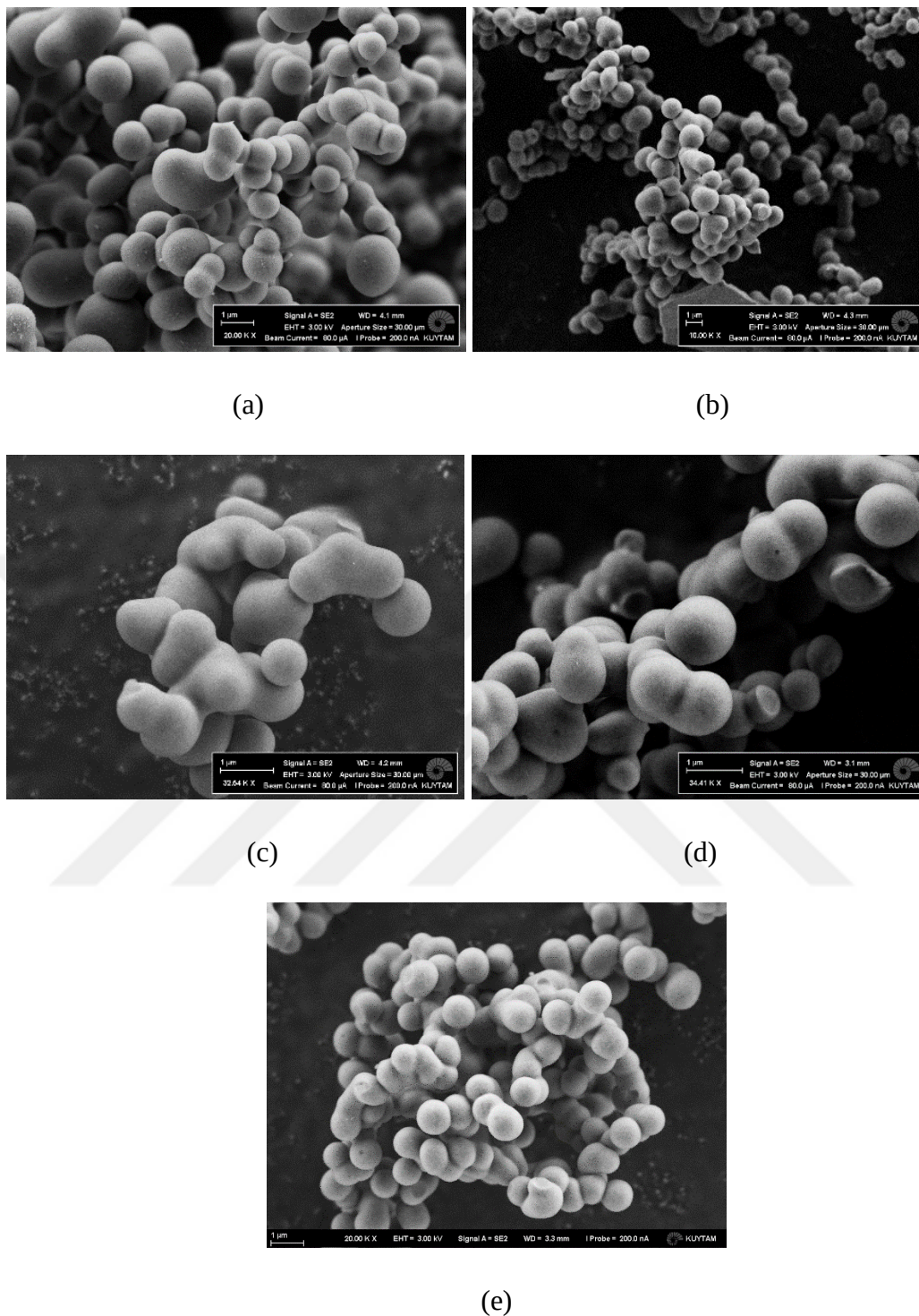


Fig. 2.7 Scanning microscope images of mesoporous silica synthesized by changing amount of Pluronic F127 in reaction mixture, a) 0.01 g, b) 0.02 g, c) 0.03 g, d) 0.04 g and e) 0.05 g. The amount of silica precursor was 0.2 mL/mL and HCl concentration was kept 7M.

The information about the porosity and specific surface area of spherical mesoporous silica particles was obtained by physisorption instrument. The adsorption isotherms of silica particles synthesized by changing Pluronic F127 amount are shown in Fig.

2.8. All these samples showed combination of Type Ib and Type II adsorption isotherms. The quantity of nitrogen adsorbed by each silica sample is increased by increasing partial pressure of nitrogen. All these isotherms are saturating at high pressure values. The probable reason for this saturation could be that surface of the silica particles may be filled with adsorbed molecules. The increase in adsorbed quantity of nitrogen at high pressure for all the isotherms is due to the adsorption of more layers on top of the first adsorbed monolayer which is shown by the concave part of the isotherms. Pluronic F127 acts as a porogen. The removal of Pluronic by calcination resulted in porosity. Therefore, sample with more Pluronic amount will have more BET specific surface area. The specific surface area of all these samples is shown in Table 2.2. The specific surface area was 318 m²/g at 0.02 g/mL Pluronic concentration and gradually increased to 399 m²/g at 0.05 g/mL Pluronic concentration. The surface area increased as the amount of Pluronic in the sample mixture increases except for the sample having least amount of Pluronic. The sample with 0.01 g of Pluronic showed the maximum specific surface area of 428 m²/g. The reason for this extra ordinary increase in the surface area could be the ordering of porous structures and will be discussed in section 2.5.3.

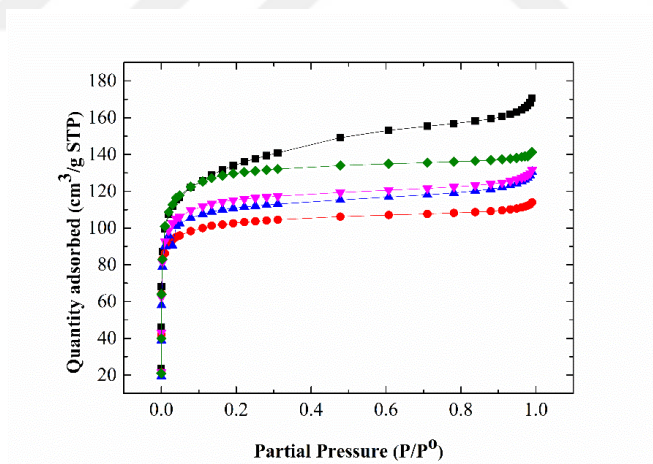
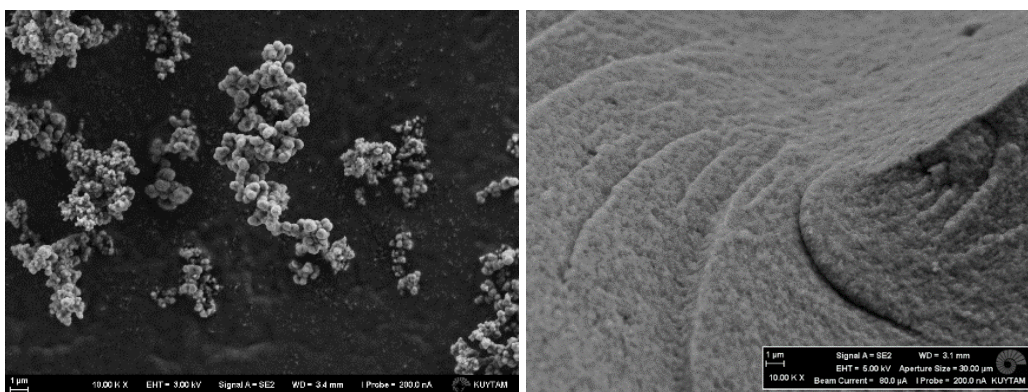


Fig. 2.8 Comparison of adsorption isotherms of mesoporous silica synthesized by changing concentration of Pluronic F127, silica synthesized with 0.01 g/mL Pluronic F127 (black squares), with 0.02 g/mL Pluronic F127 (red circles), with 0.03 g/mL Pluronic.

Table 2.2 BET specific surface area of silica synthesized by changing Pluronic F127 concentration.

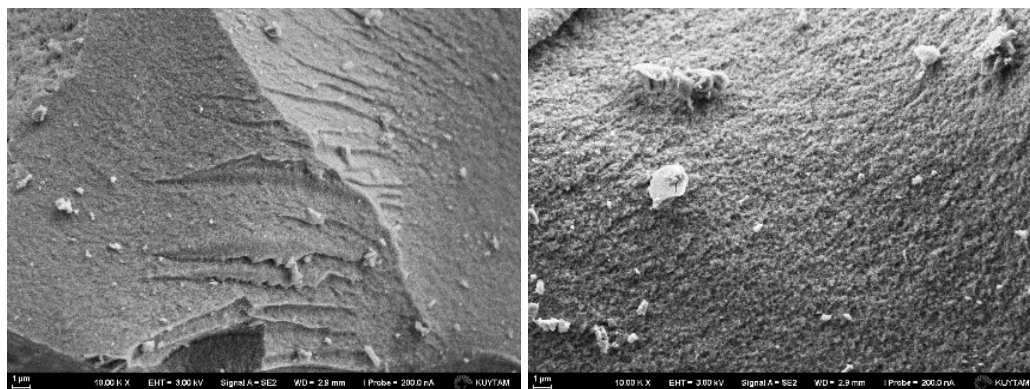
Pluronic concentration (g/mL)	BET specific surface area (m ² /g)
0.01	428
0.02	318
0.03	340
0.04	356
0.05	399

When the concentration of surfactant was further increased, the morphology of the mesoporous silica structures changed from spherical particles to monoliths. We investigated this process by increasing the surfactant concentration, rest of the parameters were kept constant. The mesoporous silica structures synthesized by increasing surfactant concentration beyond 0.05 g/mL are shown in Fig. 2.9. It was observed that the size of the particles changed as the amount of Pluronic increased from 0.05 g/mL to 0.1 g/mL. The morphology of the silica structures was changed to monoliths beyond this concentration. Under acidic reaction conditions ($\text{pH} < 1$), PEO carries positive charge and similarly silicate species carry positive charge. They interact through counter anion (Cl^-). Pluronic F127 also acts as a growth suppressant [63]. So, by increasing the concentration of pluronic at constant TEOS concentration, the excess Pluronic species would adsorb on the surface of silicate assemblies. This surface adsorbed Pluronic would result in monolith formation.



(a)

(b)



(c)

(d)

Fig. 2.9 SEM images of mesoporous silica, synthesized by increasing the concentration of Pluronic F127, at same HCl concentration (7M) and with same amount of silica precursor (0.2 mL in 1 mL surfactant solution): (a) synthesized with 0.1 g/mL Pluronic F127, (b) synthesized with 0.15 g/mL Pluronic F127, (c) synthesized with 0.2 g/mL Pluronic F127 and (d) synthesized with 0.3 g/mL Pluronic F127 (scale bar 1 μ m).

The formation of silica mesoporous assemblies was further confirmed by Fourier transform infrared spectroscopy (FTIR) analysis of calcined and as synthesized mesoporous silica structures. The FTIR spectra are shown in Fig. 2.10. The FTIR spectra of both as synthesized and calcined silica structures showed various common bands. The FTIR spectra of calcined silica confirmed the complete removal of Pluronic from the silica structures. Fig. 2.10 (a) shows the FTIR spectra of as-synthesized silica samples. The spectra contained the absorbance bands from Pluronic F127. The C-O-C stretching peak coincides with the asymmetric stretching of Si-O-Si bands at 1100 cm^{-1} . The FTIR spectra showed -CH stretching peaks between 2980 and 2860 cm^{-1} and -CH bending peaks at 1400 cm^{-1} . These peaks were observed due to the presence of Pluronic in as-synthesized silica structures. These peaks are consistent with literature [75]. Fig. 2.10 (b) showed the FTIR spectra of calcined silica samples. The broad peak at 3400 cm^{-1} corresponds to the silanol molecules. The most intense peak around 1080 cm^{-1} confirmed the synthesis of silica structures. This peak at 1080 cm^{-1} is assigned to asymmetric stretching vibrations of Si-O-Si bonds. The peak at 800 cm^{-1} showed the symmetric stretching vibrations of Si-O-Si bonds. These FTIR results confirmed the synthesis of silica structures and complete removal of Pluronic [76, 77].

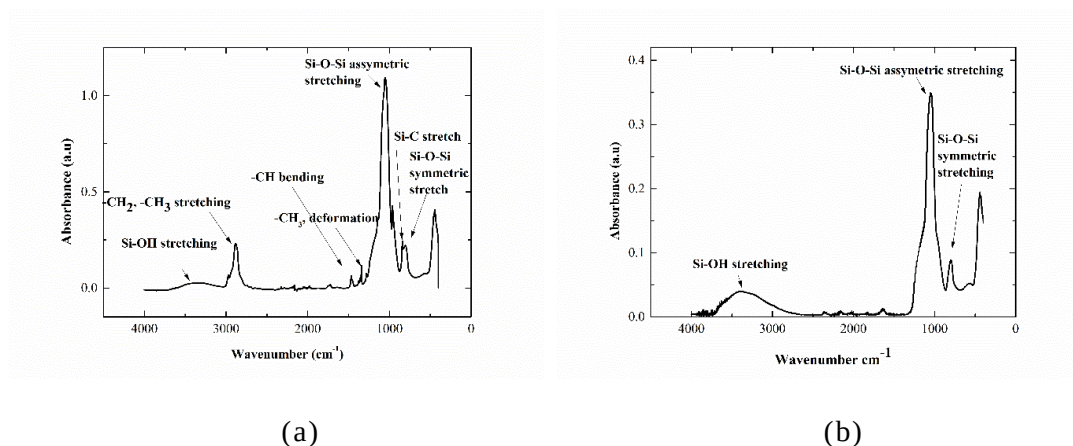
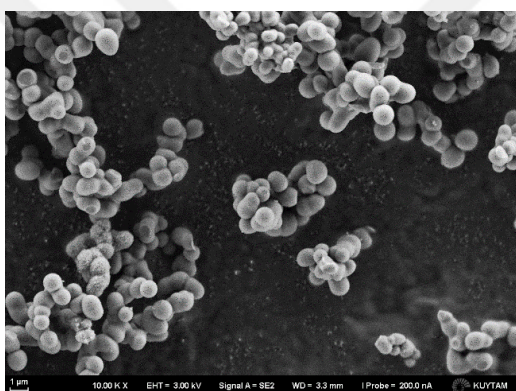


Fig. 2.10 FTIR spectrums of silica structures, (a) as-synthesized (without calcination), (b) calcined silica structure.

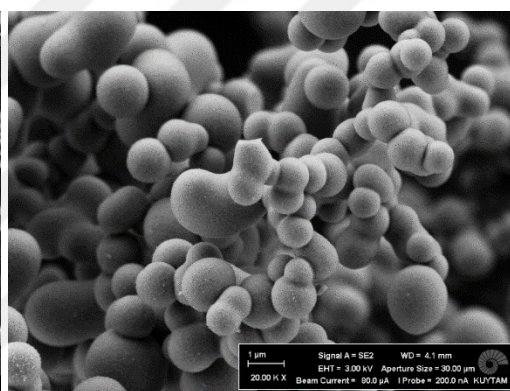
2.5.3 The effect of acid catalyzer concentration on silica morphology

Sol-gel process consists of two chemical reactions namely hydrolysis and condensation which result in formation of a network of siloxane. In this study, mesoporous silica synthesis is carried out under acidic catalytic conditions. Below pH 6, hydrolysis reaction is more favored reaction and condensation reaction is rate determining step (Fig. 2.1). The rate of both hydrolysis and condensation reactions is very fast in $\text{pH} \leq 0$. This fast reaction kinetics along with an appropriate amount of structure directing agent resulted in particle formation. We tried to observe the effect of acid catalyzer concentration on silica structure formation. So, the synthesis was carried out by changing the concentration of acid catalyzer in reaction mixture. Typically, 0.01 g of Pluronic F127 was dissolved in 1 mL aqueous solution of HCl with concentration ranging between 10^{-4} M – 8 M. The amount of TEOS used was 200 μL . The morphologies of these samples are shown in Fig. 2.11. The morphology of these silica particles changed from particles to monoliths as the concentration of HCl is decreasing in the reaction mixture. The mesoporous silica samples synthesized at higher acid concentration range of 3 M - 8 M showed spherical particle morphology. These particles showed narrow size distributions and actual yield of 88.0 % for particles synthesized at 3 M HCl concentration and 92.5 % for particles synthesized at 8 M HCl concentration. The higher yield was obtained at higher acid concentration solutions. The SEM images of mesoporous silica particles showed the presence of nano particles on the top surface of secondary particles. The synthesis of mesoporous silica assemblies relies on cooperative self-assembly of

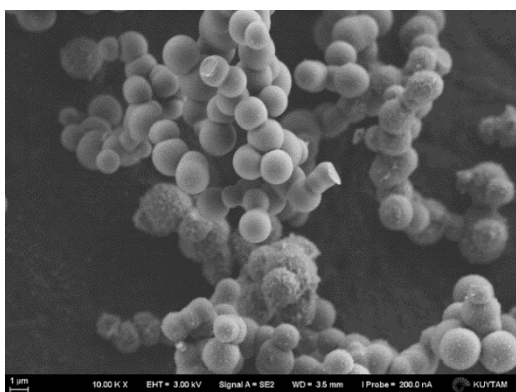
surfactant and silica species. The hydrolysis of silicon alkoxide is followed by condensation reaction that results in the formation of silica nuclei. These nuclei grow to form stable silica primary particles. The interaction of silica particles and surfactant through counter ions at this low pH resulted in the formation of dense 3D secondary particles. In case of higher acid catalyzer concentrations, the number of nucleation sites increases [78]. The effect of acid concentration on the size of mesoporous silica particles is shown in Fig. 2.12. It has been observed that the increase in the acid concentration resulted in decreased particle size. This decrease in size can be attributed to the increase in number of nucleation sites. In addition to this higher acid concentration resulted in smoothening of possibly forming edges of secondary particles [79].



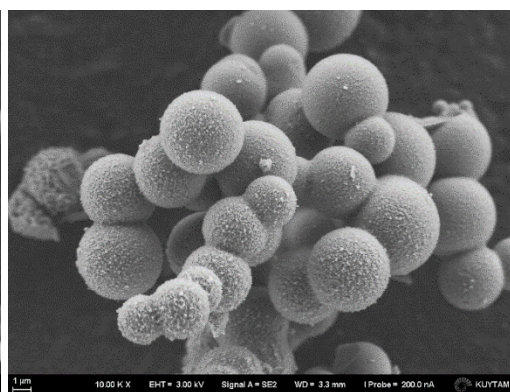
(a)



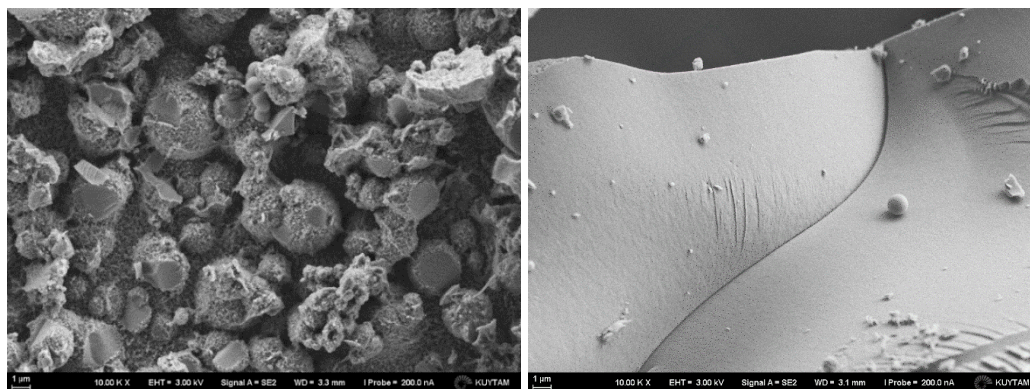
(b)



(c)

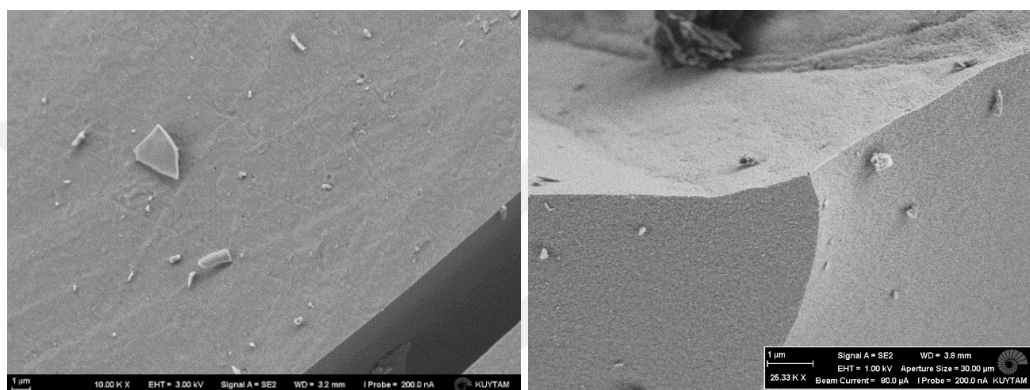


(d)



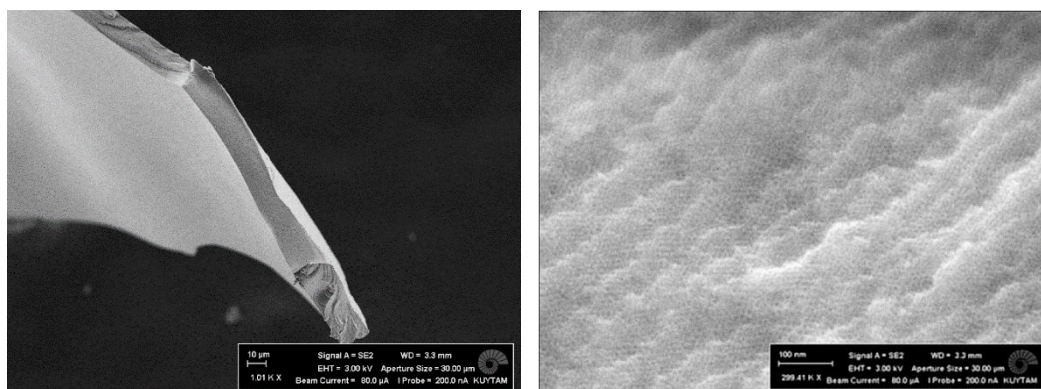
(e)

(f)



(g)

(h)



(i)

(j)

Fig. 2.11 Scanning electron images of silica particles synthesized at different acid catalyzer concentrations: (a) synthesized at 8 M HCl concentration, (b) synthesized at 7 M HCl concentration, (c) synthesized at 5 M HCl concentration, (d) synthesized at 3 M HCl concentration, (e) synthesized at 1 M HCl concentration, (f) synthesized at 0.1 M HCl concentration, (g) synthesized at 10^{-2} M HCl concentration, (h) synthesized at 10^{-3} M HCl concentration, (i) synthesized at 10^{-4} M HCl concentration and (j) the higher magnification

image of plane of monoliths shown in (i). The amount of Pluronic F127 was 0.01 g/mL and TEOS was 0.2 mL in 1 mL surfactant solutions in all the samples.

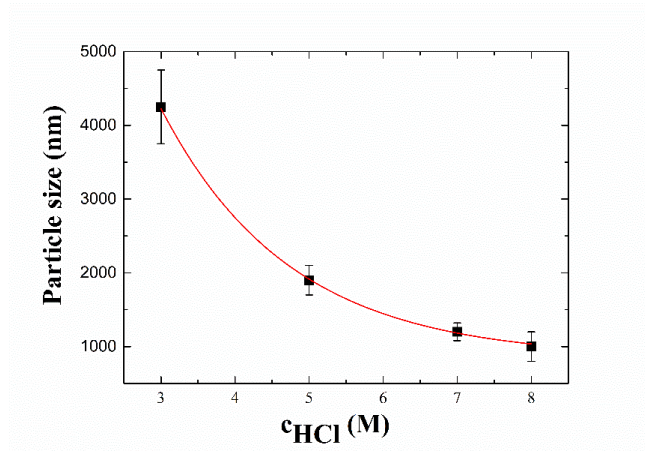


Fig. 2.12 The change in the size of mesoporous silica particles as function of the acid concentration. The results showed first order exponential decay with increasing acid concentration.

The structural investigation of mesoporous silica particles was done by TEM analysis. The TEM image of mesoporous silica particles synthesized by mixing TEOS with/without Pluronic in HCl is shown in Fig. 2.13. The TEM image of mesoporous silica particles synthesized by mixing TEOS in HCl solution containing Pluronic F127 clearly showed that the secondary silica particles are formed by the combination of smaller primary particles. The spherical morphology of mesoporous silica particles can be attributed to the aggregation of these primary particles. The mesopores having diameter of $\sim 3.3 \pm 0.4$ nm was observed in primary particles. The presence of primary particles and spherical morphology was not observed in silica sample synthesized from solution without Pluronic F127 (Fig. 2.13b). These results clearly demonstrated that the interaction between silica species and Pluronic F127 has a strong effect on the morphology of silica. The TEM image in Fig. 2.13(a) clearly showed that the ordered porous structure is formed within the primary silica particles. This ordered porosity can be attributed to the rapid cooperative self-assembly between surfactant and silica during the formation of primary particles. The high agglomeration rate of primary particles did not allow the ordered structure formation in secondary particles.

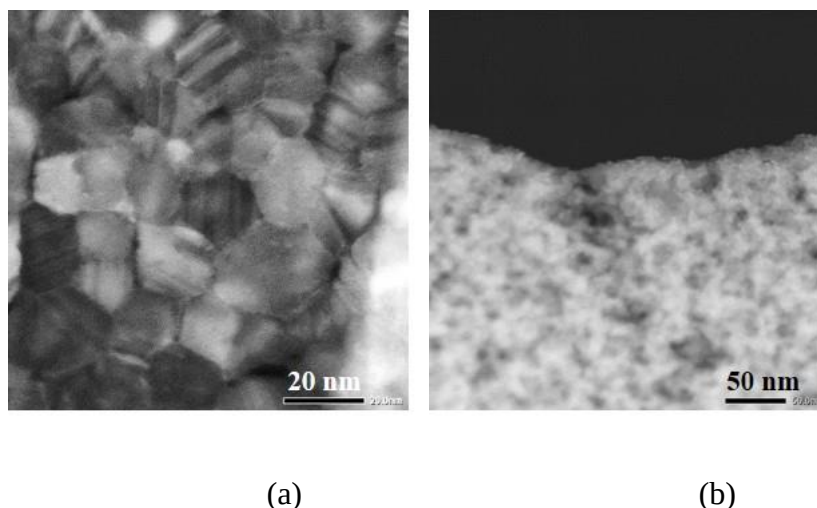


Fig. 2.13 TEM images of silica sample synthesized from TEOS in 7.0 M HCl acid solution with a) 0.01 g/mL and b) without Pluronic F127.

The sample synthesized at 1 M acid concentration (Fig. 2.11e) showed monoliths structures having spherical particles entrapped in them and on their surfaces. The samples synthesized at lower acid concentration range of 0.1 M to 10^{-4} M showed monolith morphology. The structure transition from particles to monoliths could be attributed to the change in reaction kinetics of the system. Condensation reaction slows down as the concentration of acid catalyzer decreases in the system [37]. The slowing down of condensation reaction may result in smaller number of silica nuclei which grow to form monoliths. So, the proper silica to surfactant ratio can change the morphology from particle to monoliths [80]. The SEM images of samples synthesized at acid concentration range of 0.1 M to 10^{-3} M HCl concentration showed disordered mesoporous structures for the monoliths. However, the sample synthesized at 10^{-4} HCl concentration showed hexagonally ordered mesopores in the planes of monoliths (Fig. 2.11 j). The formation of these ordered mesopores monoliths is attributed to a different mechanism as compared to the spherical mesoporous silica particles. It is formed by evaporation induced self-assembly. It is known that Pluronic F127 forms different self-assembled structures in aqueous solution such as lamellar, cubic and hexagonal structures [47]. The evaporation of solvent during the drying process increased the concentration of Pluronic 127 that resulted in the formation of hexagonally ordered cylindrical micelles of Pluronic F127. The hydrogen bonding between surfactant and silica resulted in cooperative self-assembly. The slowing down of hydrolysis and condensation reaction at pH 4 gave enough time for the assembly of silica species around the hexagonally ordered

cylindrical micelles. This synthesis mechanism was reflected in synthesis yield values. The yield of mesoporous silica synthesis method decreased from 92.5% at low pH to 57 % at pH 4. This decrease in the yield can be attributed to the evaporation of unreacted TEOS and solvent during the drying process.

Nitrogen adsorption isotherms of the silica samples synthesized by changing the acid catalyzer concentration provided the valuable information about their porosity and specific surface areas. These isotherms are shown in Fig. 2.14. The quantity of nitrogen adsorbed by each sample is increased by increasing the partial pressure of nitrogen. The mesoporous silica samples with particle morphology demonstrated the combination of type Ib and type II adsorption isotherms (Section 2.4.2.3). The type Ib isotherm is typical for the samples having both micropores and smaller size mesopores (<2.5 nm). The contribution of type II shape is due to the spherical morphology of silica particles. Type II isotherm is typical for samples having macroporous structure. It is seen due to the adsorption of nitrogen gas on the small gaps between the secondary silica particles. The presence of microporosity in spherical particles resulted in very narrow hysteresis (type H4). The samples having mixed morphology of monoliths and spheres showed type 1b isotherm due to their broad distribution of pore sizes. The silica samples synthesized at pH 2, 3 and 4 showed type IV adsorption isotherms. For all these sample with monolith morphology, the concave part of type IV isotherms showed the adsorption of monolayers and middle quasi linear section showed the formation of multilayers. Eventually at saturation vapor pressure macroscopically thick layers formed. The type IV isotherms are indicative of mesopores structures. The sample synthesized at pH 2 and 3 showed H2 type hysteresis. This hysteresis loop gave the indication that these monoliths have interconnected mesopores of different shape and sizes. However, the silica monoliths synthesized at pH 4 showed H3 type of hysteresis. This change in hysteresis loop of monoliths synthesized at pH 4 as compared to the monoliths synthesized at pH 2 or pH 3 can be attributed to their platelet structure with certain extent of order. In addition to this the opening of the pores lied in plane of monoliths (Fig. 2.11j) the entry of gas molecules is limited to this route which also affected the shape of hysteresis loop.

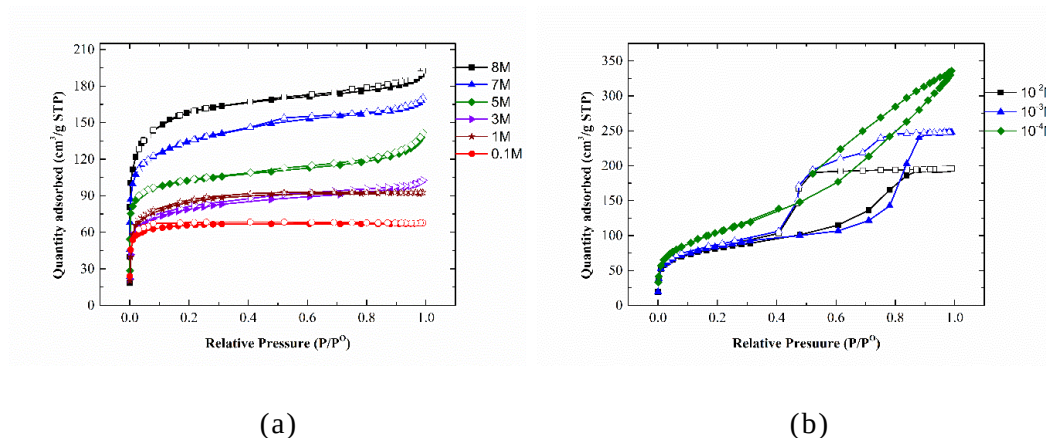


Fig. 2.14 Nitrogen adsorption isotherms of mesoporous silica synthesized by changing the concentration of acid catalyzer, (a) silica samples having particle or mixed morphology, (b) silica samples having monolith morphology.

BET surface areas of these samples as function of acid concentration is shown in Fig.2.15. It was noticed that the samples with spherical particle morphology have higher specific surface area than monoliths because surface area to volume ratio is more for the particles than monoliths. The BET surface area of the silica samples can be divided into two different regimes. The samples having spherical particles morphology showed increasing surface area with increasing acid catalyzer concentration. The maximum surface area of 498 m²/g was shown by spherical particles synthesized at 8 M acid concentration. The increase in specific surface area of the samples having spherical morphology cannot be explained only with the size difference of secondary particles (Fig. 2.12). The difference in the packing of primary particles inside the secondary particles could be the reason of this increase in surface area of samples. This difference in packing would allow different access to the pores that would affect the specific surface area of the samples. BET surface area of our mesoporous spherical particles is comparable with other mesoporous spherical silica particles [81]. In case of monolith samples, the samples having monolith morphology showed increasing surface area with decreasing acid concentration. The increase in BET surface area at lower acid concentrations can be attributed to slow reaction kinetics and attachment of self-assembled Pluronic to the surface. The surface attachment of Pluronic increased the number of pores on the surface of silica particles which resulted in more BET specific area. The more Pluronic on the surface the more will be the pores after calcination of the mesoporous silica particles. The

maximum surface area of 347 m²/g was shown by spherical particles synthesized at 10⁻⁴ M acid concentration.

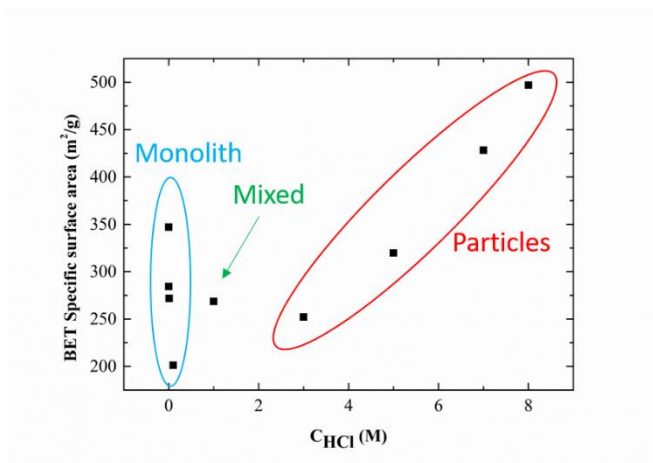


Fig. 2.15 BET specific surface area of mesoporous silica assemblies as function of the acid catalyst concentration.

2.5.4 Parameters affecting size of mesoporous silica particles

Sol-gel synthesis of the mesoporous silica in the presence of the block copolymer was performed. The mesoporous silica assemblies were obtained through acid-catalyzed synthesis using Pluronic F127 as structure directing agent and tetraorthosilicate (TEOS) as Si source. The mesoporous silica particles and monoliths were synthesized by changing surfactant concentration and by changing the amount of acid catalyst in the solution mixture. The BET results (Fig. 2.15) showed that mesoporous silica particles have higher specific surface area than mesoporous monoliths. The main aim of our study is to synthesize mesoporous silica structures with maximum specific surface area so that these structures can carry maximum corrosion inhibitors/anti-icing agent in composite coatings. In this part of the study, the synthesize of nanometer sized mesoporous silica particles was tried. An array of samples was prepared by changing the type of surfactants, pH of solution, stirring and centrifuging the solution mixture. The surface morphology of the samples was analyzed by scanning electron microscope as they were all sub-micron size particles.

2.5.4.1 Effect of surfactants on particle size of mesoporous silica

The ability of Pluronic to suppress the growth of mesoporous silica assemblies is already investigated in literature [63]. The effect of various non-ionic polyethylene-based surfactants on the size of mesoporous silica particles was investigated. Pluronic F127((PEO)₁₀₀(PPO)₆₅(PEO)₁₀₀) (M_n.12600 g/mol), F68 ((PEO)₇₆(PPO)₂₉(PEO)₇₆) (M_n. 8350 g/mol) and Brij 700 (C₁₈(PEO)₁₀₀) (M_n. 4670 g/mol) were used as structure directing agents. Typically, 0.01 g of structure directing agents was dissolved in 1 mL of 7 M HCl solution. The amount of TEOS used was 200 μL. The morphology of the synthesized mesoporous silica particles is shown in Fig. 2.16.

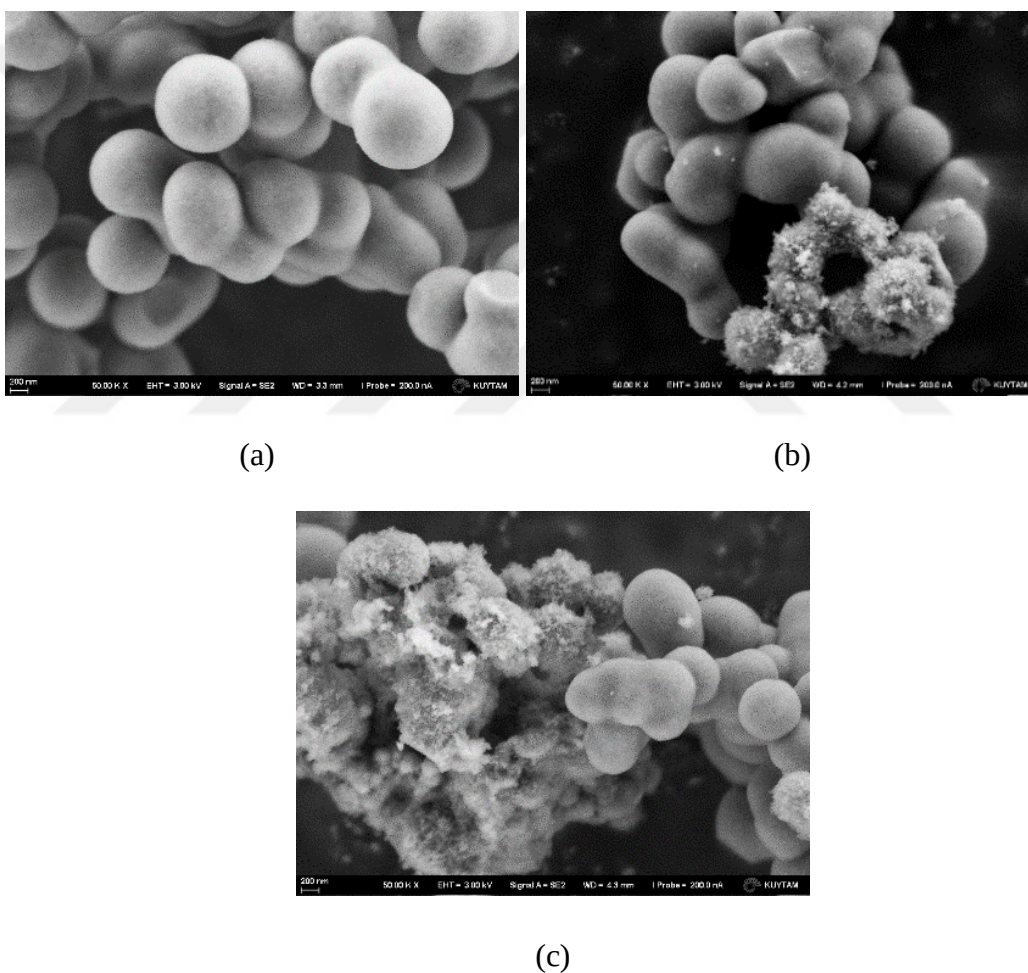


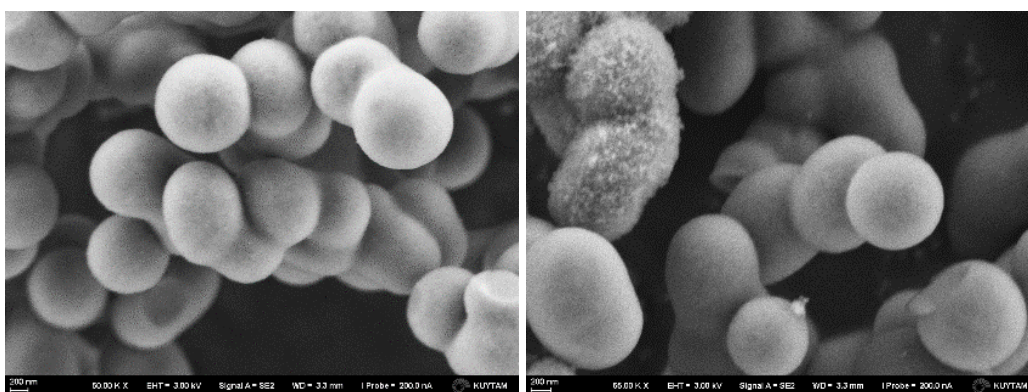
Fig. 2.16 Scanning electron microscope images of mesoporous silica synthesized with a) Pluronic F127, b) Pluronic F68, c), Brij 700 at same pH with same amount of silica precursor and surfactant concentration (scale bar 200 nm).

These images showed that the type of surfactant have no effect on the size of mesoporous silica particles. The size of mesoporous silica particles for all the

samples was in the range of 600 nm to 800 nm. The effect of surfactant molecular weight on the pore size and surface area was already reported in literature [82, 83]. The effect of Pluronic F127 and F68 on the surface area of mesoporous silica assemblies has already been discussed in section 2.5.1. The PEO or PPO block lengths have no effect on the particle size of mesoporous silica.

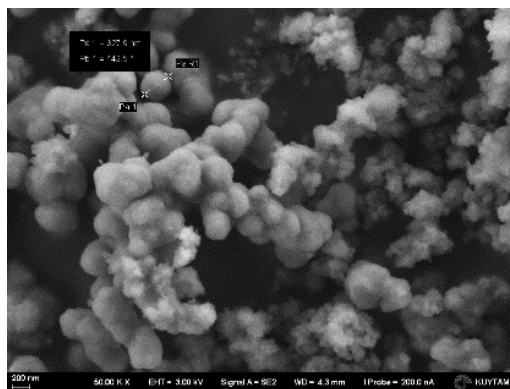
2.5.4.2 Effect of pH on the particle size of mesoporous silica particles

Sol-gel process consists of two chemical reactions namely hydrolysis and condensation. These reactions result in siloxane network formation. The kinetics of these reactions depends on the type of catalyzer. These catalyzers can be acidic or basic. In case of acidic catalyzer, the change in concentration of catalyzer strongly affects the reaction kinetics. The effect of pH change on the size of particles is investigated by changing the concentration of HCl in the reaction mixture. The concentration is changed from 7 M to 12 M. The amount of Pluronic (0.01 g/mL) and TEOS (200 μ L) was remained constant. The morphology of the samples is shown in Fig. 2.17. These images showed the size of silica particles decreased with increasing acid concentration. The size of the particles changed from 600-700 nm at 7M acidic concentration to 334 nm at 12M acid concentration. This change in size can be attributed to the fast reaction kinetics.



(a)

(b)



(c)

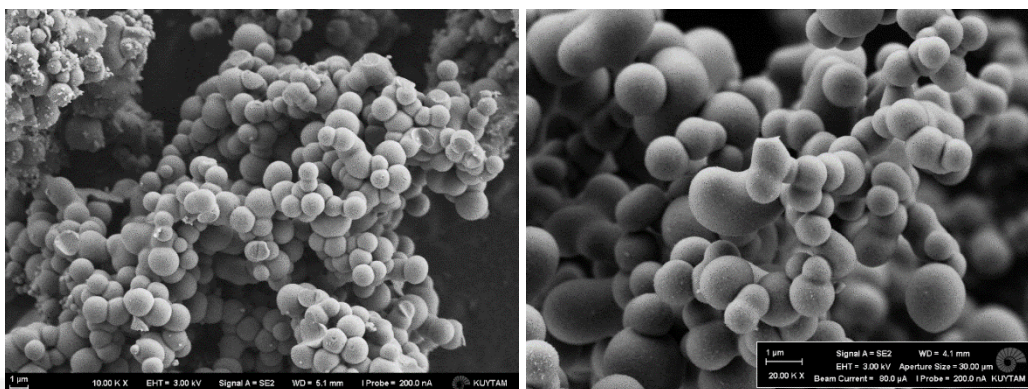
Fig. 2.17 Scanning electron microscope images of mesoporous silica particles synthesized at different acid concentration with same amount of silica precursor and surfactant concentration: (a) at 7 M concentration, (b) at 8 M concentration and (c) at 12 M concentration. The scale bar is 200 nm.

The hydrolysis and condensation reaction start at numerous sites as TEOS is added to the Pluronic containing acidic solution. This fast reaction kinetics resulted in numerous nuclei. The number of nuclei increases with the concentration of the acid in the synthesis mixture. The formation of silica nuclei at many places resulted in their cooperative interaction for the formation of particles. The preferable attachments of smaller particles formed three-dimensional silica networks. Pluronic F127 interacts and covers the surface of these colloidal particles and suppress their growth. These results that size of silica particles decreased by increasing the acid catalyzer concentration is consistent with our previous observations (Fig. 2.12).

2.5.4.3 Effect of centrifuging on the particle size

As we have discussed in section 2.5.3, the agglomeration of primary particles of ~20-30 nm resulted in secondary particles of size ranging between 700-900 nm. In order to get the smaller silica particles, we tried to reduce the agglomeration time of primary particles by centrifuging the reaction mixtures immediately after the gelation time. Typically, 0.01 g of Pluronic was dissolved in 1 mL of 7 M HCl. The amount of TEOS mixed was 200 μ L. After the gelation time of 141 s, the reaction mixture was centrifuged, washed with ethanol water mixture twice, recentrifuged and decanted. The sediments were dried in open atmosphere. The micrographs of these synthesized samples are shown in Fig 2.18. These images clearly showed that the size of samples remained in the same range of 700-900 nm even after centrifuging

the samples. These results implied that the process of secondary particle formation due to the agglomeration of primary particles was completed during gelation time. This can be attributed to faster reaction kinetics of mesoporous silica synthesis at 7 M HCl concentration.



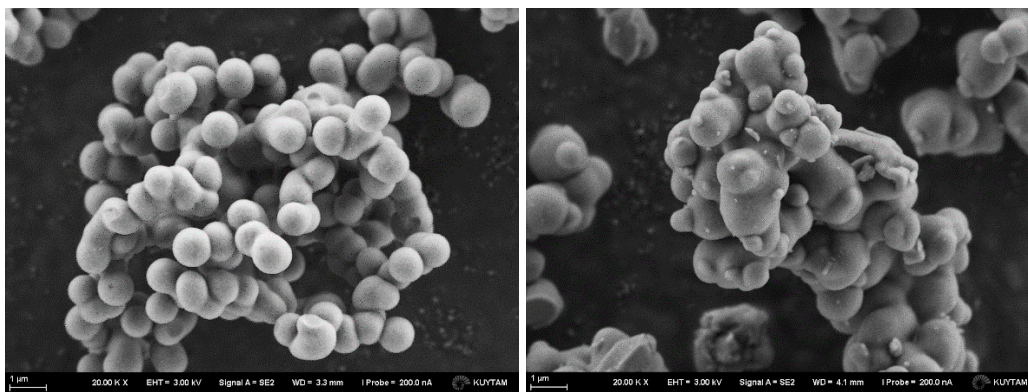
(a)

(b)

Fig. 2.18 Scanning electron microscope images of mesoporous silica synthesized at same pH with same amount of silica precursor and surfactant concentration, a) centrifuged, b) not centrifuged. The scale bar is 1 μm .

2.5.4.4 Effect of stirring on particle size

The effect of stirring on the size and morphology of mesoporous silica particles was investigated. For that purpose, 0.01 g of Pluronic was dissolved in 1 mL of 7 M HCl. The amount of TEOS mixed was 200 μL . The reaction mixture was stirred for 30 min at 1000 rpm. After stirring the reaction mixture was casted in teflon plate at ambient temperature. The mesoporous silica particles synthesized after stirring are shown in Fig. 2.19. The morphology of mesoporous silica remained same after stirring the solution. This result is consistent with literature data [84]. The size of mesoporous silica particles remained in same range of 700-900 μm even after stirring and homogenizing the reaction mixture. Silica particles for stirred sample are more closely fused than the one which was not stirred. The stirring of reaction mixture resulted in more fused particles.



(a)

(b)

Fig. 2.19 Scanning electron microscope images of mesoporous silica synthesized at same pH with same amount of silica precursor and surfactant concentration, a) without stirring, b) reaction mixture stirred for 30 min at 1000 rpm. The scale of the images is 1 μ m.

In conclusion, the mesoporous silica particles which were synthesized by increasing the acid catalyst concentration (decreasing pH of the solution) were smaller in size. Changing the type of structure directing agents, stirring or centrifuging the reaction mixture have no effect on silica particles size. Instead stirring the reaction mixture resulted in more fused mesoporous silica particles than the particles synthesized without stirring.

2.5.5 Loading and release of Rhodamine 6G in mesoporous silica particles

Mesoporous silica particles have the potential to be used as corrosion inhibitor/anti-icing agent carriers in polymeric matrices. The loading efficiency and release kinetics of these particles were investigated by loading mesoporous silica particles with Rhodamine 6G. Rhodamine 6G is water soluble dye which can be detected by UV-VIS spectroscopy. The loading capability of mesoporous silica particles was compared with non-porous silica particles of almost same size. These non-porous silica particles were synthesized by base catalyzed synthesis method.

2.5.5.1 Synthesis of non-porous silica particles

The synthesis of non-porous silica particles was carried out by Stober method [85]. This synthesis procedure was conducted under basic conditions to get non-porous silica particles. A mixture of water and ethanol having ratio of 20 to 80% by volume respectively was prepared. Then 50 μ L of each ammonia (25 wt% in water) and

Synthesis of Mesoporous Silica Particles and Controlling Their Morphologies

TEOS were added to the solution at once. This mixture was kept on the shaker for 2 h, and then the milk-white as-synthesized materials were collected by centrifugation. This white material was dried in open atmosphere and then heat treated at 450 °C. The density of the silica particles was enhanced by heat treating the as-synthesized silica particles [86]. The morphology of the silica particles was investigated by scanning electron microscope. The SEM micrographs are shown in Fig. 2.20.

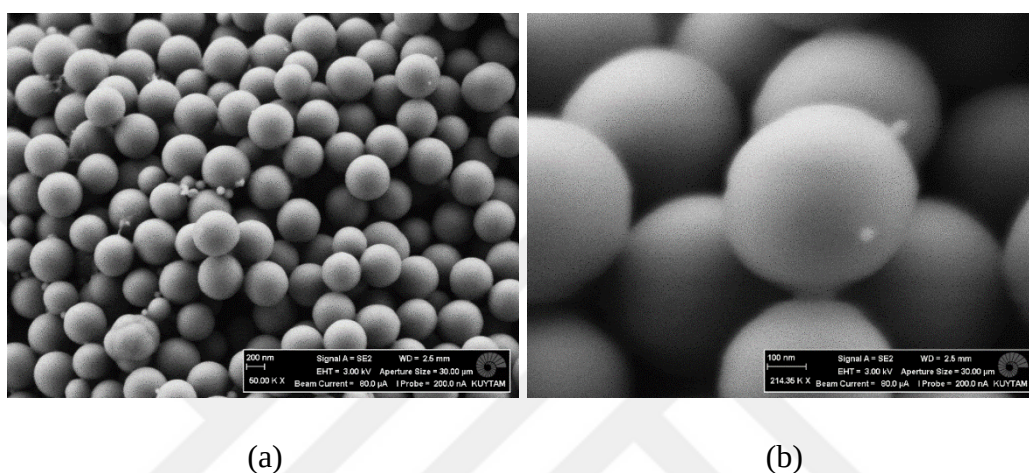


Fig. 2.20 Scanning microscope images of non-porous silica particles synthesized by Stober method, (a) image at 50 KX, (b) image at 214 KX.

The images showed monodisperse non-porous silica particles of size ranging between 400-500 nm. Nitrogen adsorption isotherm of the silica synthesized by base catalyzed method provided the valuable information about their non-porous nature and specific surface area. The isotherm is shown in Fig. 2.21. Typical Type II adsorption isotherm is shown by these base catalyzed samples. This type of isotherm is typical for non-porous materials. This type of isotherm is usually evolved due to the small gaps between the spherical particles. Nitrogen adsorption isotherm of base catalyzed silica particles showed very less quantity of nitrogen is adsorbed. This less quantity of adsorbed nitrogen suggested that these particles are not porous. The nitrogen adsorption is saturating at higher values due to multilayer adsorption. The BET specific surface area shown by this sample was 20 m²/g.

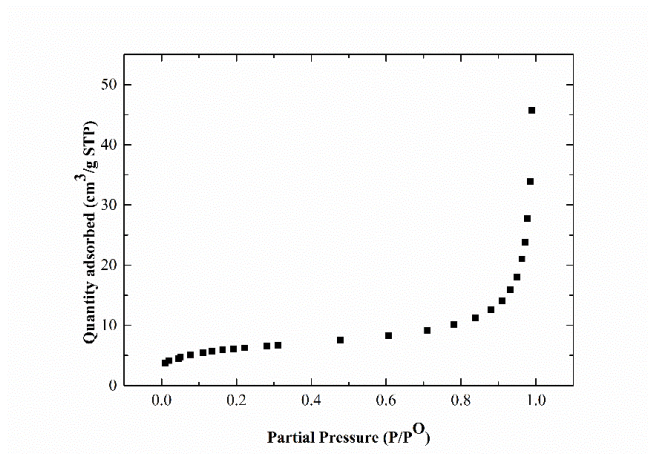


Fig. 2.21 Nitrogen adsorption isotherms of non-porous silica particles.

2.5.5.2 Loading of Rhodamine 6G in silica particles

The potential of mesoporous silica particles as corrosion inhibitor/anti-icing agent carrier was investigated by loading them with Rhodamine 6G molecules. Rhodamine 6G is a small molecule which can easily diffuse into the mesoporous silica particles and can be detected by UV-Vis spectroscopy. The mesoporous silica particles used for loading experiments have surface area of $428 \text{ m}^2/\text{g}$ and their synthesis have already been explained in section 2.5.2. To load mesoporous silica particles with rhodamine 6G, a stock solution (0.02 mg/mL) of Rhodamine 6G in water was prepared. The stock solution was diluted to prepare Rhodamine 6G solutions having various concentrations ranging from 0.002 - 0.01 mg/mL . These various concentrations of Rhodamine 6G were used to prepare a calibration curve as shown in Fig. 2.22. The solution of Rhodamine 6G showed maximum absorbance value at 530 nm [87]. Typically, 2 mg/mL mesoporous silica particles were placed in Rhodamine 6G solutions of various concentrations. The amount of Rhodamine 6G loaded in the mesoporous silica particles was investigated by UV-Vis spectroscopy. The absorbance curves are shown in Fig. 2.23. The absorption spectra of solutions containing mesoporous silica particles showed no absorbance peak at 530 nm that suggested all Rhodamine 6G is captured by mesoporous silica particles. Rhodamine 6G was loaded in mesoporous silica particles at neutral pH. The isoelectric point of mesoporous silica particles is $\text{pH}=2$. So, at the neutral pH mesoporous silica particles carry a negative charge. There is a positive amine group in Rhodamine 6G structure at neutral pH which resulted in an electrostatic interaction between mesoporous silica

particles and Rhodamine 6G molecules. In addition, Rhodamine 6G molecules can go to the pores of mesoporous silica particles.

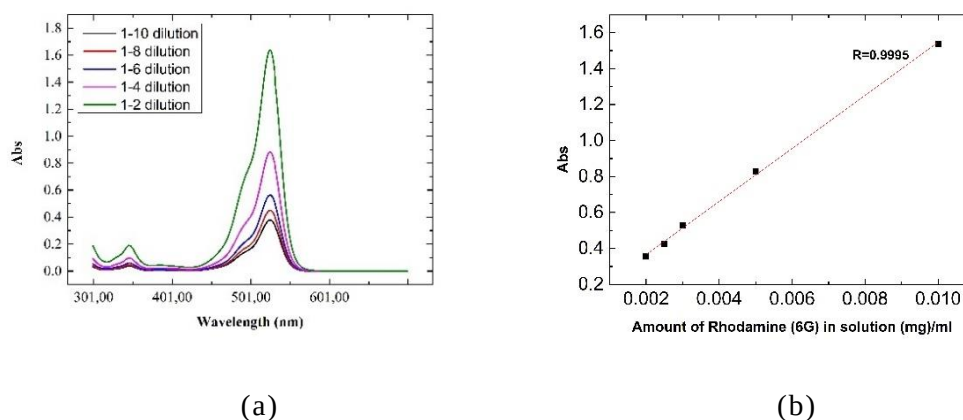


Fig. 2.22 Results obtained for Rhodamine 6G solution, (a) Absorption spectra for Rhodamine 6G with different concentrations. (b) Calibration curve for PEG at 530 nm wavelength.

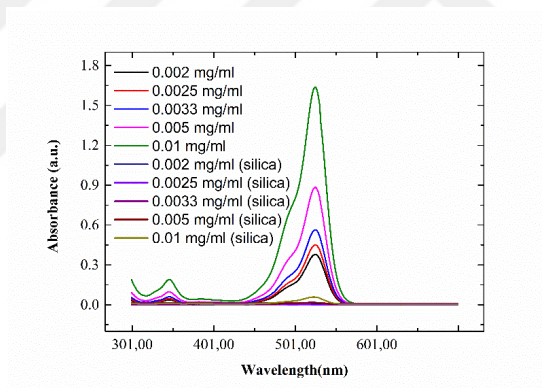


Fig. 2.23 Absorption spectra for Rhodamine 6G at various concentrations with and without mesoporous silica particles.

In order to investigate whether Rhodamine 6G will diffuse into the pores of mesoporous silica particles, 2 mg/mL non-porous silica particles were dipped in Rhodamine 6G solutions of same concentrations (0.002-0.01 g/mL). The amount of Rhodamine 6G adsorbed by non-porous silica particles was also investigated by UV-Vis spectroscopy and is shown in Fig. 2.24.

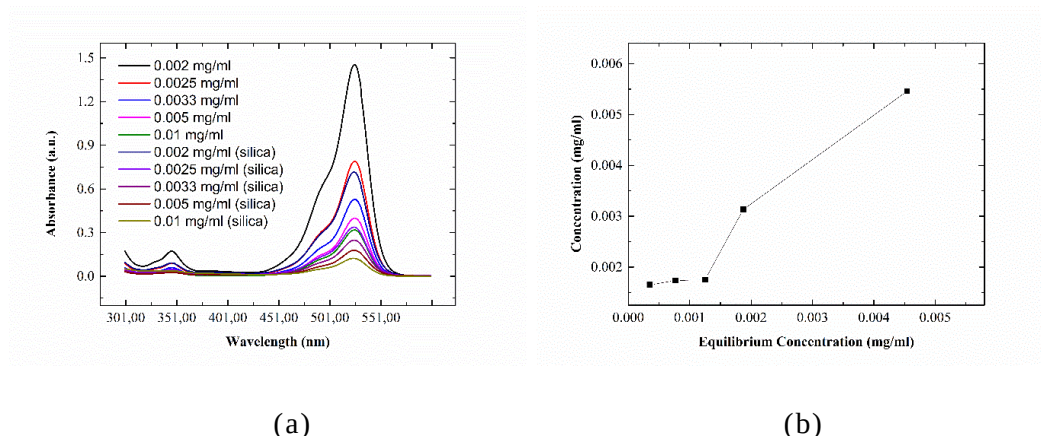


Fig. 2.24 The quantity of Rhodamine 6G adsorbed by non-porous silica particles at various concentrations, (a) Absorption spectra for Rhodamine 6G at various concentrations with and without silica particles and (b) amount of Rhodamine adsorbed by non-porous silica particles.

The absorption spectra of solutions containing non-porous silica particles showed absorbance peak at 530 nm. (Fig. 2.24 a) The presence of absorbance peak at 530 nm showed that Rhodamine 6G is not completely taken up by non-porous silica particles. The amount of Rhodamine 6G adsorbed by non-porous silica particles is significantly less compared to mesoporous silica particles. In case of non-porous silica particles, at low concentration levels, a single layer of molecules adsorbs to the surface. At intermediate concentrations, multilayers start to form. The saturation at higher concentrations is caused by the decrease in effective surface area and multilayer adsorption (Fig. 2.24 b). These loading results of non-porous silica particles confirmed that Rhodamine 6G is going into the pores of mesoporous silica particles as well as adsorbing onto the surface of mesoporous silica particles.

2.5.5.3 Release of Rhodamine 6G from mesoporous silica particles

The release kinetics is one of the most key features of mesoporous silica particles that need to be investigated when mesoporous silica particles are to be used as corrosion inhibitor/anti-icing agent carriers. The release kinetics of Rhodamine 6G loaded mesoporous silica particles was investigated at pH 7 and pH 5. Before release experiments, Rhodamine 6G was loaded in mesoporous silica particles by suspending 0.1 g mesoporous silica particles in 50 mL of Rhodamine 6G solution of 0.1 mg/mL concentration. This suspension was centrifuged after 24 h and then the supernatant was separated. The particles were washed with deionized water twice.

After washing process, the Rhodamine 6G loaded mesoporous silica particles were dried in open atmosphere. Then for release experiments, Rhodamine 6G loaded mesoporous silica particles were suspended in solutions with desired pH values. Typically, 0.05 g of Rhodamine loaded mesoporous silica particles was suspended in 50 mL of aqueous solutions at pH 7 and pH 5 respectively. A 3mL aliquot was removed from the suspension after every 15 min and centrifuged. The absorbance of supernatant was observed with UV-VIS spectroscopy. The release profile of Rhodamine 6G from mesoporous silica particles at pH 7 and pH 5 solutions is shown in Fig. 2.25. The release of Rhodamine 6G from mesoporous silica particles at pH 5 is more than the release at pH 7. The amount of Rhodamine released at pH 7 is 2.1 $\mu\text{g/mL}$ and gradually increased by a factor of 6 to 13 $\mu\text{g/mL}$ at pH 5 after 2 hr. These results are consistent with the results reported in literature where the release of Rhodamine 6G increased in acidic medium [88]. The electrostatic interactions between negatively charged mesoporous silica particles and positively charged Rhodamine 6G molecules decreased in more acidic pH. The negative charge of silica mesoporous silica particles decreases as the solution pH approaches towards isoelectric point (pH=2). This decreased negative charge resulted in decreased electrostatic interactions with Rhodamine 6G molecules. The fast release at pH 5 could be due to these decreased electrostatic interactions.

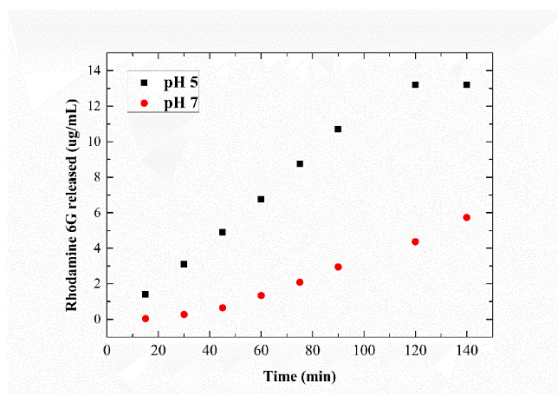


Fig. 2.25 Comparison of Rhodamine 6G release from mesoporous silica particles, (a) release at pH 5 and pH 7.

2.6 Conclusion

Mesoporous silica structures for various applications were successfully synthesized by using various amphiphilic block copolymers as structure directing agents and TEOS as silica precursor in highly acidic region. The higher specific surface area

was obtained by using Pluronic F127 as structure directing agent due to longer PEO block length that resulted in additional micro-porosity. The effect of surfactant concentration and acid catalyst concentration on the morphology of mesoporous silica structures was investigated. The morphology of mesoporous silica structures changed from spherical particles to monoliths by increasing the surfactant concentration from 0.01 g/mL to 0.3 g/mL in synthesis mixture. The morphology of mesoporous silica structures changed from particles to monoliths as well by decreasing the acid concentration from 8 M to 10^{-4} M in reaction mixture. The change in morphology can be attributed to the decrease in rate of hydrolysis and condensation reactions. The slow reaction kinetics resulted in less nucleation sites and monolith morphology. The BET surface area of these mesoporous structures decreases as the morphology changed from particle to monoliths. The highest specific surface area of 500 m²/g was shown by mesoporous silica having spherical morphologies compared to 347 m²/g for monoliths. This change in specific surface area is attributed to the decrease in surface area to volume ratio of monoliths as compared to particles. The mesoporous silica structures were synthesized for using as corrosion inhibitor/anti-icing agent carriers in anti-corrosive/anti-icing composite coatings. The mesoporous silica particles due to their higher specific surface area were preferred for these applications. The specific surface area of mesoporous particles can be further enhanced by decreasing the particle size of the mesoporous silica particles. The effect of surfactant type, acid catalyzer concentration such as 1M to 12 M, centrifuging the reaction mixtures versus evaporating in open air and stirring of reaction mixture at 100 rpm on the size of particles was investigated. The mesoporous silica particles synthesized by using 12 M HCl concentration in reaction mixture were smaller in size. The mesoporous silica particles prepared by changing the type of non-ionic surfactant, centrifuging or stirring the reaction mixture remained same in size and shape. The loading and release kinetics of Rhodamine 6G in mesoporous silica particles were investigated by UV-Vis spectroscopy. The loading capacity of mesoporous silica particles was compared with non-porous silica particles. These non-porous silica particles were prepared by using Stober method in basic medium. The amount of Rhodamine 6G loaded in mesoporous silica was greater than non-porous silica particles as expected. The loading results showed that Rhodamine 6G is not only electrostatically adsorbing onto the surface but also going into the pores of mesoporous silica particles. The release of Rhodamine 6G from

mesoporous silica particles was investigated at pH 5 and pH 7. The enhanced release of Rhodamine 6G from mesoporous silica particles at pH 5 was attributed to the weakening of electrostatic interactions between silica and Rhodamine 6G molecules. The loading and release results confirmed the potential of these mesoporous silica particles as corrosion inhibitor/anti-icing agent carriers in anti-corrosion/anti-icing composite coatings.



Chapter 3: Anti-Icing Composites

3.1 Motivation

Icing, frost formation and ice adhesion can cause major problems in transportation services, in daily life and in various industries. Ice formation can be prevented by lowering the freezing temperature or delaying the freezing time of water droplets so that supercooled water droplets can roll off the surfaces due to gravity, wind and centrifugal forces before solidification. Conventional methods such as active heating, mechanical removal of ice and chemical spraying are used to avert or impede ice accumulation [12, 89-91]. Although these methods have proven effective in preventing ice formation and accumulation, they have issues to be enhanced related to cost and environmental impacts [92]. Passive icephobic surfaces have attracted great interest due to their economic and safety benefits in inhibition and easy ice removal in various applications [93]. Superhydrophobic surfaces having micro and nanoscale textures and hydrophobic surface chemistry have been effective in preventing ice formation by enhancing the free energy barrier for heterogeneous nucleation [94-97]. Despite all this, these surfaces lose their anti-icing ability under harsh conditions of humidity, pressure and physical damage [15, 16]. Slippery liquid infused porous surfaces (SLIPS) have been proposed to overcome all these shortcomings of superhydrophobic surfaces. These surfaces have low contact angle hysteresis, low surface energy and low sliding angles which results in better anti-icing ability even in humid and high pressure conditions [18]. The issue related to the liquid depletion due to evaporation or entrainment with rolling droplets have not been addressed [98]. . However, to date, composites having porous micro/nanoparticles in polymer matrices which can be filled with anti-icing agents have not much studied. The release of the anti-icing agent from the porous particles upon contact with water will decrease the freezing temperature of the water. The approach has the advantage of maintaining the anti-icing agent at the top surface even if the coating is damaged by scratches.

In this work, we intended

- To prepare polymer/porous particle composites,
- To incorporate anti-icing agents in polymer/porous particle composites,

- To investigate the filling of porous particles with anti-icing agents and characterize the anti-icing ability of these composites,
- To investigate the release of anti-icing agent from these polymer/porous particles composites.
- To compare the anti-icing ability of two different porous particles containing composites.

The release of the anti-icing agent from the porous particles upon contact with water will decrease the freezing temperature of the water. The approach has the advantage of maintaining the anti-icing agent at the top surface even if the coating is damaged by scratches.

3.2 Anti-icing systems

In spite of numerous developments in the field of anti-icing coatings, the issue of ice accumulation still persists. The stress caused by accumulated ice is damaging critical structures such as buildings, transmission towers and power lines. Ice accumulation in natural environments takes place over a broad spectrum of temperature, wind condition and humidity levels. The ideal anti-icing composites need to withstand a wide range of environmental conditions. The commercially used strategies for preventing icing problems include active heating, mechanical removal methods and chemical anti-icing fluids. These processes are time consuming, suboptimal, costly and environmentally unfavorable [99]. Therefore, the use of passive methods based on icephobic coatings has attracted significant interest [94, 95, 100].

3.2.1 Superhydrophobic surfaces for ice prevention

The surfaces which can avert, or delay ice formation would be an ideal solution to eliminate the use of active anti-icing methods. These surfaces can prevent ice formation or reduce ice adhesion depending on their surface chemistry and topography. The anti-icing surface can be divided in three main groups namely hydrophilic, hydrophobic and superhydrophobic [101]. Hydrophobic surfaces have low wettability and static contact angles between 90° and 150°. These surfaces prevent ice formation by increasing the free energy barrier to ice nucleation and higher contact angle makes the droplet rolling process easier [14, 102]. The extent of anti-icing effect of these coatings is proven to be inefficient.

Superhydrophobic surfaces consist of micro and nano textures. Inspired by self-cleaning and non-wetting properties of organisms such as lotus leaf [103], rose petals [104] and water strider legs [105] superhydrophobic surfaces have been fabricated. These surfaces have low surface energy, extremely high contact angle ($\geq 150^\circ$) and low sliding angle ($<5^\circ$). These surfaces prevent ice formation by decreasing the probability of heterogeneous nucleation. This ice prevention mechanism can be tailored by the combination of surface roughness and chemistry [106].

Wang et al. synthesized superhydrophobic surfaces with surface modified calcium carbonate nanoparticles [107]. They used FAS-17 as surface modifying agent and polyacrylate as a binder for nanoparticles. They investigated the anti-frosting ability of the surfaces with different hydrophobicity. The water contact angle of the newly synthesized superhydrophobic surface was 155° and of bare copper surface was 64° . The initial frost formation on the superhydrophobic surface was delayed as compared to the copper surface. The anti-frosting ability of these surfaces were enhanced by tilting their position.

He et al. investigated the anti-icing ability on hydrophobic and superhydrophobic films [95]. The water contact angles of hydrophobic and superhydrophobic films were 98.1° and 155.3° respectively. The anti-icing ability of these films were investigated at -10°C and relative humidity of 50%. Due to the condensation of water vapors the surface wettability of hydrophobic surfaces increases while oscillates in case of superhydrophobic surfaces. Superhydrophobic surfaces retard ice formation as compared with hydrophobic surfaces.

Mishchenko et al. studied the behavior of dynamic droplets impacting on tilted superhydrophobic surfaces [108]. The temperature of dynamic droplets was ranging between -5 to 60°C , the surfaces were tilted between 0 - 60° and the temperature of superhydrophobic surface was changed between -30 to 20°C . They concluded that the ice formation depends only on the surface temperature. The ice formation process was fully prevented till -25°C surface temperature as impinging droplets retracted from the superhydrophobic surfaces while ice formation occurred on hydrophilic and hydrophobic surfaces.

Zuo et al. fabricated a superhydrophobic surface with surface modified ZnO nanorods [109]. The radio frequency magnetron method was used to synthesize these

superhydrophobic surfaces. The surface of ZnO was modified with FAS-17. The anti-icing ability of these superhydrophobic surface was compared with bare glass slides and permanent room temperature vulcanized rubber (PTRV) coated glass slides. The superhydrophobic surfaces showed freezing delay of 140 min at -10°C . These surfaces showed excellent durability against 30 repeated icing/deicing cycles.

Guo et al. fabricated microstructured (M), nanostructured (N), and micro/nanostructured (MN) surfaces [94]. The micrometer ratchet arrays were combined with ZnO nanohair to form micro/nanostructured surfaces. The contact angle for MN and N surfaces almost remained same with decreasing the temperature below 0°C . The MN surfaces showed longest freezing delay of almost 7200 s at -10°C . This freezing delay was attributed to the discontinuous three phase line on MN surfaces which resulted in more trapped air. In addition to longer freezing delay these surfaces showed low ice adhesion strength as well.

Cao et al. studied the effect of particle size on anti-icing ability of polymer nanocomposites [110]. The polymer nanocomposites were synthesized by using particle diameters up to $20\text{ }\mu\text{m}$. The polymer nanocomposites prepared with particle sizes up to $10\text{ }\mu\text{m}$ were all superhydrophobic. The anti-icing ability of all these superhydrophobic coatings were completely different. The coatings made with 20 and 50 nm diameter particles were completely icephobic. They concluded that critical radius of nucleating ice crystal is 21.6 nm. The probability of icing increases as the particle size increases beyond the critical particle diameter.

Jung et al. investigated the anti-icing ability of various surfaces ranging from hydrophilic to superhydrophobic [111]. The temperature of supercooled droplets and specimen surfaces was maintained at -20°C . They observed the longest freezing delay on hydrophilic surfaces with roughness ranging from 1.4 to 6 nm. They concluded that superhydrophobic surfaces with micro/nanostructured textures may not be the best choice for ice prevention purposes. These surfaces showed best ability to roll off the liquid water and proved a better choice against ice buildup on them.

Eberle et al. quantified the anti-icing ability of various surfaces by using ice nucleation temperature and ice nucleation delay time [112]. They found that ice nucleation temperature for both hydrophobic and hydrophilic surfaces is the same. The quasi-liquid layer at solid/liquid interface is the major reason for reduced ice

nucleation. Superhydrophobic surfaces with micro/nanostructures showed lower nucleation temperature than hydrophobic surfaces with nanostructures. The reason for this lower ice nucleation temperature is reduction in effective contact area of water droplets. They showed that superhydrophobic surfaces at temperature slightly above than ice nucleation temperature showed almost 25 h freezing delay in sessile droplets.

Alizadeh et al. investigated the ice nucleation and nucleation rate on the surfaces with variable wettabilities [113]. The combination of IR thermometry and high-speed imaging was used to detect the droplet freezing and observe the temperature of water droplets during phase transition. The delayed freezing was observed on superhydrophobic surfaces. The high contact angle on superhydrophobic surfaces resulted in increased free energy barrier and reduced water-substrate surface area, which delayed the water droplet freezing. They concluded that ice nucleation can be delayed by controlling surface texture and chemistry.

Suzuki et al. investigated the freezing of supercooled water droplets on silicon surfaces coated with various silane compounds [114]. The silicon surfaces were coated with fluoroalkylsilanes and alkylsilanes. Differential scanning calorimetry was used to investigate the freezing temperatures of supercooled water droplets. They concluded that fluoroalkylsilane coated surfaces suppressed the freezing of water droplets more than alkylsilane coated surfaces. They speculated that the interaction between water molecules and fluorocarbon resulted in this delayed freezing of water droplets.

Zhang et al. discussed both experimentally and numerically the effect of contact angle on freezing of sessile water droplets on cold surfaces [115]. The movement of ice/water interface and freezing process was recorded with CCD camera. The numerical and experimental results showed that the freezing time of sessile water droplets increases exponentially with contact angles.

Heydari et al. has investigated the water wettability and freezing delay of water droplets on a set of surfaces with similar chemistry but different surface topography [116]. The wettability of superhydrophobic surfaces was affected by temperature. The condensation of water and frost formation at lower temperature resulted in decrease in contact angle. They observed the same freezing delay for all surfaces.

They concluded that icing on superhydrophobic/hydrophobic surfaces is not controlled by surface topography. The ability to roll off the water droplets faster makes superhydrophobic surfaces important for anti-icing applications.

Varanasi et al. studied the impact of frost formation on the anti-icing ability of superhydrophobic surfaces [117]. The frost nucleation occurs indiscriminately over all surface textures of superhydrophobic surface without any preferences. They observed the anti-icing ability of superhydrophobic surfaces is greatly compromised by the frost nucleation over all surface. The ice adhesion strength increased linearly with surface area. Frost formation on superhydrophobic surfaces limits their use as icephobic surfaces in most on-ground and in-flight applications.

Wier et al. investigated the effect of water condensation on various ultra-hydrophobic surfaces [118]. They observed the condensation of water droplets on top of surface pillars and between them as well. The water droplets coalesce with condensed water on the surfaces and change its state from Cassie-Baxter to Wenzel. This water droplets pinning reduced their surface mobility. The water condensation on ultra-hydrophobic surfaces increases contact angle hysteresis. They concluded that a smooth surface can be used to overcome this water mobility and contact angle hysteresis problem.

Superhydrophobic surfaces have shown excellent water repellency due to their high contact angle and lower contact angle hysteresis. The ice formation on superhydrophobic surfaces can be prevented by increasing the free energy barrier to ice nucleation and by minimizing the contact time of falling water droplets with surfaces. The superhydrophobic surfaces having microscale textures showed the disadvantage of water condensation below the dew point. This disadvantage was reduced by decreasing the length scale of surface texture. However, the anti-icing properties of superhydrophobic surfaces were affected under extreme conditions of shear, pressure and humidity [99].

3.2.2 Slippery liquid infused porous surfaces (SLIPS)

Superhydrophobic surfaces have unprecedented ability to discard liquid water and impede ice accumulation. Despite all this, they are still plagued with a handful of problems that restrict their applications as anti-icing surfaces. These problems include failure under harsh conditions of humidity and pressure [15], failure upon

physical damage [16], lack of self-healing ability and production cost [15, 16]. To address all these shortcomings of superhydrophobic surfaces, Wong et al. introduced slippery liquid infused surfaces (SLIPS) with excellent self-healing ability, extremely low contact angle hysteresis and pressure stability. The lubricant fluid was infiltrated in micro/nanostructured substrates. These surfaces showed low contact angle hysteresis ($\leq 2.5^\circ$), low sliding angle ($\leq 5^\circ$) and performed at high pressures (676 atm). They showed the ability of SLIPS to repel various liquids such as water, oil, blood and hydrocarbons and to restore water repellency within 0.1-1 s upon mechanical damages. They concluded that the properties of SLIPS are independent of the underlying substrate geometrical structures [18].

Kim et al fabricated SLIPS on aluminum surfaces [19]. They formed SLIPS by electrodepositing polypyrrole on aluminum substrates then fluorination of coated substrates and filling with lubricant fluid. They compared the anti-icing ability of SLIPS with bare aluminum, hydrophobically modified and superhydrophobic aluminum. The contact angle hysteresis of SLIPS ($2^\circ \pm 1^\circ$) was significantly smaller than all other surfaces. The ability to remove the water of condensation was better for SLIPS. They observed a freezing delay of 100 minutes on SLIPS as compared to all other surfaces at higher relative humidity (60%) and lower temperature (-2°C). SLIPS showed 1-2 order of magnitude less ice adhesion strength than all other materials under consideration.

Kim et al. have studied the effect of surface roughness of the underlying solid substrate on the performance of SLIPS [119]. They used aluminum as substrate. Sandblasting was used to fabricate micro/nanostructures on aluminum substrate. The ability of these micro/nanostructures to retain lubricant under various shear rates was observed. The results showed that all coatings maintained low contact angle hysteresis ($<6^\circ$) at low shear rate (~ 1000 rpm). The coatings with micro and hierarchically textured surfaces showed increase in contact angle hysteresis with increase in shear rate. The coatings with nanostructured maintained low contact angle hysteresis ($<3^\circ$) at high shear rates (~ 10000 rpm). They concluded that nanotextured surfaces showed excellent nonwetting behavior and shear tolerance in contrast to the superhydrophobic surfaces which shows low contact angle hysteresis and pressure stability with hierarchically textured surfaces.

Anand et al. compared the water droplets condensation on superhydrophobic surfaces and SLIPS [20]. They fabricated liquid infused hierarchically textured substrate surfaces to reduce the pinning of water droplets. The lubricating fluid must be selected while considering the surface energies of all the phases in the system. The droplets with size less than 100 μm move faster on SLIPS than on micro/nanotextured superhydrophobic surfaces. The enhanced water droplet mobility is due to the reduced availability of solid fraction for droplet pinning. This enhanced mobility resulted in sweeping effect which makes these surfaces a best option for anti-icing applications.

Yao et al. investigate the ability of SLIPS to form a new class of adaptive surfaces [17]. The liquid lubricant was filled in porous elastic solid substrate. The surface changes its topography from a smooth surface to a rough surface upon the deformation of solid substrate. This mechanical stimulus changes the wettability of the surfaces. They observed that the application of strain increased the sliding angle of water droplets due to exposed roughness and pinning of water droplets. They suggested that stimuli response can be finely tuned by increasing the amount of lubricant amount. The selection of lubricant and pore structures can affect the surface properties.

Rykaczewski et al. investigated the frost formation on micro/nanostructured superhydrophobic and perfluorinated oil infused surfaces [21]. The detailed analysis was conducted by using cryogenic scanning electron microscopy. The frost formation was observed at $-10\text{ }^{\circ}\text{C}$ and relative humidity of 25%. The liquid infused surfaces showed excellent anti-frosting ability. The self-healing ability of these surfaces made them better choice for anti-frosting applications. However, after some frosting/defrosting cycles these surfaces have lost their self-healing ability. The reason for this loss was the migration of lubricant oil onto the water droplets. They observed that microstructured liquid infiltrated surfaces lost their self-healing ability in one frosting/defrosting cycle. But nanostructured liquid infiltrated surfaces lasted for two frosting/defrosting cycles. They emphasized that further research is needed to overcome frosting problems in SLIPS. They suggested for better lubricant and textured surface pairs to limit this frosting.

3.2.3 Strategies based on anti-icing agent release

Ice formation can be delayed/prevented using freezing point depressants such as salts or other small molecules. These freezing point depressants decrease the chemical potential of water. As we increase the amount of freezing point depressant, the chemical potential of water decreases more. These properties depend on the amount of freezing point depressants and so termed as colligative properties.

Sun et al. developed a new anti-icing coating that secretes anti-icing agent upon accumulation of ice on the surface [120]. They combined an outer superhydrophobic surface with an inner porous hydrophilic membrane filled with anti-icing agent. Under dry conditions, the surface behaves as an ordinary superhydrophobic surface which sheds liquid drops. However, in conditions of high humidity and pressure, superhydrophobic surfaces easily covers with ice, the coating structure responds by releasing antifreeze liquid. This antifreeze liquid mix with water and prevents ice accumulation on the surface. They observed that the presence of lubricating water layer between ice and coating surface reduced the adhesion strength of ice.

Kanyas et al. studied the freezing delay of water droplets on a composite surface by the release of Potassium formate (KCOOH) salt [121]. They observed the freezing delay of 70 minutes at -14 °C plate and -5 °C chamber temperatures. They concluded that this freezing delay of water droplets is due to release of salt molecules from the composite surface. These salt molecules decrease the chemical potential of water and increase the freezing delay. They observed that the increase in the amount of nanoparticles have a negative effect on freezing delay of water droplets. This group further used these polymeric composites and modified bitumen. They investigated the anti-icing ability of composite modified bitumen. The anti-icing properties were investigated in humidity and temperature-controlled chamber. They observed that modified bitumen showed longer freezing delay than unmodified bitumen. They further demonstrated the release of anti-icing agent from the modified bitumen. The amount released was in range of 1.07-10.8% (w/w) in 67 days.

Ayres et al. synthesized a new anti-icing coating system [122]. This system is based on titanium alkoxide sol gel coatings. These coatings showed a mass loss of 25% as compared to 85% for isolated sol-gel systems. The addition of organic groups in the system helps in slowing the release of glycerol and tripropylene glycol from the coating surfaces.

The icing problem can be prevented by synthesizing composite systems based on the release of anti-icing agents. The ionic salts and glycols were mostly used anti-icing agents in these systems. The release of anti-icing agent decreases the chemical potential of water that resulted in freezing delay of water droplets. The fast release of anti-icing agents from the coating systems is a limitation in their longer-term durability. The anti-icing ability of anti-icing agent releasing coatings is affected by physical damage. In addition to this, the anti-icing ability of these coatings cannot be restored by refilling the anti-icing agents.

3.2.4 Glycols as anti-icing agents

Ethylene glycol and polypropylene glycol are the most common used anti-icing agents in anti-icing applications [123]. Ozbay et al. compared the anti-icing ability of hydrophilic and hydrophobic liquids impregnated in hydrophilic filter papers and hydrophobic mat respectively [124]. The results indicated that hydrophilic surfaces filled with hydrophilic liquids are better choice for anti-icing applications. These surfaces decreased both ice adhesion strength and ice accretion at -2 °C temperature. They used ethylene glycol and glycerine as hydrophilic liquids.

Polyethylene glycol (PEG) is a biocompatible, water soluble, biodegradable and commercially available polymer. Inada et al. investigated the anti-ice nucleating properties of PEG [125]. They studied the effect of anti-ice nucleating ability of anti-freezing proteins, poly vinyl alcohol (PVA) and PEG on the ice nucleation ability of silver iodide particles. The heterogenous ice nucleation activity of silver iodide was completely inactivated by anti-freeze proteins which are already used for this purpose, also by PEG and PVP. They observed that silver iodide possesses discrete nucleation sites and these polymers adsorbs on those sites and inhibit ice nucleation process.

Zobrist et al. studied the melting and ice nucleation temperatures by differential scanning calorimetry [126]. They demonstrated the freezing behavior of aqueous PEG solution with the help of ice nucleation theory based on water activity data. They compared the water activity of various PEG solutions. The results showed that water activity of PEG solutions decreases with temperature. They used PEG with different molar masses. The decrease in water activity was stronger as the molar mass of PEG increases. This decreased water activity resulted in longer supercooling

of PEG water solutions. They concluded the existence of liquid phase spinodal controls the ice nucleation in aqueous solutions.

Micheltmore et al. determined the rates of ice nucleation as function of temperature in PEG aqueous solutions and undercooled water by differential scanning calorimetry [127]. They observed that PEG decreased the freezing temperature of water. They concluded that PEG acts as cryoprotectant by affecting the diffusional motion of water molecules.

Vringer et al. investigated the solution properties of aqueous PEG 1550 by differential scanning calorimetry [128]. They cooled the PEG solutions down to -60 °C and then heated to 90 °C. They observed a secondary melting around -16 °C due to the melting of PEG and water eutectic mixture. They also observed hydrogen bonding between etheric oxygen of ethylene glycol unit with 2 water molecules. This hydrogen bonded water molecules did not freeze till -60 °C.

PEG is a non-toxic and commercially available compound. PEG is an effective anti-icing agent. PEG decreased the freezing temperature of water either by effecting the diffusional motion of water molecules or by making hydrogen bonds with water molecules through etheric oxygen present in PEG. PEG is not much used in release based composite coatings as anti-icing agent.

3.2.5 Diatomaceous earth as a filler material

Diatomaceous earth (DE) is very fine grained, soft and earth sedimentary rock. It is light brown in color and chemically inert. DE is biocompatible and inexpensive natural material with micro/nano porous structure. DE have been immensely used in applications including drug delivery, gene delivery, bio sensing, complex structure formation and as adsorbent materials [129-131].

Puretskiy et al. synthesized superhydrophobic surfaces by using diatomaceous earth particles. They grafted thin polymer layers on top of these diatomaceous earth. The anti-icing ability of these superhydrophobic surface/es was investigated. They concluded that the hierarchical shape of these diatoms helped in achieving the required superhydrophobic characteristics [132].

Sedai et al. developed superhydrophobic surfaces by using three different type of diatomaceous earth particles. They used polystyrene as matrix material for these

Anti-Icing Composites

composite coatings. They treated DE with 3-(heptafluoroisopropoxy)propyltrimethoxysilane (HFIP-TMS). The superhydrophobic properties of all these coatings were investigated by contact angle measurements. They calculated the minimum amount of DE particles required for superhydrophobicity [133].



3.3 Materials, Methods and Techniques

In this section the materials and methods used to synthesize polymer/micro- and nano-particles composite films filled with anti-icing agents will be introduced.

3.3.1 Polymer/silica-based fillers composites containing anti-icing agent

3.3.1.1 Materials

Styrene-Butadiene-Styrene (SBS) triblock copolymer with 30% styrene content and number average molecular weight of 140,000 g/mol was used as polymeric matrix. SBS is normally used as an additive to enhance mechanical properties of asphalt as well as in construction and automotive sectors. SBS was kindly supplied by Arçelik company. The anti-icing agents and reference material used in this work are tabulated with their properties (Table 3.1). The properties of porous fillers used for filling the polymer matrix in this study are shown in table 3.2. Mesoporous silica particles were synthesized from TEOS and Pluronic F127 by using HCl acid as a catalyzer. Acetone, diethyl ether and chloroform were purchased from Merck. Untreated DE, bismuth nitrate (BiONO_3), hydrochloric acid (HCl), Potassium iodide (KI) were bought from Sigma Aldrich.

Table 3.1 Properties of anti-icing agents used in this work with their specifications.

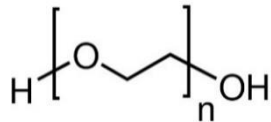
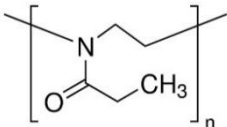
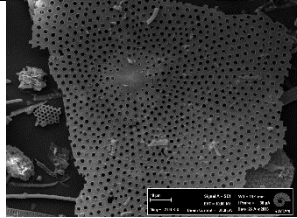
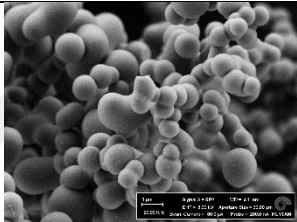
Anti-icing agent	Molecular weight (g/mol)	Chemical structure	Company
Polyethylene glycol (PEG)	600 2000 10000		Merck
Ethylene glycol (EG)	62	$\text{HOCH}_2\text{CH}_2\text{OH}$	Sigma Aldrich
Poly-2-ethyl-2-oxazoline (PEOX)	5000		Sigma Aldrich

Table 3.2 Properties of silica-based fillers used in this work with their specifications.

Fillers	Specific surface area (m ² /g)	Particle size (μm)	Shape	Company
Diatomaceous earth	35 [134]	14 [135]		Sigma Aldrich
Silica nano/micro particles	428	1.2		Self-synthesis

3.3.1.2 Sample preparation

3.3.1.2.1 Investigation of anti-icing agent intake ability of DE

The anti-icing agent intake ability of DE pores was determined by filling EG, PEG-2K and PEOX-5K in acetone solutions. 0.2 g of DE was placed in 2 mL solution of 30 volume% EG, 0.3g/mL PEG-2K or 0.3 g/mL PEOX-5K in acetone. These dispersions were left in shaker at 200 rpm for 24 h. The samples were then centrifuged. The sediments were re-dispersed in acetone and centrifuged to remove the physically adsorbed anti-icing agent from the surface of DE. This purification process was repeated twice. The product was dried in open atmosphere. The amount of anti-icing agents incorporated in DE pores was determined by thermogravimetric analysis (TGA).

3.3.1.2.2 Composite preparation

To prepare DE/SBS composite, SBS (100mg/mL) was dissolved in chloroform to prepare stock solution. DE was dispersed in SBS stock solution to obtain 30 mass % of DE in final composites. The sample solution was shaken at 900 rpm for 24 h to get homogeneous dispersion. Solvent casting method was used to prepare free standing composite films. The DE/SBS dispersion was dispensed on 6 x 4.5 cm² Teflon

templates. Composite were ready after 24 h drying in open atmosphere. The thickness of these free-standing DE/SBS composite is approximately 0.2 mm.

3.3.1.2.3 Loading of anti-icing agent in DE/SBS composites

The anti-icing agents (EG, PEG and PEOX) were loaded in DE/SBS composite by dipping the free-standing film in anti-icing agent solution in acetone or diethyl ether/acetone binary mixture. The binary solvent mixture of acetone and diethyl ether was carefully chosen to fill the pores of DE with anti-icing agent in free standing composite films. SBS is dissolved in diethyl ether and it is not soluble in acetone. The binary solvent mixture of acetone/ diethyl ether (30/70 by volume) gives maximum swelling of DE/SBS composites. Anti-icing agent are soluble in this binary solvent mixture. The penetration of anti-icing agents containing solvents into swollen SBS allowed filling of pores of DE in composite films.

EG and PEG-600 were dissolved in binary solvent mixture up to 50% by volume. PEG-2K, PEG-10K and PEOX-5K were dissolved in binary mixture up to 0.5 g/mL. Composite films were dipped in these solutions for 24 h at room temperature. These composites were removed and rinsed by water to remove any loosely adsorbed molecules. The anti-icing agent loaded composite films were then dried for 24 h.

3.3.2 Characterization

3.3.2.1 Thermogravimetric analysis

The compositions of DE and anti-icing agents were analyzed by thermogravimetric analysis. Thermogravimetric measurements were carried on TA instruments Q500. The samples were heated with 10 °C/min from room temperature to 700 °C under 40 mL/min of continuous air flow.

3.3.2.2 Scanning Electron Microscope

Field emission scanning electron microscope (ZEISS Ultra Plus SEM) was used to analyze the filled DE pores with anti-icing agent and surface morphology of the DE/SBS composites. The elemental composition was determined by Energy-dispersive X-ray (EDX) spectroscopy in SEM. DE/SBS composite samples for SEM were coated with a very thin layer (10 nm) of gold metal to make them conductive. The gold layer was deposited using a sputter coater (Cressington 108).

3.3.2.3 Wettability measurements

The wettability of composite films was analyzed by using optical contact angle system (OCA 20, DataPhysics). The contact angles were measured between 25 °C and -10 °C. Water droplets having 4 μL volumes were placed onto 1 x 2 cm^2 substrates in three distinct positions to obtain average static contact angle value.

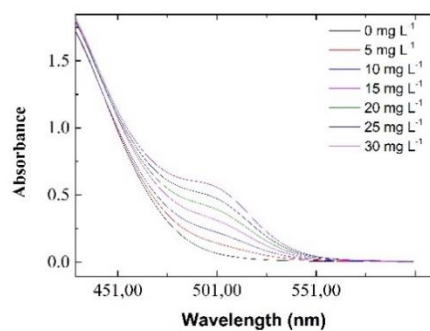
3.3.2.4 Freezing experiments

Freezing experiments as function of temperature were also carried out in optical contact angle system. The samples were placed in the cell at room temperature. Then the cell temperature was decreased down to measurement temperature (-12 to -15 °C). Water droplets having 4 μL volumes were placed onto the composite surface after the measurement temperature was stabilized. The freezing time of all the droplets was determined using a video camera.

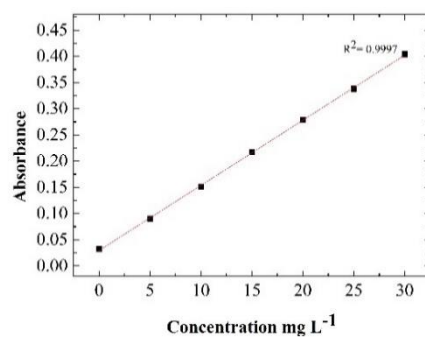
3.3.2.5 Anti-icing agent release from DE/SBS composite films

The amount of PEG released from the DE/SBS composite films into water was determined by UV-VIS spectroscopy using modified Dragendorff method [136]. The modified Dragendorff method is more susceptible for higher molecular weight PEG, thus PEG-10k was used as anti-icing agent for release experiments.

To prepare Dragendorff reagent (DR) solution [136], solution 1 was prepared by dissolving 0.8 g of BiONO_3 in 50-mL 1 M HCl and solution 2 was prepared by dissolving 20 g of KI in 50 mL of deionized water. Then 5 mL of solution 1 and 5 mL of solution 2 was added into a 100-mL brown volumetric flask and diluted to volume with distilled water. The addition of PEG in DR resulted in an orange red complex formation. This complex is detected at 514 nm wavelength with UV-VIS spectrophotometer. The calibration curve was prepared by measurements of solutions prepared by adding 5mL of aqueous PEG-10 solutions of known concentrations (5-30 mg/L) into 3 mL of 0.05 M HCl and 1 mL of DR respectively and filling it to 10 mL with DI water. Fig. 3.1 shows the calibration curve using PEG-10k in DR solution. The amount of PEG-10K released from the loaded DE/SBS composites was determined by keeping the composites in fixed amount of deionized water at room temperature, sampling 5 mL aliquots at different time intervals and measuring the absorbance by UV-VIS spectroscopy after adding DR.



(a)



(c)

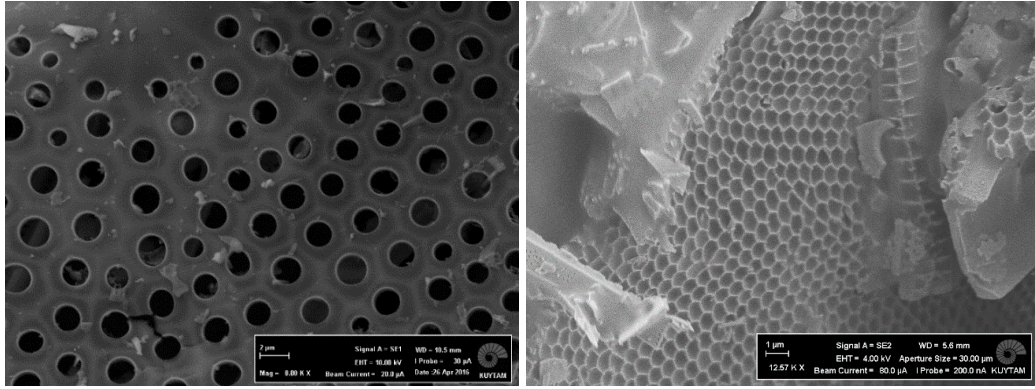
Fig. 3.1 Calibration for PEG-10K into water by UV-Visible spectroscopy using modified Dragendorff method: (a) Absorption spectra of the orange red complex formed by mixing PEG-10K at various concentrations and DR. (b) Calibration curve for PEG-10K at 514 nm wavelength.

3.4 SBS/DE composites for anti-Icing applications

The anti-icing agent filled DE/SBS composites have been prepared as novel anti-icing agent releasing surfaces for anti-icing applications. The release of the anti-icing agent from the porous DE particles upon contact with water decrease the freezing temperature of the water and thus prevents ice formation. Diatomaceous earth has been used as anti-icing agent carrier due to its porous structure in hydrophobic styrene-butadiene-styrene matrix. Ethylene glycol and polyethylene glycol have been used as anti-icing agents. These anti-icing agents were successfully infused in DE/SBS composite coatings. The anti-icing ability of these coatings was characterized by freezing delay of water droplets on these composite surfaces. Surface wettability of these coatings was investigated by contact angle measurements on these composite surfaces and its relationship with anti-icing filling in composite coatings was inferred. These coatings can be synthesized with variable thickness. These coatings have an advantage of maintaining the anti-icing agent at the top surface even if the coating is damaged by scratches.

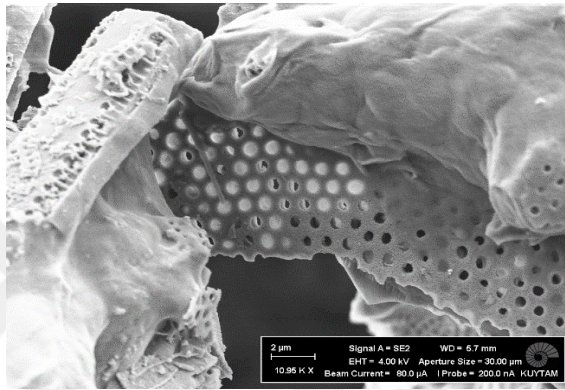
3.4.1 Investigation of anti-icing agent intake capacity of DE pores

Polyethylene glycol and ethylene glycol were used as anti-icing agents. Poly(2-ethyl-2-oxazoline) (PEOX) was also used as a pore filling agent. PEOX contains nitrogen that can be easily detected by EDX analysis from diatomaceous earth pores. The particles of DE usually had very irregular shapes but dominated by planar flakes. These flakes contain rows of holes perpendicular to the surface of plane. SEM image of untreated diatomaceous earth particles under high magnification in Fig. 3.2(a) shows the presence of empty pores having micrometer size diameters. The DE particles were dipped in anti-icing/pore filling agent solutions in acetone for 24 h. Then the particles were separated by centrifuging. The particles of DE were filled by anti-icing agents. Fig. 3.2(b) shows PEOX-5K filled DE pores and Fig. 3.2(c) shows pores of DE filled with PEG-2K. The filling of DE pores in case of PEG-2K and PEOX-5K shows the favorable interaction of these hydrophilic agents with DE pores. The EDX analysis was performed on the DE samples containing PEOX-5K. The results are shown in Fig. 3.3. The presence of nitrogen peak at 0.39 keV showed that pores of DE are filled with PEOX-5K. The results taken on the PEOX containing model system indicated that filling the DE pores with PEG has a good potential. This result suggests that pores of DE in Fig. 3.2 (c) are filled with PEG.



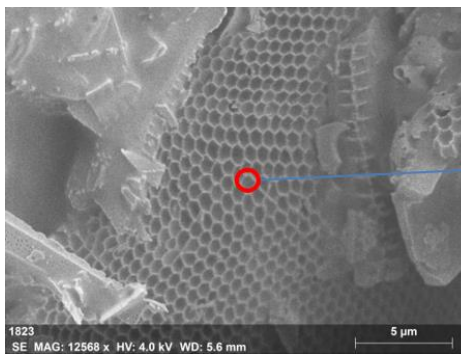
(a)

(b)

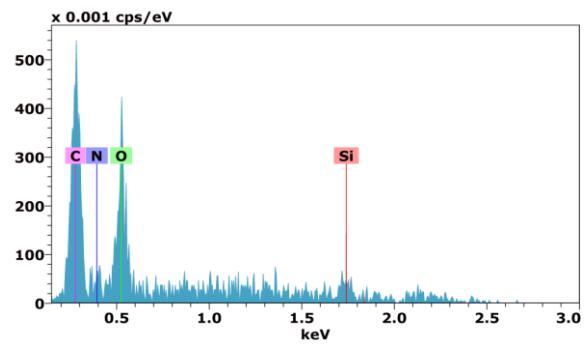


(c)

Fig. 3.2 SEM pictures for a) untreated diatomaceous earth particles, b) diatomaceous earth particles centrifuged with PEOX-5K and c) diatomaceous earth particles centrifuged with PEG-2K. The pores of diatomaceous earth particles are filled in case of PEOX and PEG loading. This image is taken from reference [137].



(a)



(b)

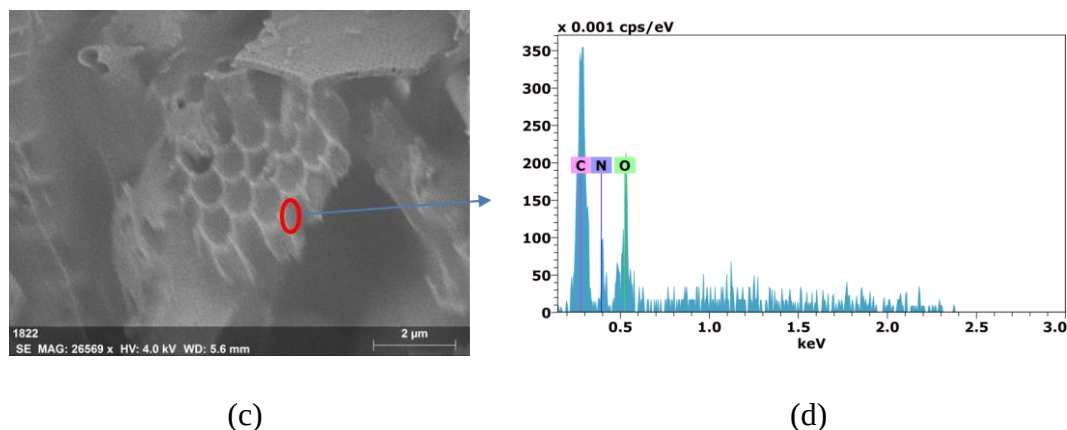


Fig. 3.3 Scanning electron microscope micrographs (a, c) and EDX analysis (b, d) for diatomaceous earth particles kept in PEOX-5K solution in acetone and centrifuged. The red arrow shows the point where EDX analysis was performed. The presence of nitrogen peaks in EDX results confirms the filling of DE pores with PEOX. This image is taken from reference [137].

The amount of EG, PEG-2K and PEOX-5K filled in the pores of DE pores was determined by TGA analysis. The weight loss curves of unreacted DE and DE filled EG, PEG-2K and PEOX-5K are shown in Fig. 3.4 The amount of anti-icing agents and PEOX were determined by the difference between weight losses of untreated diatomaceous earth and their respective mixtures.

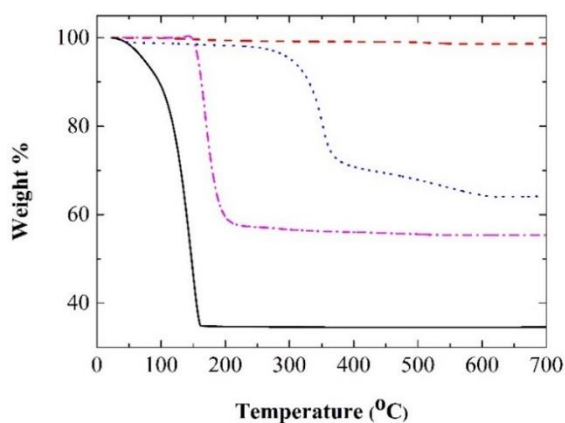
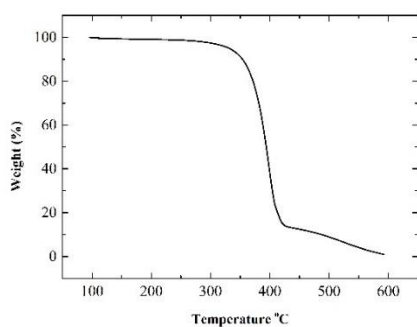


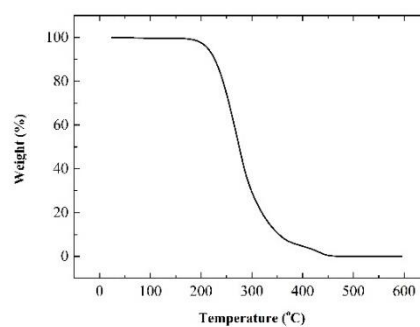
Fig. 3.4 TGA plots showing weight losses for untreated DE particles (dashed line), DE Particles filled with PEOX-5K (dotted line), DE particles filled with PEG-2K and DE particles filled with EG (solid line). The amount of anti-icing agents and PEOX were determined by the difference between mass losses of untreated diatomaceous earth and their respective mixtures. This image is taken from reference [137].

The thermogram of untreated diatomaceous earth particles showed mass loss (1.2%) in two different regions. The first mass loss, in temperature range of 90-180 °C was likely due to the loss of physically bound water molecules and removal of some hydroxyl groups present in diatomaceous earth particles. The second mass loss in the temperature range of 350-600 °C is expected due to various inorganic substances such as Al_2O_3 and Fe_2O_3 present in diatomaceous earth particles [138]. The thermogram of DE particles filled with PEOX-5K showed mass loss of 35% at 350 °C which is the decomposition temperature of PEOX-5K as shown in Fig. 3.5 (a). This mass loss was due to the decomposition of physically adsorbed PEOX molecules in DE particles. The thermograms of DE particles filled with PEG-2K showed mass loss of 42% at decomposition temperature (200 °C) of PEG-2K. The decomposition temperature of PEG-2K is shown in Fig. 3.5 (b). The DE filled with EG showed a mass loss of 65% in the temperature range of 50-140 °C. This range is consistent with decomposition of EG as shown in Fig. 3.5 (c).

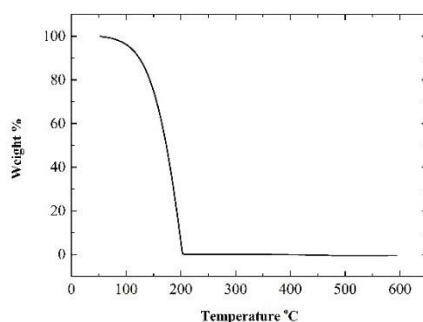
Considering that PEOX-5K, PEG-2K and EG have same density and assuming all the molecules are in the pores of DE particles, these TGA results indicate that most pores are filled in case of EG and least in case of PEOX-5K. This difference in pore filling can be attributed to the kinetic effects related to the molecular sizes. Smaller molecule will easily go into the pores of diatomaceous earth which results in more pore filling. The difference in hydrophilicity of these molecules can also affect the pore filling. The adsorption of these molecules on the flat surfaces of DE particles can contribute to the mass loss. The contribution due to the adsorption will be smaller considering that the pore surface area will dominate the interfacial area compared to flat surfaces.



(a)



(b)



(c)

Fig. 3.5 TGA characterization of the anti-icing agents used showing the weight loss as a function of temperature: a) PEOX-5K, b) PEG-2K, c) EG. This image is taken from reference [137].

3.4.2 Investigation of pore filling of DE and DE/SBS composites

The anti-icing agents were incorporated into the pores of DE in DE/SBS composites with a different method due to the chemical incompatibility of hydrophilic anti-icing agents and hydrophobic SBS. The DE/SBS composite films of 0.2 mm thickness were synthesized by solvent casting method. The solvent casted films were dipped into EG, PEG or PEOX containing solutions at various concentrations in binary mixture of diethyl ether/acetone. SBS is soluble in diethyl ether and insoluble in acetone. The anti-icing agents (EG, PEG or PEOX) were soluble in binary mixture. The binary mixture was used to swell SBS so that anti-icing agents could be carried to the pores of DE particles in DE/SBS composite. The composite coatings were removed from the solution of anti-icing agent/binary mixture after 24 h. The films were rinsed with distilled water to remove any excess solvent from the surface and then dried in open air. To investigate the filling of DE pores with anti-icing agent in DE/SBS composite coatings, the dried films were cut with liquid nitrogen. The fractured cross sections of DE/SBS films were characterized by SEM. The SEM images at the cross section of PEG-2K filled DE/SBS composite films are shown in Fig. 3.6. The SEM image in Fig. 3.6 (a) shows that most pores of DE particle are filled while few of them are partially filled. The image in Fig. 3.6 (b) shows the embossed pattern of pores of DE particles which indicates that the DE particle may be fractured during nitrogen cutting of composite coatings. The presence of PEG in

pores of DE particle cannot be confirmed by EDX analysis because the elements in PEG (O, H, C) are same as those in SBS (H, C) and DE (Si, O).

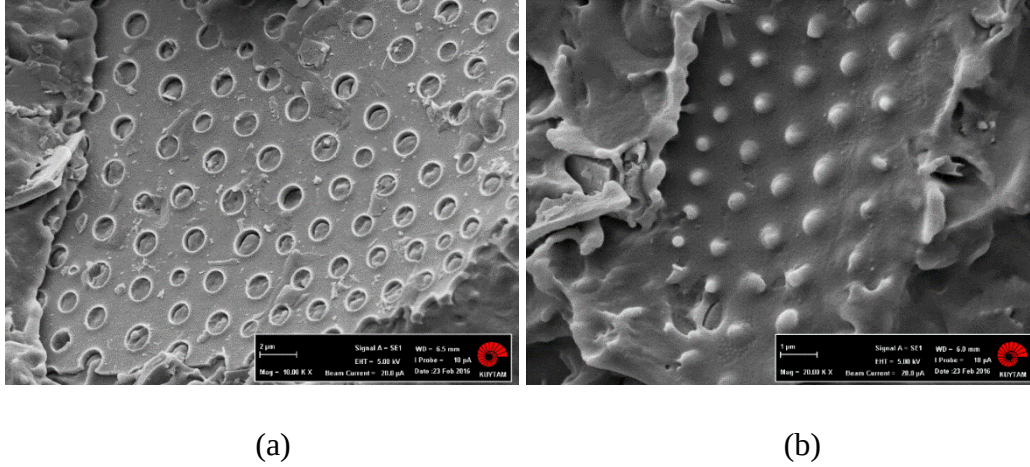
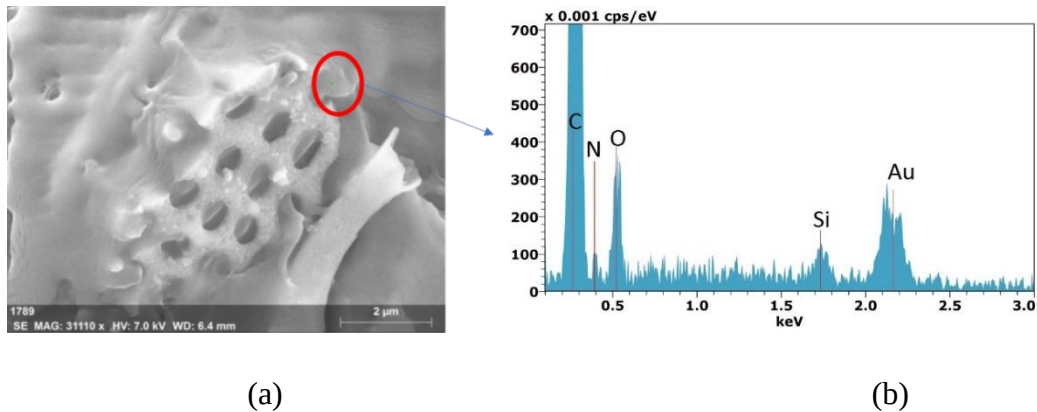


Fig. 3.6 Scanning electron microscope images of PEG-2K filled DE/SBS composite films. To confirm that the pores of DE are filled with hydrophilic anti-icing agents, PEOX-5K was incorporated into the DE/SBS composite films by same loading process.

The SEM images at the cross section of PEOX-5K loaded DE/SBS composite coatings are shown in Fig. 3.7. The SEM image in Fig. 3.7 (a) shows the pores of DE particle are filled. The SEM image in Fig. 3.7 (c) shows similar embossed pattern of pores of DE particle as shown in Fig. 3.7 (b). The EDX spectrum of the material filled in pores and that raised pattern is shown in Fig. 3.7 (b, d). The presence of Nitrogen peaks at 0.39 keV along with oxygen (0.53 keV), carbon (0.28 keV), silicon (1.73 keV) and gold (2.10 keV) confirms that the pores of DE particles in DE/SBS composite were filled with PEOX.



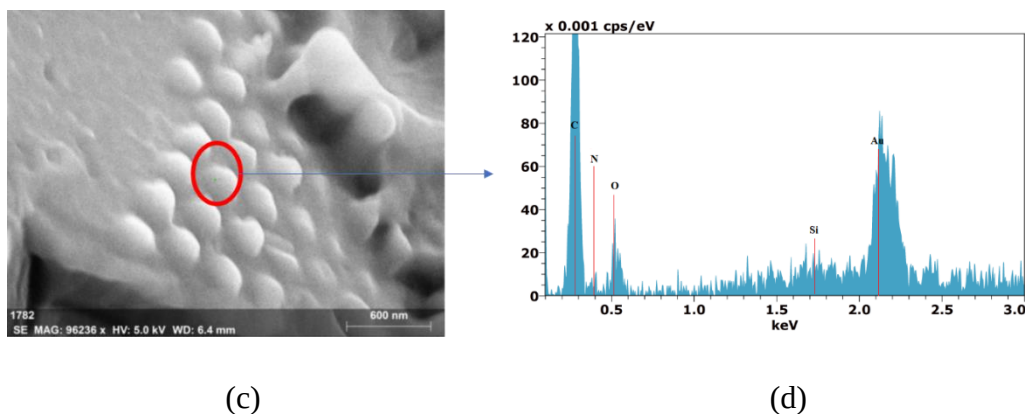


Fig. 3.7 Scanning electron microscope images (a,c) and EDX analysis (b,d) of PEOX-5K filled DE/SBS composite films. The red arrow shows the point where EDX analysis was performed. The presence of nitrogen peaks in EDX results confirms the filling of DE pores with PEOX.

The thermodynamic incompatibility of anti-icing agent and SBS and favorable interaction between hydrophilic anti-icing agents and DE particles cause the anti-icing agents to fill the pores of DE. There is a probability that anti-icing can be kinetically trapped in the hydrophobic SBS matrix after the loading and drying process. However, the phase separated domains of anti-icing agent in SBS matrix were not observed with SEM analysis.

3.4.3 Loading of anti-icing agents in DE/SBS composite coatings

Anti-icing agents (EG or PEG-600) were loaded in DE/SBS coatings by swelling the composite coatings in acetone/diethyl ether binary mixtures. The amount of EG or PEG-600 retained in DE/SBS composite coatings was determined both gravimetrically and thermogravimetrically. The composite coatings were having 30% by mass DE in SBS matrix. Figure 3.8 shows the gravimetrically determined mass fraction of EG or PEG-600 retained in DE/SBS coatings as function of concentration of these anti-icing agents in binary solvent mixture in which these composite coatings were dipped for 24 h. The mass fraction of EG retained in DE/SBS composite coatings was 0.004 at 2.5% by volume of EG in binary mixture. This retained mass fraction of EG in DE/SBS composites gradually increased and reached to 0.04 at 40% by volume of EG in binary solvent. The mass fraction of PEG-600 retained in DE/SBS composite coatings also increased with increased amount of PEG-600 in binary solvent mixture. The mass fraction of PEG-600 retained in composite coatings is almost 1.5 times that of EG at same anti-icing

concentration in dipping solution. The effect of swelling agent on the ability of composite coatings to retain anti-icing agent was investigated gravimetrically. The DE/SBS coatings were dipped in EG solutions in acetone only. The concentrations of EG selected were 30% and 40% by volume in acetone. Fig. 3.9 shows the comparison of mass fraction of EG retained in DE/SBS composite coatings dipped in EG solution in acetone and binary solvent mixture as function of drying time of loaded composite coatings in open air.

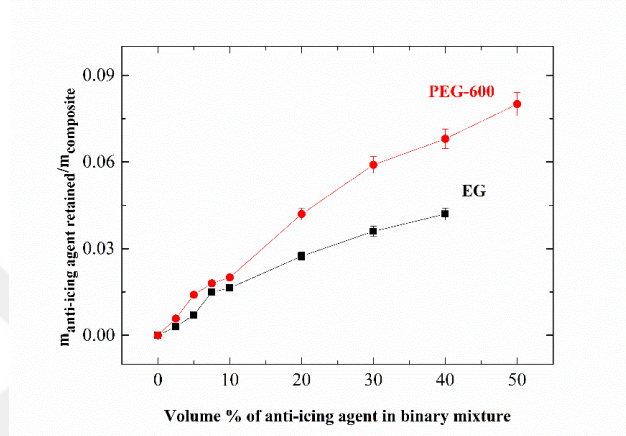


Fig. 3.8 Mass fraction of EG/PEG-600 retained in DE/SBS composite coatings dipped in binary solvent mixture for 24 h then rinsed and dried in air as a function of concentration of EG or PEG-600 solutions. The amount of EG/PEG-600 retained in coatings increases with increased amount of EG/PEG-600 in dipping solutions. This image is taken from reference [137].

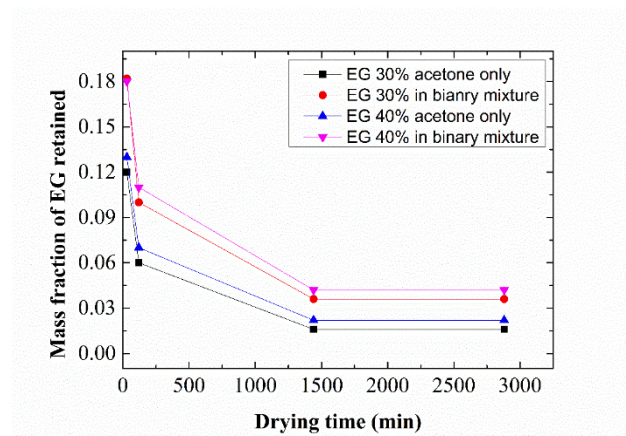
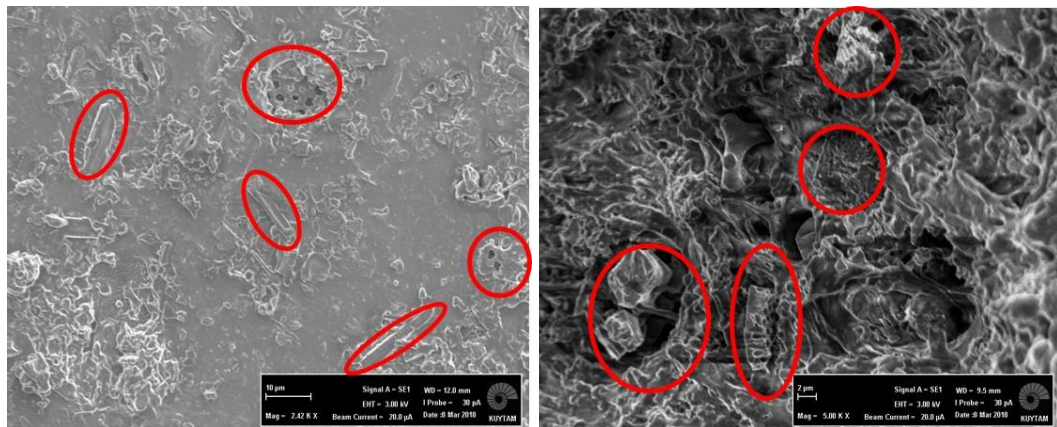


Fig. 3.9 Comparison between the mass fraction of Ethylene glycol retained by composite coatings dipped in anti-icing agent solutions (EG is dissolved in acetone and binary solution containing acetone and diethyl ether separately) for 24 h and then dried in open air for 24 h. The amount of EG retained in coatings is more in case of binary solvent.

The amount of EG retained in coatings dipped in acetone only was 1.6% at 30% by volume EG concentration and 2.2% in 40% by volume EG concentration compared to 3.6% and 4.2% respectively for coatings dipped in binary solvent mixture. These results showed that swelling of SBS by diethyl ether in binary mixture resulted in more EG intake into the DE/SBS coatings. This increase in amount of EG in binary solvent can be due to the penetration of EG into the DE pores which were buried deeper in the composite coatings. But in case of acetone only the coating is not swollen so the pores exposed onto the surface can be filled by EG. Fig. 10 shows the SEM images of surface and cross section of DE/SBS composite coatings. The distribution of DE particles in SBS matrix is visible in these images. Fig. 10 (a) shows the DE particles exposed to the surface. These particles can be easily filled by anti-icing agents. Fig. 3.10 (b) shows the cross-section of DE/SBS composites. The distribution of DE particles in SBS matrix is random. The swelling of SBS matrix by diethyl ether in binary solvent can fill these randomly distributed DE particles in the composite. The filling of these inner DE particles or physical entrapment of anti-icing agent in SBS matrix can enhance the mass fraction of anti-icing agent loaded in coatings exposed to binary solvent.



(a)

(b)

Fig. 3.10 SEM images of DE/SBS composite coatings, (a) surface of the coating, (b) cross section of the coating. The red circles in the image highlights the DE particles in SBS matrix. This image is taken from reference [137].

In order to investigate the maximum amount of anti-icing agent that can be retained in the composite coatings, the coatings were dipped in different concentrations of

anti-icing agent containing binary solvent mixture. The amount of PEG retained in DE/SBS coatings is more than the amount of EG retained in the composite coatings, so PEG-600 was used for this experiment. The maximum mass fraction of anti-icing agent retained in coatings was determined by dipping them in PEG-600 solution of 30-60% by volume concentration in binary mixture. Fig. 3.11 shows the mass fraction of PEG-600 retained in composite coatings as function of concentration of PEG-600 in binary solvent mixture. The mass fraction of PEG-600 retained in coatings was 0.06 at 30% concentration by volume and increased up to 0.08 at 50% concentration but then decreased to 0.059 at 60% by volume concentration of PEG-600. The amount of PEG-600 retained by coatings dipped in 60% (v/v) PEG solution is less as the amount of swelling agent dipping solution is decreased to 40 % (v/v). This decrease in swelling agent amount to 40 % (v/v) might affected the swelling of polymeric matrix. These results suggested that the maximum amount of anti-icing agent can be retained at 50% by volume concentration of both anti-icing agent and swelling agent in dipping solution.

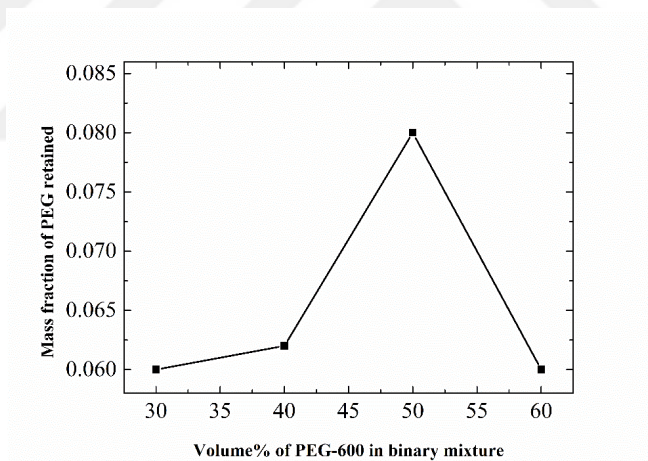


Fig. 3.11 Mass fraction of PEG-600 retained in DE/SBS composite coatings dipped in binary solvent mixture as function of concentration of PEG-600 solutions for 24 h and then rinsed and dried in air. The maximum amount of PEG-600 retained in coatings was at 50% by volume concentration of PEG-600 in binary mixture.

The amount of anti-icing agent retained in DE/SBS composite coatings was determined thermogravimetrically as well. The DE/SBS coatings were dipped in PEG-600 solutions in binary mixture. The concentrations of PEG-600 selected were 10%, 30% and 50% by volume in binary mixture. Fig. 3.12 shows the thermograms of PEG-600 loaded SBS/DE composite coatings.

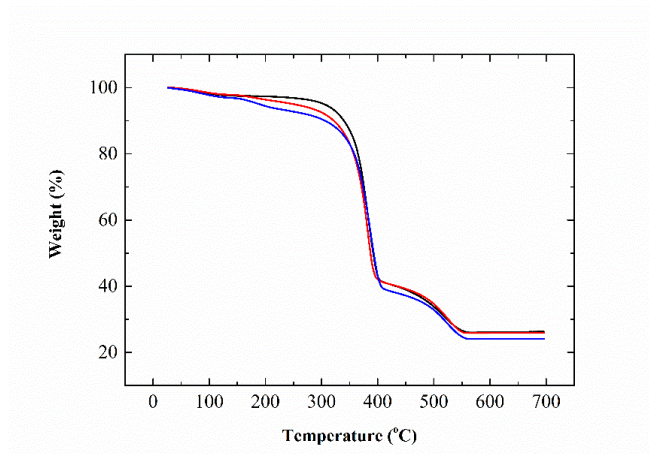


Fig. 3.12 TGA characterization of the anti-icing agent filled DE/SBS composites showing the weight loss as a function of temperature: DE/SBS filled in 10 v% PEG-600 (black line), DE/SBS filled in 30 v% PEG-600 (red line), DE/SBS filled in 50 v% PEG-600 (blue line). This image is taken from reference [137].

The thermograms of PEG-600 filled shows the mass loss as function of temperature. The weight loss at 250 °C is attributed to the amount of PEG, since the decomposition of PEG is completed at this temperature. The amount of PEG retained increases as the PEG concentration in binary mixture increases. The mass loss in the temperature range of 400-550 °C was attributed to the loss of SBS from DE/SBS composite coatings. The amount of PEG-600 was calculated to be 3.24% at 10% filling concentration, 5.25% at 30% filling concentration and 7.82% at 50% filling concentration. The amount of PEG-600 retained in DE/SBS composite coatings were determined both gravimetrically and thermogravimetrically. The amount determined by both methods were compared and shown in table 3.3. The results obtained by thermogravimetric and gravimetric method are almost same.

Table 3.3 Comparison of mass fraction of PEG-600 retained in DE/SBS composite coatings.

Volume % of PEG-600 in binary mixture	Amount of PEG-600 retained (gravimetrically)	Amount of PEG-600 retained (Thermogravimetrically)
10	2.0%	3.25%
30	5.90%	5.25%
50	8.0%	7.82%

The DE/SBS composite coatings were prepared by mixing 30% by mass DE in SBS matrix. This composition of these coatings was same throughout our research work

for anti-icing composite coatings. The amount of DE in SBS matrix is the same as shown by thermogravimetrically results of SBS/DE composite coatings filled with PEG-600. The amount of sample left after TGA characterization is almost 25% in all these coatings as shown in Fig. 3.12.

3.4.4 Surface wettability of anti-icing agent loaded DE/SBS composite coatings

The surface wettability of the DE/SBS composite coatings was investigated by contact angle measurements of water droplets as function of temperature. The temperature range was chosen between 25 °C and -10 °C for these experiments. The water contact angles of bare glass slides and SBS films were used as controls. The evolution of water contact angles on anti-icing agent loaded composite coatings and controls as function of plate temperature is shown in Fig. 3.13.

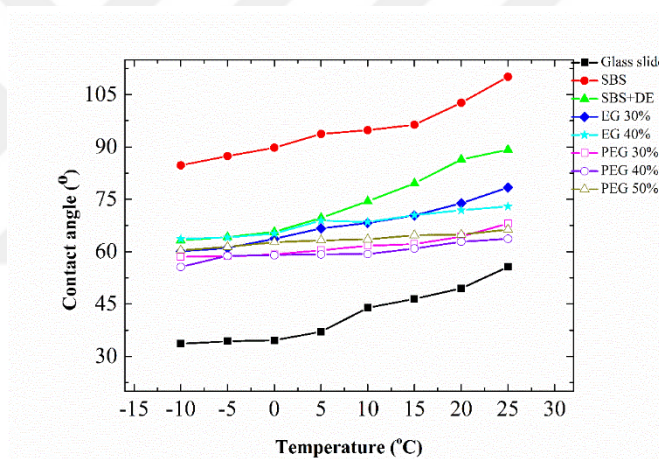


Fig. 3.13 Change in water contact angles on composite coatings (dipped in anti-icing agent solutions of various concentration in binary mixture and dried) as a function of plate temperature. The hydrophilicity increased by decreasing plate temperature. In several cases, the standard deviations of the measurements were between 0.2-1.2°. This image is taken from reference [137].

The contact angles of water droplets on the bare glass slides gradually decreased from 55° at 10 °C to 35° at -10 °C. The reason of decrease in contact angles is the formation of thin water film on the surface. When droplet is deposited onto film, it coalesces with the existing water film resulting in low water contact angle values. Some research groups have reported similar temperature dependent decrease in water contact angles and they attributed this decrease to the water condensation with

decreasing temperature [139, 140]. The water contact angle on SBS coated glass slide was 110° at 25 °C. Like the bare glass slide this value decreased to 85° at -10 °C, which means coatings remains almost hydrophobic even at lower temperatures. The addition of 30% by mass DE particles in SBS matrix lowered the contact angle values by 20° compared to SBS coated glass slides. The presence of hydrophilic DE particles in SBS matrix resulted in this much lower contact angles. The loading of EG or PEG-600 into the DE particles decreased further the contact angles compared to DE/SBS composite coatings.

The values of water contact angles on EG filled DE/SBS composite coatings increased gradually with increasing plate temperature from -10 °C to 25 °C. These water contact angle values ranged between 60° to 75°. The water contact angle values on PEG-600 filled DE/SBS composites in the same temperature range are slightly lower and ranged between 55° to 65°. These results are in line with the amounts of these anti-icing agents retained in DE/SBS composites at same concentrations of anti-icing agents in binary mixture (Fig. 3.8). The increase in amount of hydrophilic anti-icing agent in diatomaceous earth particles results in decrease of contact angle values. These anti-icing agents filled DE/SBS composite films showed much weaker temperature dependence compared to the controls and without anti-icing agent DE/SBS composites. The decrease in contact angle for EG loaded composites was 10° to 15° and 6° to 10° for PEG-600 loaded composite coatings. This weaker temperature dependence can be attributed to the presence of water-soluble anti-icing agents on the surface. The presence of these water-soluble anti-icing agents resulted in lower contact angle values at room temperature even when there is less tendency of water condensation. Despite the presence of water-soluble anti-icing agents on the surface, the most notable point is that the water contact angle value on anti-icing filled DE/SBS composites were measured between 60°-70°. This result suggested that the filling of DE particles exposed to top surface (Fig. 3.10 (a)) resulted in isolated islands of anti-icing loaded particles on DE/SBS composite surface.

3.4.5 Anti-icing ability of anti-icing agent loaded DE/SBS composites

The anti-icing ability of composite coating surfaces was investigated by freezing delay of water droplets placed on them. The freezing time of 4 µL water droplets on the composite surface was measured at a constant temperature. The plate temperature was decreased from -12 °C till -15 °C. The freezing time delay for controls and anti-

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icing agent loaded composite surfaces as a function of plate temperature are shown in Fig. 3.14 (a). The freezing time of water droplet on a simple glass slide increases from 10 s at $-15\text{ }^{\circ}\text{C}$ to 50 s at $-12\text{ }^{\circ}\text{C}$. The reason for this short freezing time is the hydrophilic nature of glass slides. The freezing time of water droplets increases on DE/SBS composite surfaces compared to glass slides from 40 s at $-15\text{ }^{\circ}\text{C}$ to 150 s at $-12\text{ }^{\circ}\text{C}$. The larger surface hydrophobicity and relatively small contact area on DE/SBS composites compared to glass slide resulted in longer freezing time. There is more probability of water droplet freezing by heterogeneous nucleation at water/composite interface. The unfavorable interaction between water and hydrophobic polymeric matrix together with larger contact angle decreases nucleation probability and increases the freezing time of water droplets on these DE/SBS composite surfaces.

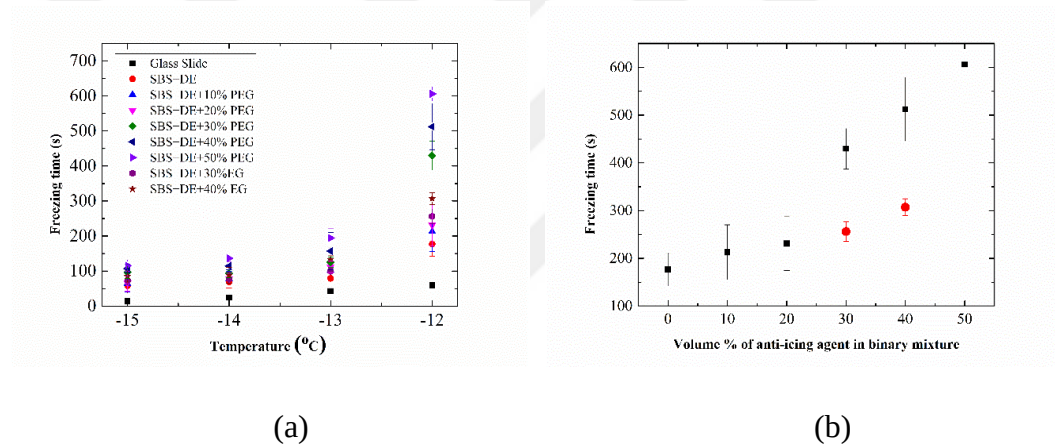


Fig. 3.14 Anti-icing ability of various coatings a) freezing time of water droplets on various coatings as function of temperature b) freezing time delay at $-12\text{ }^{\circ}\text{C}$ for EG filled (red circle) and PEG-600 filled DE/SBS composites (black squares). Freezing time is longer on coatings with more anti-icing agent. PEG is better anti-icing agent than EG. This image is taken from reference [137].

The DE/SBS composites filled with anti-icing agents showed longer freezing times than DE/SBS composites without anti-icing agents. The increase in freezing time of water droplets on anti-icing agent filled DE/SBS composites compared to unfilled DE/SBS composites is due to the release of anti-icing agents from composite coatings. The freezing time increases with the amount of anti-icing agent retained in DE/SBS composite coatings. The largest freezing times were observed on DE/SBS

composites filled with PEG-600 in 50% volume concentration solution. The freezing time measured on these coatings were 150 s at -15 °C and 600 s at -12 °C.

The freezing times of water droplets on EG and PEG-600 filled DE/SBS composites as a function of anti-icing agent concentration in dipping solution are shown in Fig. 3.14 (b). The freezing time is increasing with increasing the concentration of EG/PEG-600 in dipping solution. This result indicates that more anti-icing agent loaded in DE/SBS composites at higher anti-icing agent concentrations resulted in longer freezing delay and supports data on the amount of anti-icing agent retained in composites in Fig. 3.8. The more amount of anti-icing agent retained in the composite coatings allowed more release of anti-icing agents into the water droplets placed on the surface of composites. This mixing of anti-icing agent with water droplets decreases the melting temperature of water droplets and their probability to freeze at a given temperature. The rinsing of composite surfaces prior to freezing experiments removes the loosely bounded anti-icing agents, so it is expected that the anti-icing agents are released from the pores of DE on the top surface of composites in contact with water droplets. For prevention of icing on composites, the minimum concentration of EG in water droplets should be around 25-30 wt% in temperature range of -12 °C to -15 °C [141]. Below this minimum concentration range, the presence of EG (or PEG) in water droplets only delays the freezing of water droplets. The release of PEG is slower than EG due to the larger size of PEG-molecules. The freezing delay (Fig. 3.14), contact angle (Fig. 3.13) and release results (Fig. 3.16) indicated that the amount of EG (or PEG) was lower than the critical value required for freezing. The volume of water droplets used for freezing experiments was 4 μL . The contact angles of the water droplets were between 75-55 ° for anti-icing agent filled DE/SBS coatings. The area of the water droplets changed from 0.03 cm^2 to 0.09 cm^2 . The concentration of anti-icing agent released from DE/SBS composites in 4 μL water droplets was calculated to be between 3.8 wt% to 11.5 wt% at room temperature. The water droplets containing 11.5 wt% EG does not freeze at temperatures below -5 °C [141] in consistent with the measurements.

Fig. 3.14 (b) shows that PEG-600 is more effective in delaying the freezing time of water droplets than EG. One of the reasons for this effectiveness can be that more PEG-600 is loaded at a given concentration compared to EG (Fig. 3.8). In addition, this freezing delay can be attributed to the interaction of water and PEG molecules

because PEG effects the diffusional motion of water molecules [127]. In addition to that formation of PEG hydrate contributes to the freezing delay of water droplets. Water molecules can form several types of hydrogen bonded bridges with adjacent etheric oxygen groups. PEG with low molecular weight forms less PEG hydrates as compared to higher molecular weight PEG. The increase in PEG concentration also enhances PEG hydrate formation and results in more freezing delay. The water activity is decreased more for the larger PEG molecules than smaller EG molecules which results in more freezing delay for PEG containing water droplets [126].

3.4.6 Release of anti-icing agent from DE/SBS composites

To prove that the release of anti-icing agents into the water droplets is responsible for freezing delays, the amount of anti-icing agent released in time from the anti-icing agent loaded composites was determined by UV-Vis spectroscopy. The anti-icing agent loaded composites were dipped in DI water for different time intervals. PEG released from DE/SBS composites was complexed with Dragendorff reagent. This complex had orange-red color and absorbed visible light at 514nm [136]. Dragendorff method is sensitive with higher molecular mass PEG so PEG-10K was used for this spectroscopic determination of the amount of PEG released from DE/SBS composites. First, the calibration curve using the PEG-10K standard solution was prepared as shown in Fig. 3.15 then the absorbance was measured by UV-Vis spectrophotometer.

The calibration curve is used to determine the value of PEG-10K released from DE/SBS composite coatings by UV-Vis spectroscopy. The release profile of PEG-10K from composite coatings as function of time for DE/SBS composite coatings filled in 0.3 g/mL, 0.4 g/mL and 0.5 g/mL PEG-10K concentrations in binary solvent mixtures is shown in Fig. 3.16. The amount of PEG-10K loaded in 1mg of composite was 0.1 mg at 30% PEG concentration, 0.33 mg at 40% PEG concentration and 0.42 mg at 50% PEG concentration in binary solvent mixture. The amount of PEG-10K loaded in DE/SBS coatings increases with the concentration of PEG-10K in binary mixture. Similarly, the amount of PEG-10K released was more for composites filled at higher PEG concentrations. This observation of larger amount of PEG released from the DE/SBS composites filled at higher PEG concentrations is consistent with the data of mass fraction of PEG retained (Fig.3.8), surface wettability differences (Fig 3.13) and freezing time delays (Fig. 3.14).

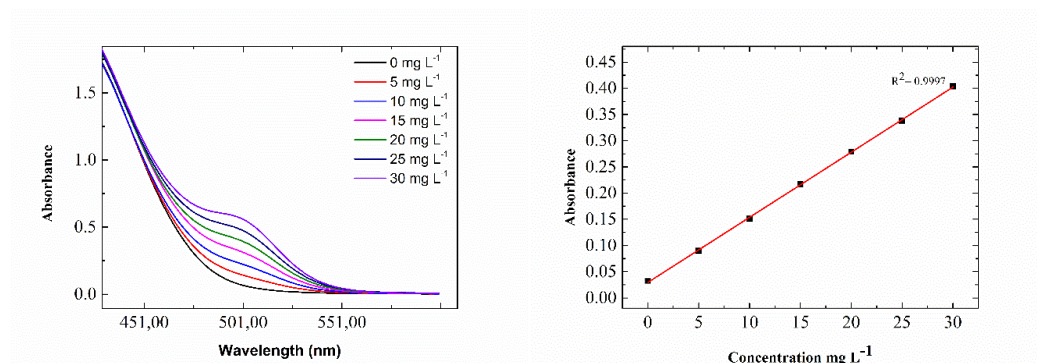


Fig. 3.15 Calibration for PEG-10K released from the composite into water at room temperature by UV-Visible spectroscopy using modified Dragendorff method: (a) Absorption spectra of the complex formed by mixing PEG-10K at various concentrations and Dragendorff reagent (DR). (b) Calibration curve at 514 nm for PEG-10K. This image is taken from reference [137].

The rate of PEG release from the composite coatings increased with the amount of PEG retained in the composites and reached steady state faster. However, the fraction of amount released to the fraction of amount loaded was larger for composites loaded at lower PEG concentrations. This indicates that at lower filling concentrations (0.3 g/mL), the pores of DE particles near to the surface are filled with PEG. The burst release of PEG was observed from these pores upon their contact with water droplets. But at higher PEG filling concentrations (0.4 g/mL and 0.5 g/mL) PEG can penetrate further and fill the pores of DE particles buried deep inside the matrix. Since water cannot swell SBS, so upon contact with water only surface exposed PEG releases and PEG filled in the inner DE particles remain intact.

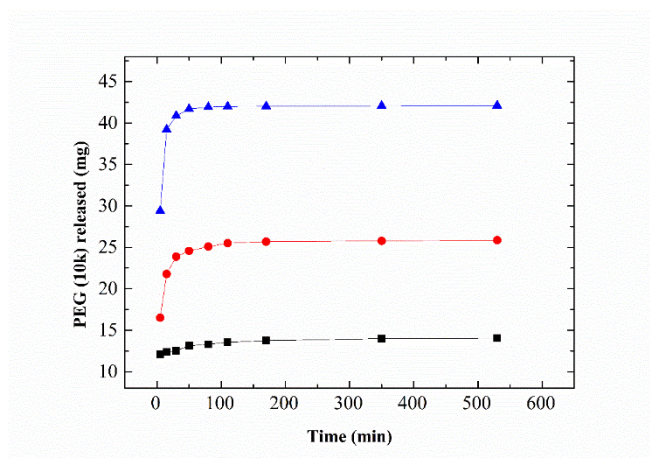


Fig. 3.16 The amount of PEG-10K released (mg) into 10 mL as function of time from DE/SBS composites coatings dipped in 0.5 g/mL (blue line), 0.4 g/mL (red line) and 0.3

g/mL (black line) PEG-10K solution in binary solvent mixture respectively. This image is taken from reference [137].

The gravimetrically determined PEG-10K amount retained in DE/SBS composites as function of PEG-10K concentration in binary mixture is shown in Fig. 3.17. These coatings were used for determining the amount of PEG-10K released in DI water by UV-Vis spectroscopy. For all these composite coatings, the amount of PEG released in DI water as determined by UV-Vis spectroscopy was significantly less than the amount of PEG-10K retained in these composites as determined by gravimetric method. The comparison of the PEG amount released (Fig. 3.16) and amount of PEG retained (Fig. 3.17) showed that the release of PEG-10K originates from the pores of DE particles exposed to the surface and in touch with water. Since water cannot swell SBS, PEG-10K in the pores of DE particles buried in SBS matrix cannot be solubilized and remained intact. The amount of PEG-600 released from DE/SBS composites was determined gravimetrically. The amount of PEG-600 released as function of time from the coatings dipped in 30% and 40% by volume PEG-600 concentrations in binary solvent mixture is shown in Fig. 3.18. These results are in line with the spectroscopic results obtained for PEG-10K (Fig. 3.16).

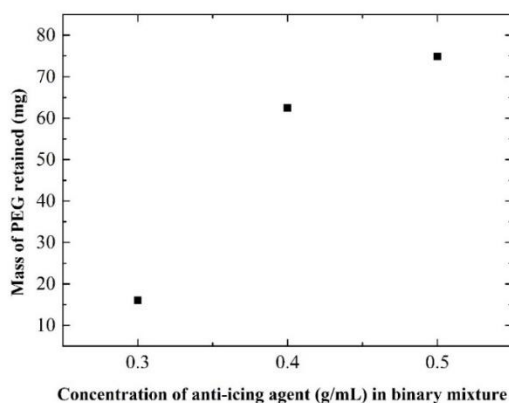


Fig. 3.17 Mass (in mg) of PEG-10K retained in DE/SBS composites filled in different concentrations of PEG-10K solutions in binary mixture of diethyl ether and acetone. The more amount of PEG is retained by the coating dipped in higher PEG concentration solution. This image is taken from reference [137].

The presence of PEG in the inner pores of DE particles buried in SBS matrix was investigated. The DE/SBS films with 0.2 mm thickness and lateral dimension of 1.8 cm x 1.3 cm were filled in 0.5 g/mL PEG-10K solution. This PEG-10K filled coating

was cut into 6 pieces and kept in water. The release of PEG-10K from 6 pieces in water was compared to that released from 0.2 mm thick single piece having same lateral dimensions (1.8 cm x 1.3 cm) and same volume. Fig. 3.19 shows the amount of PEG-10K released as a function of time from the coating cut into 6 pieces in reference to a single piece having same surface thickness and same top and bottom surface area. The amount of PEG-10K released from 6 pieces was 1.5 times greater than that released from single piece. The newly produced side areas of single piece by cutting it into 6 pieces increased the total surface area from 4.80 cm² to 5.06 cm². The sample cut into 6 pieces released almost 50% more PEG-10K compared to the single uncut sample. This increase in released amount was due to the exposure of more DE particles to the water/composite interface and the connectivity of DE particles in composite. The connectivity of DE particles within the composite allowed the water to penetrate deeper into the film and solubilize more PEG molecules. These results clearly showed that anti-icing ability of these coatings are enhanced by wear in time and clearly demonstrates their potential longer-term use in harsh conditions. These results prove our hypothesis that anti-icing agent loaded composite coatings will retain their anti-icing ability even if they are scratched. Scratches and wear allow the anti-icing agent filled DE particles buried in SBS matrix to be exposed to the top surface with possibility of new anti-icing agent released when in touch with water.

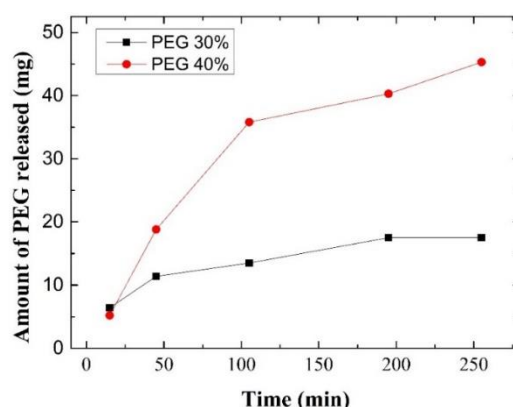


Fig. 3.18 Mass (in mg) of PEG-600 released from filled DE/SBS composites into 10 mL water as a function of time. The amount released was determined gravimetrically. DE/SBS composites filled in 30% by volume PEG in binary mixture (black line); DE/SBS composites filled in 40% by volume PEG in binary mixture (red line). This image is taken from reference [137].

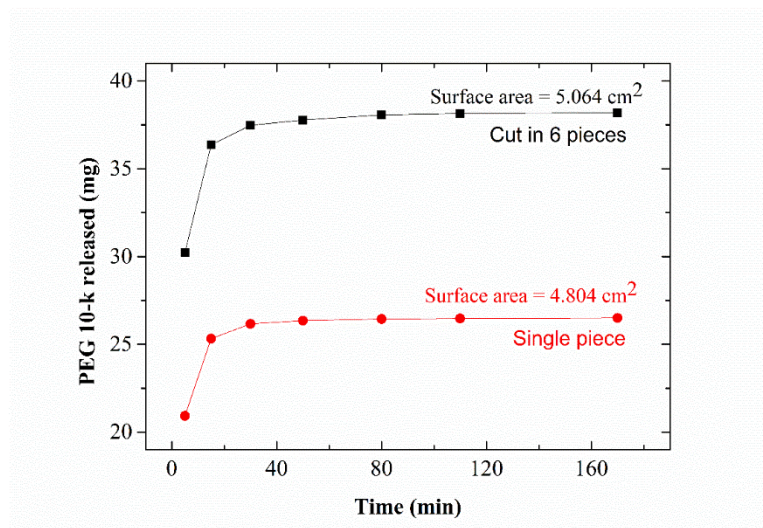


Fig. 3.19 The mass of PEG-10K released into 10 mL water from DE/SBS composites filled in 0.5 g/mL PEG-10K solution in binary solvent mixture: from sample cut into 6 pieces (black line) and from single piece having same volume of the 6 pieces (red line). This image is taken from reference [137].

3.4.7 Comparison of anti-icing ability of mesoporous silica/SBS composite coatings and DE/SBS composite coatings

The aim of this study is to enhance the anti-icing ability of composites. The anti-icing ability of composites can be enhanced by increasing the release of anti-icing agent from the surface exposed particles in composites. This can be achieved by decreasing the size of porous fillers that will enhance their specific surface area and anti-icing agent loading and release ability. Mesoporous silica particles can be used as an alternative of DE particles in SBS matrix. The average particle size of mesoporous silica and DE is 1.2 μm and 14 μm respectively [135]. Due to smaller size, mesoporous silica particles have higher specific surface area than DE particles (Table 3.2). The higher specific surface area of the mesoporous silica particles will enhance the loading of anti-icing agent and smaller pore size will result in controlled release of anti-icing agents. Mesoporous silica particles used in this study were synthesized by mixing Pluronic F127 and TEOS in 7M HCl solution. The details of mesoporous silica particles synthesis are given in Chapter 2. For synthesizing silica/SBS composites, mesoporous silica particles were dispersed in SBS solution to have 30% by mass mesoporous silica particles in final coatings. The mesoporous silica/SBS coatings were loaded with anti-icing agents in similar way as DE/SBS coatings were filled by swelling the SBS films and allowing the diffusion of PEG-

600 in pores of mesoporous silica particles. Similar to anti-icing agent filled DE/SBS composite coatings, the anti-icing ability of mesoporous silica/SBS composite coatings were characterized by freezing delay of water droplets on these composite surfaces. Surface wettability of mesoporous silica/SBS coatings was investigated by contact angle measurements on these composite surfaces and its relationship with the amount of anti-icing agent in composite coatings was inferred.

3.4.7.1 Loading of anti-icing agent in composite coatings

Anti-icing agent (PEG-600) was loaded in mesoporous silica/SBS coatings by swelling the composite coatings in acetone/diethyl ether binary mixtures. The amount of PEG-600 retained in silica/SBS composite coatings was determined gravimetrically. The composite coatings were having 30% by mass mesoporous silica particles in SBS matrix. Figure 3.20 shows the gravimetrically determined mass fraction of PEG-600 retained in silica/SBS coatings as function of concentration of PEG-600 in binary solvent mixture in which these composite coatings were dipped for 24 h. The amount of PEG-600 retained in composite coatings was increased by increasing the concentration of PEG-600 in binary solvent mixture. The mass fraction of PEG-600 retained in silica/SBS composite coatings was 0.013 at 5% by volume concentration of PEG-600 in binary solvent mixture. This mass fraction retained by silica/SBS composite coatings increased gradually to 0.17 at 50% by volume concentration of PEG-600 in binary solvent mixture. When compared with the mass fraction of PEG-600 retained in DE/SBS composite coatings, the amount of PEG-600 retained in silica/SBS composite coatings was ~2 times higher at same PEG-600 concentration in binary solvent mixture. The ability of silica/SBS composite coatings to retain more amount of PEG-600 than DE/SBS composite coatings can be attributed to the difference in specific surface area of mesoporous silica particles and DE. The Specific surface area of mesoporous silica particles and DE is 428 m²/g and 35 m²/g respectively [134, 142]. This higher specific area of mesoporous silica particles resulted in higher loading of PEG-600 in silica/SBS composite coatings.

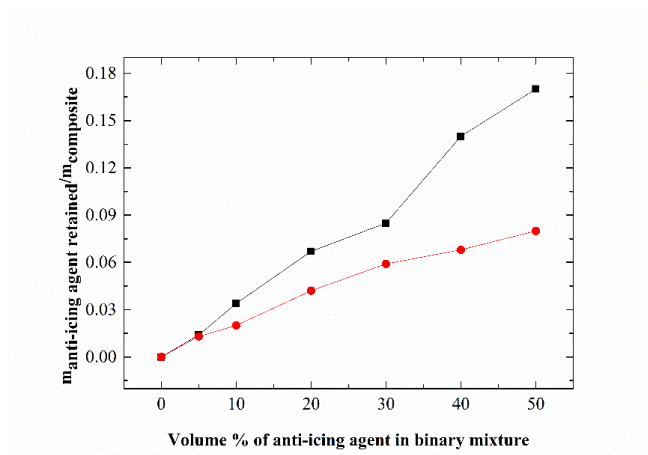


Fig. 3.20 Mass fraction of PEG-600 retained in silica/SBS composite coatings dipped in binary solvent mixture for 24 h then rinsed and dried in air as a function of concentration of PEG-600 solutions. The amount of PEG-600 retained in coatings increases with increased amount of PEG-600 in dipping solutions.

3.4.7.2 Surface wettability of anti-icing agent loaded silica/SBS composites

The surface wettability of the silica/SBS composite coatings was investigated by contact angle measurements of water droplets as function of temperature. The temperature range between 25 °C and -10 °C was chosen for these experiments. The water contact angles of bare glass slides and silica/SBS composite film were used as controls. The evolution of water contact angles on PEG-600 loaded composite coatings and controls as function of plate temperature is shown in Fig. 3.21. The contact angles of water droplets on anti-icing agent filled composite surfaces and controls decreased with decreasing temperature. This decrease in contact angle values with temperature was more pronounced in controls compared to the PEG-600 filled composite coatings. This temperature dependent decrease in contact angles was attributed to the condensation of water vapors on the surfaces [139, 140]. This weaker temperature dependence of PEG-600 filled silica/SBS composites can be attributed to the presence of water-soluble PEG-600 on the surface. Fig. 3.21 shows that the increase in the amount of PEG-600 in silica/SBS composite coatings resulted in slightly lower contact angle values. The presence of water-soluble anti-icing agent (PEG-600) resulted in this lower contact angle values. Fig. 3.21 (b) shows the comparison of contact angles of DE/SBS and silica/SBS composites filled with same PEG-600 concentrations as function of plate temperature. Despite the higher mass fraction of PEG-600 retained in silica/SBS composites, the water contact angle

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values on PEG-600 filled DE/SBS composites and silica/SBS composite were measured in almost same range of 52-68° for composites having same PEG-600 concentrations in binary solvent mixture. In case of composites filled with PEG-600 in 50 volume % solutions, the contact angle values measured on silica/SBS composites were lower compared to the contact angles measure on DE/SBS composites. But in case of composites filled with PEG-600 in 40 volume% solutions, the contact angle values measured on silica/SBS composites were higher till 10 °C and then slightly lower till -15 °C as compared to contact angles on DE/SBS composites. The difference in contact angle values of both composites were in range of 2-4°. These contact angle values suggested that surfaces of both composite coatings consisted of isolated islands of PEG-600 filled pores.

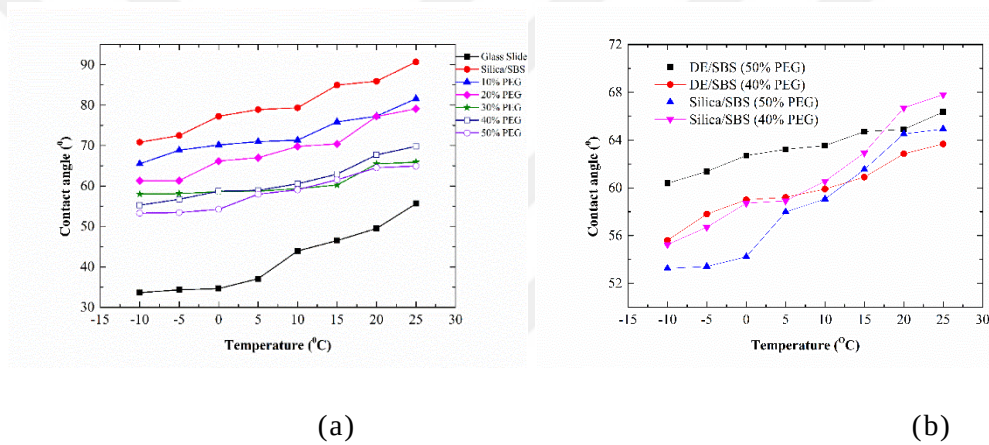


Fig. 3.21 (a) Change in water contact angles on silica/SBS composites (dipped in PEG-600 solutions of various concentration in binary mixture and dried) as a function of plate temperature. (b) comparison of water contact angles on DE/SBS and silica/SBS composites (filled with same PEG concentrations) as function of plate temperature. The hydrophilicity increased by decreasing plate temperature. In several cases, the standard deviations of the measurements were between 0.2-1.2°.

3.4.8 Anti-icing ability of anti-icing agent loaded composites

The anti-icing ability of composite coating surfaces was investigated by freezing delay of water droplets placed on them. The freezing time of 4 μ L water droplets on the composite surfaces was measured at a constant temperature. Fig. 3.22. shows the freezing times of water droplets on PEG-600 filled DE/SBS composites and silica/SBS composite coatings at -14 °C as function of PEG-600 solution concentration in which composites were filled. For both anti-icing agent filled

composites, the freezing time was increasing with increasing concentration of PEG-600 in dipping solution. Retaining more amount of PEG-600 resulted in release of more PEG-600 in the water droplets placed on the surface of composites. This mixing of anti-icing agent with water droplets decreases the melting temperature of water droplets and their probability to freeze at a given temperature.

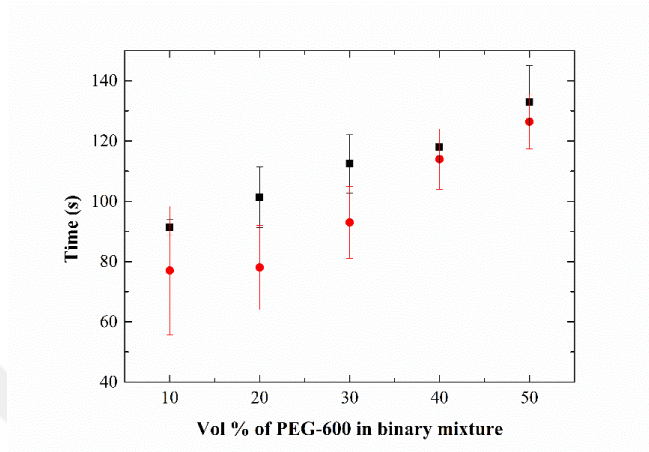


Fig. 3.22 Freezing time delay at -14°C for PEG-600 filled DE/SBS composites (red circle) and PEG-600 filled silica/SBS filled composites (black squares). The more surface exposed silica particles resulted in larger release of PEG-600 that resulted in longer freezing delays.

The results suggested that silica/SBS composite coatings showed longer freezing delay as compared to DE/SBS composite coatings. The amount of PEG-600 retained in silica/SBS was more than that retained in DE/SBS composites (Fig 3.20). Since water cannot swell SBS, the release of PEG-600 from surface exposed pores of DE or silica from their respective composites mixed with water droplets and resulted in freezing delays. It is expected that due to the smaller size of silica, more silica particles were exposed on the top surface of silica/SBS composites as compared to DE particles of DE/SBS composites. The higher amount of surface exposed pores of silica allowed larger release of PEG-600 into water droplets placed on the surface of silica/SBS composites which resulted in longer freezing delays on these surfaces. In addition to this, when the amount of surface exposed particles is same in case of both silica and DE/SBS composites, the larger specific surface area of silica particles will retain and ultimately release more amount of PEG-600 into water droplet placed on the surface of silica/SBS composites than DE particles of DE/SBS composites.

3.4.9 Release of anti-icing agent from Silica/SBS composites

To prove that the release of anti-icing agent from silica/SBS composite coatings into the water droplets is responsible for freezing delays, the amount of anti-icing agent released in time from the anti-icing agent loaded composites was determined by UV-Vis spectroscopy. The anti-icing agent loaded composites were dipped in DI water for different time intervals. PEG released from silica/SBS composites was determined by using the same method as explained in section 3.4.6. Similar calibration curve was prepared by using PEG-10K standard solutions as shown in Fig. 3.15. The calibration curve was used to determine the value of PEG-10K released from silica/SBS composite coatings by UV-Vis spectroscopy. The gravimetrically determined PEG-10K amount retained in DE/SBS composites as function of PEG-10K concentration in binary mixture is shown in Fig.3.23. These coatings were used for determining the amount of PEG-10K released in DI water by UV-Vis spectroscopy. The amount of PEG-10K loaded in 1 mg of silica/SBS composite was 0.17 mg at 0.3 g/mL PEG-10K concentration, 0.37 mg at 0.4 g/mL PEG-10K concentration and 0.46 mg at 0.5 g/mL PEG-10K concentrations. The amount of PEG-10K loaded in silica/SBS composite coatings is higher than the amount loaded in DE/SBS composite coatings (Fig. 3.17) at similar PEG concentrations in dipping solutions. These observations that larger amount of PEG-10K was loaded in silica/SBS composites than DE/SBS composites coatings were consistent with mass fraction of PEG-600 retained (Fig. 3.20) in these coatings.

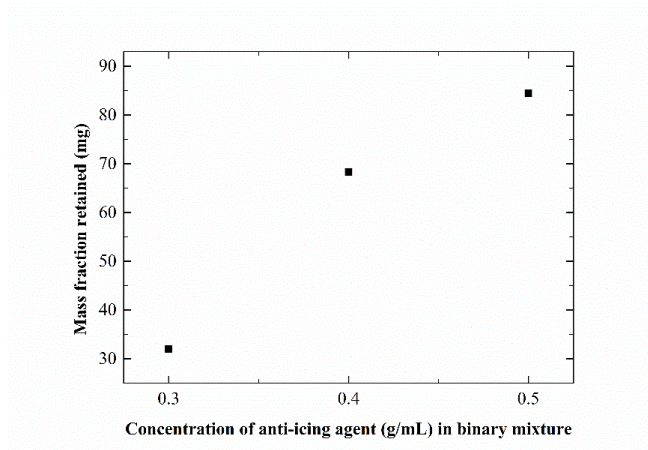


Fig. 3.23 Mass of PEG-10K retained in silica/SBS composites filled in different concentrations of PEG-10K solutions in binary mixture of diethyl ether and acetone.

The release profile of PEG-10K from silica/SBS composite coatings as function of time for composite coatings filled in 0.3 g/mL, 0.4 g/mL and 0.5 g/mL PEG-10K concentrations in binary solvent mixtures is shown in Fig. 3.24. The results showed that more amount of PEG-10K was released from the composite coatings filled at higher PEG-10K concentrations. The rate of PEG-10K release increased with the amount of PEG in silica/SBS composite coatings and reached a steady state. Similar to the release results of DE/SBS composites (Section 3.4.6), the fraction of amount PEG-10K released to the amount loaded was higher for coatings loaded at lower PEG concentrations. But the amount of PEG-10K released from silica/SBS composites was higher than DE/SBS composites (Fig 3.16) filled at similar PEG concentrations. The release of PEG-600 is originated only from the pores of silica particles exposed to the surface of silica/SBS composites and in touch with water molecules. Due to small size of silica particles, the amount of mesoporous silica particles exposed to the composite surface could be higher than DE particles. The anti-icing agent filling of these surface exposed particles resulted in larger burst release of PEG-10K from the surface of silica/SBS composites upon contact with DI water.

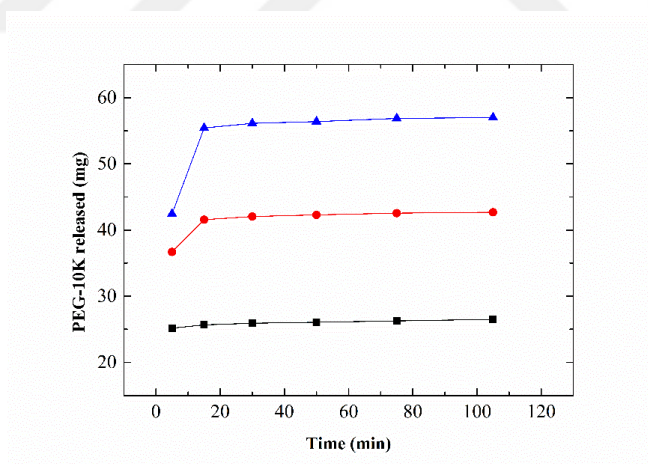


Fig. 3.24 The amount of PEG-10K released (mg) into 10 mL as function of time from silica/SBS composites dipped in 0.5 g/mL (blue line), 0.4 g/mL (red line) and 0.3 g/mL (black line) PEG-10K solution in binary solvent mixture respectively.

The amount of PEG-10K released from all silica/SBS composites coatings as determined by UV-Vis spectroscopy was less than the amount of PEG-10K loaded in them as determined gravimetrically (Fig. 3.23). These results are in line with release profile of PEG-10K from DE/SBS composite coatings. The comparison of the PEG

amount released (Fig.3.24) and amount of PEG retained (Fig. 3.23) showed that the release of PEG-10K originates from the pores of DE particles exposed to the surface and in touch with water. Since water cannot swell SBS, PEG-10K in the pores of silica particles buried in SBS matrix cannot be solubilized and remained intact.

Similar to DE/SBS composites, the presence of PEG in the inner pores of mesoporous silica particles buried in SBS matrix was investigated. The silica/SBS films with 0.2 mm thickness and lateral dimension of 1.7 cm x 1.2 cm were filled in 0.5 g/mL PEG-10K solution. This PEG-10K filled coating was cut into 6 pieces and kept in water. The release of PEG-10K from 6 pieces in water was compared to that released from 0.2 mm thick single piece having same lateral dimensions (1.7 cm x 1.2 cm) and same volume. Fig. 3.25 shows the amount of PEG-10K released as a function of time from the coating cut into 6 pieces in reference to a single piece having same surface thickness and same top and bottom surface area. The amount of PEG-10K released from 6 pieces was 1.5 times greater than that released from single piece. The newly produced side areas of single piece by cutting it into 6 pieces increased the total surface area from 4.19 cm² to 4.68 cm². The sample cut into 6 pieces released almost 50% more PEG-10K compared to the single uncut sample. This increase in released amount was due to the exposure of more mesoporous silica particles to the water/composite interface.

Despite the smaller surface areas of silica/SBS composite samples exposed to DI water, the amount of PEG-10K released from single piece sample and sample cut into 6 pieces of silica/SBS and DE/SBS composites (Fig. 3.19) was almost same. The amount of PEG-10K released from 1 cm² of both composites is shown in Table 3.4. The amount of PEG-10K released from 1 cm² single piece sample and sample cut into 6 pieces of silica/SBS composites is higher than the amount released from their respective counter parts of DE/SBS composites. These results confirmed the ability of mesoporous silica particles to retain and release more anti-icing agent due to their higher specific surface area and smaller size. The more release of anti-icing agent from the silica pores buried in SBS matrix (Table 3.4) showed the anti-icing ability of silica/SBS composites will be enhanced by wear.

Table 3.4 Comparison of the amount of PEG released from composite coatings

Sample properties	Amount of PEG released from (1 cm ²) (mg)
DE/SBS composites single piece	5.41
Silica/SBS composites single piece	5.72
DE/SBS composites cut into 6 pieces	7.30
Silica/SBS composites cut into 6 pieces	7.97

The results of mass fraction of PEG-600 retained in (Fig. 3.20), surface wettability (Fig. 3.21), water droplets freezing delays (Fig. 3.22) and mass fraction of PEG-10K retained and released (Fig. 3.24) showed that silica particle containing composite exhibit superior anti-icing ability compare to diatomaceous earth filled composites. These superior anti-icing ability of silica/SBS composite coatings can be attributed to the smaller particles size, large pore volume and higher specific surface area of mesoporous silica particles. The smaller particle size of mesoporous silica particles resulted in better dispersion and more surface exposed porous particles. The large pore volume and higher specific surface area of mesoporous silica particles resulted in higher loading of anti-icing agents. The larger release of anti-icing agent from surface exposed pores of silica particles resulted in better anti-icing ability of silica/SBS composites.

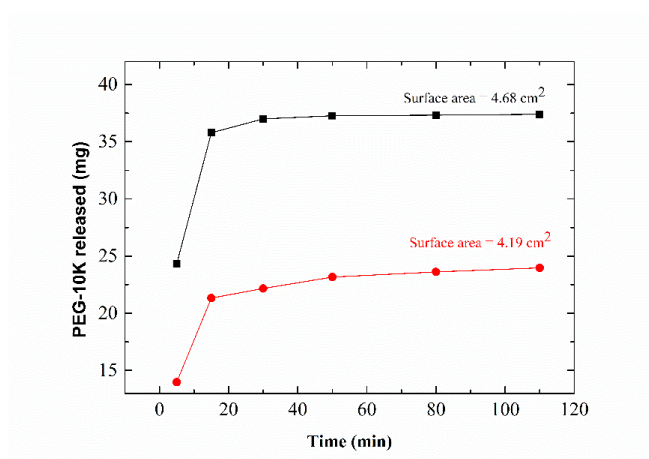


Fig. 3.25 The mass of PEG-10K released into 10 mL water from silica/SBS composites filled in 0.5 g/mL PEG-10K solution in binary solvent mixture: from sample cut into 6 pieces (black line) and from single piece having same volume of the 6 pieces (red line).

3.5 Conclusion

DE loaded SBS composites were developed for anti-icing applications. 30 % by weight DE containing SBS composites were filled by keeping them in EG or PEG solutions in diethyl ether/acetone binary solvent mixture. The anti-icing agent is soluble in binary solvent mixture. The anti-icing agent dissolved in binary mixture penetrated into the swollen DE/SBS composite. The results of SEM and EDX analysis showed that anti-icing agents were in the pores of DE particles. The anti-icing agents were driven into the pores of DE by favorable interaction of hydrophilic anti-icing agents and hydrophilic DE particles. The amount of anti-icing agents retained in the DE/SBS composite coatings is increased by increasing the concentration of anti-icing agent in binary mixture. The wettability of DE/SBS composite coatings loaded with anti-icing agents were characterized by contact angle measurements. The contact angles of water droplets on these anti-icing agents loaded DE/SBS composites was measured between 60-70°. These contact angle values indicated that the surface of DE/SBS composites contained isolated islands of anti-icing agents, most probably in the pores of DE particles exposed to the top surface. The anti-icing ability of the composite surfaces was characterized by the freezing delay of water droplets. The freezing time of water droplets increased with the amount of anti-icing agents retained in composite coatings. At -12 °C, the freezing time on the DE/SBS composites filled in 50 volume % PEG-600 solution in binary solvent was ~600 s compared to ~170 s on unfilled composites. The release of anti-icing agent upon contact with water decreased the freezing temperature of water. The amount of PEG released was more for the DE/SBS coatings loaded at higher PEG concentrations which was consistent with surface wettability results and freezing time delays. The amount of PEG released in water was significantly lower than the amount filled in DE/SBS composites. This release result indicates that PEG released from the composite coatings originate from the pores of DE particles exposed to the composite surface and in touch with water. Since water cannot swell SBS, PEG loaded in the pores of DE particles buried in SBS matrix couldn't be solubilized. The release of PEG from the inner pores was enabled by increasing the water composite interfacial area. This water/composite interfacial area was enhanced by cutting the anti-icing agent loaded DE/SBS composite coatings into smaller pieces. The composites developed maintain their anti-icing ability for longer time in the presence

of wear and scratches. The scratches and wear allow the inner DE particles buried in SBS matrix to be exposed to the top surface with possibility of new anti-icing agents released when in touch with water. The anti-icing ability of DE/SBS composite coatings and mesoporous silica/SBS composite coatings was compared. For that purpose, the DE particles were replaced by mesoporous silica particles in SBS matrix. The mass fraction of PEG-600 retained by silica/SBS composite coatings was ~ 2 times of that amount retained by DE/SBS composite coatings at same PEG-600 concentration. The surface wettability of silica/SBS composite coatings was also investigated by contact angle measurements. The results showed that contact angles of PEG-600 filled silica/SBS composite coatings were measured in same range as for PEG-600 filled DE/SBS composite coatings. At -14°C , the freezing time on silica/SBS composite coatings was 140 s as compared to 120 s for DE/SBS composite coatings filled with same PEG concentration solutions. The anti-icing agent release results for silica/SBS composites were consistent with release profiles of DE/SBS composite coatings. Overall, the results of mass fraction of PEG-600 retained, water droplets freezing delays and mass fraction of PEG-10K retained and released showed that silica/SBS composites exhibit superior anti-icing ability compared to DE/SBS composites. These superior anti-icing ability of silica/SBS composite coatings can be attributed to the better dispersion, more surface exposure and higher specific surface area of mesoporous silica particles. The higher specific surface area of surface exposed silica particles resulted in more loading and release of anti-icing agent that ultimately enhanced the anti-icing ability of silica/SBS composites.

Chapter 4: Anti-Corrosive Composites

4.1 Motivation

Corrosion is the chemical or electrochemical interaction between metals and their environment that leads to metallic deterioration. The environment is described as all species in contact with metals. All environments are corrosive to some extent, but inorganic materials are more corrosive than organics. Corrosion is affecting society with great economic impact, loss of natural resources and environmental damages. Metallic corrosion can be beneficial or detrimental. The enticing effects of metallic corrosion include chemical milling of excessive metallic parts and anodizing of metals to get better surface appearances. The deleterious effect of metallic corrosion include, high maintenance and operating costs, appearance and contamination of materials, plant shutdowns, safety and reliability and loss of valuable products [143].

The development of corrosion protection system for metallic substrates remains an important challenge for many industrial problems. Corrosion resistant coatings protect metallic substrates against degradation due to moisture, corrosive media or exposure to many hazardous industrial chemicals. The protection mechanism of composite coatings having porous nano/microparticles filled with corrosion inhibitors in polymeric/metallic matrix is based on diffusion of the inhibitor upon contact with the corrosive media to the metal surface. We showed that polymer composite coatings significantly slowed down the corrosion rate of the investigated copper metal. Similarly, we showed that the metallic composites slowed down the corrosion rate of Iron.

In this work, we intended

- To load silica-based nano/microparticles with corrosion inhibitors,
- To prepare polymer/nano- and micro- filler composites and dip coat them on metal substrate,
- To characterize the anti-corrosive ability of composite coated metal substrates in various corrosive environments,
- To deposit Fe-P alloy films on copper substrate at various conditions,

- To investigate the electrochemical properties of electrodeposited Fe-P thin films,
- To incorporate inhibitor loaded silica particles and/or halloysite nanotubes in Fe-P alloy thin films,
- To characterize the anti-corrosive ability of silica-based fillers containing Fe-P alloy thin films.

4.1.1 Corrosion mechanism

Corrosion is an electrochemical process as it can be divided into two partial reactions of oxidation and reduction. The anodic reaction in every corrosion process is the oxidation of metal atoms to their respective ions. The electrons released at the anode during metal dissolution process are consumed at the cathode during reduction reactions. There are several cathodic reactions that include hydrogen evolution, oxygen reduction, metal reduction and metal deposition. The anodic and cathodic reactions are shown below [1].

Anodic reaction: $M \rightarrow M^{n+} + ne^{-}$

Cathodic reactions: $2H^{+} + 2e^{-} \rightarrow H_2$ (Hydrogen evolution)

$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$ (Oxygen reduction (acid solution))

$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$ (Oxygen reduction (Basic /neutral))

$M^{3+} + e^{-} \rightarrow M^{2+}$ (Metal ion reduction)

$M^{+} + e^{-} \rightarrow M$ (Metal deposition)

4.2 Corrosion protection mechanism

The prevention of corrosion is an important challenge in the industrial world. There is a variety of methods used for corrosion protection of materials. The two common approaches used for corrosion protection include active and passive approach. The aim of active corrosion protection system is to influence the corrosion reactions in a manner that corrosion is avoided. It is done by the addition of corrosion inhibitor or developing corrosion resistant alloys etc. Inhibitors are commonly used to prevent the corrosive attack by suppressing the chemical reactions [22-24]. The passive corrosion protection is achieved by depositing anti-corrosion coatings that protect metal surfaces and act as a barrier to inhibit the contact between

chemical compounds or corrosive materials [22]. The passive corrosion protection methods include cathodic protection [25, 26], anodic protection [27], coating [28] and alloying. The combination of both approaches can provide long-term corrosion protection to the metallic surfaces [23, 24].

Surface modifications of metallic substrates with inorganic and organic coatings is a common method for enhancing their corrosion resistance. The three basic protective mechanisms of anticorrosive coatings include effective barrier protection, passivation of the substrate and galvanic protection. The overall performance of these coatings is affected by many internal and external factors. The inhomogeneities such as air bubbles, cracks, voids and trapped solvents will influence the transport of corrosive agents through the coatings which will affect the corrosion process [144].

Metals and alloys having low oxidation potential are most commonly used for corrosion resistance of metallic substrates. Zinc electroplating is a widely used process for corrosion protection of steel and enhancing its surface life [145, 146]. The anticorrosive ability of zinc coated steels is investigated in different corrosive environments [145, 147]. The service life of zinc coated materials was enhanced by treating it with electro active compounds. These compounds form passive adsorption layer or a complex with metal and prevent its degradation [148-150]. Zinc composite coatings have shown better potential as corrosion protection coatings for steel than their traditional counterparts. These coatings have better properties such as high corrosion resistance, chemical stability, wear resistance and low friction due to the presence of small filler particles in zinc matrix [28, 151]. Chromates are widely used to protect the corrosion of active metals such as iron, steel, aluminum alloys and zinc. Chromates are used due to their strong oxidizing ability, ease of application, their passive nature and relatively low cost [152-154]. The use of chromate conversion coatings is the most common method to inhibit corrosion on metal surfaces. These coatings provide extra protection layer to electroplated zinc coatings [153, 155, 156]. The presence of hexavalent and trivalent chromium ions provide high corrosion resistance and self-healing ability to these coatings [157]. These coatings provide corrosion inhibition by inhibiting the cathodic reaction and passivating the metallic surface [158]. The strong oxidation properties of chromates make them environmentally unsafe. The penetration of chromium ions in human organisms is through skin contact, inhalation and ingestion. The conversion of

hexavalent ions (Cr^{6+}) to pentavalent ions (Cr^{5+}) through reduction is the main reason for DNA damage. The solutions containing Cr^{4+} are carcinogenic. The extreme toxicity and carcinogenicity of hexavalent chromium ion-based compounds have limited their use in almost all sectors except aerospace industry [159, 160]. The phosphate, silicate and molybdate-based coatings are introduced as an alternate to chromate-based coatings as they are environmental and effective inhibitors [161-164].

4.2.1 Sol-gel coatings for corrosion protection

Sol-gel derived protective coatings have shown excellent potential as substitute of chromate conversion coatings. These coatings possess excellent chemical stability, oxidation control and corrosion resistance for metallic substrates. Since the inception of the sol-gel coatings, a great deal of work has been done to make corrosion resistant sol-gel coatings [165]. Sol-gel coatings can be deposited to the metal substrates using different methods, such as spraying [166], spinning [167], dipping [168] and electrodeposition [169]. The electrochemical deposition technique is superior than dipping or spinning methods for complex geometries and structures. These electrodeposited sol-gel coatings showed higher thickness, lower porosity and better barrier properties [169]. Silica, zirconia, titania and alumina-based sol-gel coatings possess better corrosion protection abilities due to their chemical stability [166-171]. The major drawbacks of sol-gel coatings such as brittleness, high temperature treatment, internal stresses, thickness limits and crackability limits their use on metallic substrates [172]. These limitations can be overcome using organic-inorganic hybrid sol-gel coatings. The inorganic part increases durability and adhesion with the metal substrate. The organic part provides flexibility to the film. The advantage of these hybrid films is the possibility to make thick and stress-free coatings [173, 174]. The increase in organic component enhances the thickness of the film. However, too high concentration of organic constituent decreases the wear resistance and adhesion of coatings to the metallic substrates. This decrease in adhesion results in coating breakdown and lower corrosion protection [175, 176]. The crackability and barrier properties of polymeric sol-gels can be improved by dispersing inorganic particles in the matrix. The suspensions containing nanoparticles show better corrosion resistance than the particles with higher diameter. These improved properties depend on the size and concentration of

particles in hybrid matrix [171, 177, 178]. These thick sol-gel coatings provide a dense barrier for corrosive agents. The presence of pores and cracks can reduce the corrosion protection ability of these coatings.

4.2.2 Desorption dependent release of corrosion agents

Hybrid sol-gel coatings containing inorganic nanoparticles provide better mechanical barrier to the corrosive agents. The formation of cracks or any defect can disrupt these barrier effect and enhance corrosion of the substrate surface. The encapsulation of organic or inorganic corrosion inhibitors within these coatings imparts a self-healing effect [179-181]. The addition of corrosion inhibitors to the hybrid coatings leads to the improvement of active corrosion protection ability of the coatings. The excess of corrosion inhibitor can affect the barrier properties of the coatings. This limitation can be reduced by using nanoparticles as reservoirs for inhibitors [182].

Khramov et al. has investigated the corrosion properties of organo-silicate hybrid coatings with encapsulated ionizable and non-ionizable corrosion inhibitors [183]. They concluded that non-ionizable inhibitors outperforms ionizable inhibitors. The slow release of non-ionizable inhibitor and its continuous delivery to the corrosion sites provides better corrosion protection.

Zheludkevich et al. has investigated the use of zirconia nanoparticles as reservoir for the storage of cerium ions (Ce^{3+}) [184]. Zirconia nanoparticles reinforce the hybrid matrix and adsorb cerium ion. These cerium ions are released upon contact with moisture. The prolonged release of cerium ions from zirconia particles provides better corrosion protection compared to their direct addition in matrix. They suggested that this prolonged release is due to the chemisorption of cerium ions to the zirconia surface and/or incorporation in the structure of nanoparticles.

4.2.3 pH dependent release of corrosion inhibitors

Corrosion process is always accompanied by local changes of pH in cathodic and anodic areas. Some research groups used a different strategy to provide self-healing ability to the hybrid coatings, based on the intelligent release of corrosion inhibitor. The release of corrosion inhibitor can be regulated by pH, light and humidity. The local change of pH during corrosion process makes it most preferable trigger option in corrosion protection systems. Polyelectrolyte multilayers can be used as storage

medium for corrosion inhibitors. The use of these multilayers preserve the stability of coatings by minimizing the negative effect of corrosion inhibitors [185, 186].

Shchukin et al. investigated the self-healing effect of layer by layer (LbL) assembled nanocontainers doped in $\text{ZrO}_x/\text{SiO}_x$ hybrid coating [185]. The silica nanoparticles were coated with poly(ethylene imine)/poly(styrene sulfonate) (PEI/PSS) using layer by layer assembly method. Benzotriazole was encapsulated between multilayers of polyelectrolytes. The release of benzotriazole was triggered with local changes of pH in defective areas during corrosion of metal substrate. The corrosion protection ability was investigated by scanning vibrating electrode technique (SVET). This method reveals the localized current activity by mapping the cathodic and anodic current along the substrate surface.

Zheludkevich et al. protected aluminum alloy AA2204 surface with unloaded $\text{ZrO}_x/\text{SiO}_x$ hybrid coating and $\text{ZrO}_x/\text{SiO}_x$ coating loaded with coated silica particles [186]. The silica particles were coated layer by layer with polyelectrolyte and benzotriazole layers. The alloy coated with hybrid film containing coated silica nanoparticles showed better corrosion protection behavior. These results show that the local change of pH results in the release of benzotriazole. This released inhibitor hinders the corrosion process. The introduction of benzotriazole filled nanocontainers in $\text{ZrO}_x/\text{SiO}_x$ hybrid coatings provides active corrosion protection.

Shchukin et al. demonstrated the ability of halloysite nanotubes as nanocontainers for anti-corrosive coatings [187]. They used 2-mercaptobenzothiazole as corrosion inhibitor and loaded it in halloysite nanotubes. The surface of the corrosion inhibitor loaded halloysite nanotubes was modified with alternating multilayers of (poly(allylamine hydrochloride)/poly(styrene sulfonate)). These surface modified halloysite nanotubes were incorporated in sol-gel coatings. The presence of these polyelectrolyte multilayers around the halloysite nanotubes make them pH sensitive. The release of corrosion inhibitor is controlled by the local pH changes in the surrounding of halloysite nanotubes due to corrosion process.

Andreeva et al. investigated the corrosion protection ability of polyelectrolyte multilayers on aluminum substrates [188, 189]. They deposited multilayers of polyelectrolytes with corrosion inhibitors. They concluded that these coatings protect corrosion process by passivating the metal due to the controlled release of inhibitor

and by buffering the pH changes at the corrosive area due to the polyelectrolyte layers.

Borisova et al. investigated the anti-corrosive ability of inhibitor loaded mesoporous silica particles in hybrid zirconia-silica coatings [190]. They loaded mesoporous silica particles with 1H-benzotriazole without any further surface modifications. The homogeneous distribution of inhibitor loaded mesoporous silica particles improved the wet corrosion protection ability of hybrid sol-gel coatings. The local pH change induced by corrosion activity triggers the release of inhibitor from mesoporous silica nanoparticles.

Hollamby et al. functionalized mesoporous silica nanoparticles and dispersed them in polyester resin-based matrix [191]. The surface functionalization helped in homogeneous dispersion of particles in the coating. They compared the anti-corrosive ability of the coatings doped directly with inhibitor to the coating doped with inhibitor loaded mesoporous silica nanoparticles. They concluded that coatings coated with inhibitor loaded mesoporous silica particles in polyester resin matrix strongly impeded the corrosion process. The concentration of directly doped inhibitor required to get the same corrosion impedance was tenfold greater.

Fix et al. demonstrated the self-healing effect of the sol-gel coatings doped with inhibitor filled halloysite nanotubes [192]. They compared the anti-corrosive ability of benzotriazole and 8-hydroxyquinoline. They loaded halloysite nanotubes with these inhibitors and incorporated in hybrid sol-gel matrix. The amount of benzotriazole loaded into halloysite was 3 (wt.%) compared to 8-hydroxyquinoline (17 wt.%). They concluded that benzotriazole showed stronger anti-corrosive effect than 8-hydroxyquinoline. The higher loading of 8-hydroxyquinoline destabilizes the sol-gel matrix which resulted in lower corrosion protection.

Shchukina et al. investigated the effect of inhibitor loaded mesoporous silica and halloysite particles on the corrosion protection of polyester powder coatings [193]. They used 8-hydroxyquinoline as corrosion inhibitor. They concluded that only 2 wt.% of inhibitors encapsulated nanocontainers can suppress the corrosion process. The release of inhibitor is triggered by local pH change due to corrosion process. They further concluded that coatings containing inhibitor loaded nanocontainers perform better than coatings with directly added inhibitor.

Shchukina et al. compared the corrosion protection ability of inhibitor loaded halloysite doped polyepoxy based autonomic corrosion protection coatings with standard polyepoxy paints [194]. They used Korantin SMK, Halox 520 or $(\text{NH}_4)_2\text{TiF}_6$ as corrosion inhibitors. The amount of corrosion inhibitors loaded in the halloysite nanotubes was 1 wt.%. The amount of zinc sulphate in commercial polyepoxy paints is 20 wt.%. Despite the 20 times decrease in inhibitor amount, the coatings doped with inhibitor loaded halloysite nanotubes showed similar corrosion protection as shown by commercial polyepoxy paints. The encapsulation of inhibitors in halloysite nanotubes isolate them from polymeric matrix and release them only in locally damaged areas. They observed the same magnitude of corrosion protection with all three inhibitors.

Borisova et al. investigated the effect of concentration and position of mesoporous silica nanoparticles filled with inhibitor on the anti-corrosion performance of hybrid sol-gel coatings embedded with these nanocontainers [195]. They used 2-mercaptobenzothiazole as corrosion inhibitor. The concentration of embedded mesoporous silica particles affects the anti-corrosion efficiency of coatings. The low concentration (0.04 wt.%) of loaded silica particles led to better barrier performance but less active corrosion inhibition. This unsatisfactory active corrosion inhibition at this low concentration attributed to the insufficient amount of 2-mercaptobenzothiazole. The coating was damaged at too high concentration (0.8-1.7 wt.%) of embedded silica nanoparticles due to the introduction of diffusion paths for aggressive electrolyte species. They concluded that the coatings doped with 0.7 wt.% of silica nanoparticles showed the best active and passive corrosion protection. Regarding the position of inhibitor loaded silica nanoparticles in the hybrid coatings, it is concluded that the introduction of these nanoparticles into the coating near the metal surface improves the anti-corrosion ability of these coatings. The proximity with the metal substrate facilitates a fast transport of the inhibitor upon corrosion attack. This helps in improving active corrosion resistance and self-healing ability of these coatings [196].

Chen et al. demonstrated the anti-corrosion and self-healing ability of acid and alkaline responsive hollow mesoporous silica nanoparticles doped hybrid sol-gel coatings [197]. They modified hollow mesoporous silica nanoparticles with 3-chloromethyl triethoxysilane and N-phenylaminomethyltriethoxysilane to obtain

alkaline and acid responsive behavior respectively. Benzotriazole was used as corrosion inhibitor and all the hallow mesoporous silica nanoparticles were loaded with it. The anti-corrosive coatings were synthesized with equal amount of acid and alkaline responsive particles in sol-gel matrix. Both pH responsive coatings showed better corrosion protection ability than the undoped sol-gel coating. They attributed these better corrosion protection abilities of these coatings to the release of benzotriazole from the hallow mesoporous silica nanoparticles after local pH changes in the corroded areas.

Fu et al. investigated the role of inhibitor loaded nanoparticles in self-healing process and long-term corrosion protection of metal substrates [198]. They synthesized acidic and alkaline dual stimuli responsive hallow mesoporous silica nanoparticles, using supramolecular nanovalves. They used bistable CB[7]/hexylammonium unit-ferrocenecarboxylic acid unit pseudorotaxanes as supramolecular nanovalves. These nanovalves have the ability to capture corrosion inhibitor at neutral pH values and release them quickly under any pH change Caffeine was used as corrosion inhibitor. These mechanized mesoporous silica nanocontainers were dispersed in self-assembled nanophase particle coatings and deposited on aluminum substrate. These coatings demonstrated excellent self-healing ability by repairing the damaged oxide layer and by showing excellent barrier resistance to maintain long-term corrosion protection.

A.H. Jafari et al. investigated the inhibitor release properties of polyelectrolyte modified silica, polyelectrolyte modified halloysite and polyelectrolyte capsules [199]. They modified these particles with layer by layer assembly of polyelectrolytes. The effect of solution parameters such as pH, temperature and stirring on inhibitor release were studied. They concluded that the release of inhibitor depends on polyelectrolyte components and inhibitor amount. Their results revealed that lower pH, higher temperature and higher stirring speed enhanced the inhibitor release.

Li et al. reported stimuli responsive silica/polymer double walled hybrid nanocontainers [200]. They synthesized these nanocontainers having hallow cavity and stimuli responsive polymeric outer wall by surface-graft precipitation polymerization. The surface grafts on these hallow particles consists of redox, pH or temperature responsive polymers. These silica/polymer double walled coatings

served as intelligent coatings for better anti-corrosion protection of metal substrates with better self-healing ability.

4.2.4 Mechanical rupture dependent release of corrosion inhibitors

The corrosion protection coatings are susceptible to damages in the form of cracks. These cracks can lead to coating degradation and ultimately making the metallic substrates accessible to the corrosion attacks. The use of self-healing polymers can help to overcome this issue. The synthesis of self-healing polymer coatings involves the incorporation of self-healing agent into nanocontainers and then, they are mixed in polymeric matrices. These nanocontainers fractures upon coating degradation, releasing the self-healing agent for curing the cracks [201-203].

Kumar et al. developed the self-healing coatings by encapsulating formaldehyde microcapsules loaded with corrosion inhibitors and healing agents into commercially available paints [204]. These coatings were applied on outdoor structures made of steel. They used tung oil and spar varnish as healing agents. Camphor and alkylammonium salt of succinic acid were used as corrosion inhibitors. They concluded that whether the coating is damaged by a direct cut or by some other mechanisms like aging, healing agent and corrosion inhibitors will flow into the affected area from the microcapsules.

Raps et al. synthesized polymeric microcapsules by oil in water polymerization method [205]. They loaded these microcapsules with oil soluble corrosion inhibitors and incorporated them in paints. The capsules prevent the interaction between inhibitor and compounds of paint matrix. The benefit of using oil soluble inhibitor is the ability of these inhibitors to displace water which can repel the electrolyte from the metal surface and assisting the adsorption of these compounds to the substrate. The use of interfacial polymerization method increases the amount of organic inhibitors in the paint matrix. These coatings showed active corrosion protection of mechanical defects. They concluded that the performance level of these coatings is comparable with chromate loaded coatings.

The effective solutions for corrosion protection depend on the complexities of conditions that trigger corrosion process. There is no single solution to enhance the corrosion protection of various materials. The combination of different corrosion inhibitors and different micro/nanocontainers can help to achieve better corrosion

performance [206]. Montemor et al tried to combine two distinct types of nanocontainers in same polymer matrix to provide corrosion protection and self-healing ability in a synergistic manner [207]. They used cerium molybdate hollow spheres and layered double hydroxide as nanocontainers. 2- mercaptobenzothiazole was used as corrosion inhibitor. The addition of both inhibitors filled nanocontainers in the matrix resulted in synergistic corrosion inhibition effect. The different activation mechanism of both nanocontainers helps in early corrosion protection and long-term stability.

4.2.5 Corrosion inhibitors for copper

Copper is most widely used in many applications due to its good thermal and electrical conductivity, ductility and strength. Copper metal is resistant towards corrosion except in highly aggressive environments. The use of corrosion inhibitors can prevent copper corrosion in aggressive mediums. The corrosion inhibitors can be inorganic and organic compounds. Organic compounds are investigated in greater numbers as they are more environment friendly. The corrosion protection mechanisms are different for both inorganic and organic compounds. Inorganic compounds form a protective oxide layer on the metallic substrate. Organic compounds either adsorb to the surface or form a complex with metal atoms. The efficiency of corrosion inhibition process can be enhanced by increasing the inhibitor solution concentration and longer exposure of metal to the inhibitor solution. Organic compounds containing heteroatoms having free electron pairs and aromatic hydrocarbons with delocalized electrons improve corrosion inhibition because these compounds enhance the probability of chemisorption. The barrier properties of higher molecular weight organic compounds are better due to their strong physical adsorption efficiency [208].

Sherif et al. demonstrated the effect of azole compounds as corrosion inhibitor on copper corrosion in various aggressive environments [209-211]. They studied the effect of 2-amino-5-ethylthio-1,3,4-thiadiazole on copper dissolution in 0.5 M HCl solution. The inhibition efficiency increases with the concentration of inhibitor in the solution. The maximum inhibition efficiency value was 78% for copper metal with this inhibitor. They also investigated the effect of 2-amino-5-(ethylthio)-1,3,4-thiadiazole and 2-Amino-5-ethyl-1,3,4-thiadiazole on the copper dissolution in 3% sodium chloride solutions. The corrosion inhibition efficiency increases with the

amount of inhibitor in the solution. The presence of heteroatoms in these azole compounds helped in complex formation with copper ions that resulted in corrosion prevention of copper.

Finšgar et al. studied the corrosion inhibition properties of 2-Mercaptobenzoxazole [212]. They concluded that 2-Mercaptobenzoxazole inhibits the corrosion process of copper metal in NaCl solution. The corrosion inhibition ability of this azole compound can be increased by changing oxygen atom with nitrogen atom.

Mihajlović et al. investigated the effects of imidazole and its derivatives as corrosion inhibitors for copper in sea water [213]. The results show that the corrosion inhibition efficiency of these compounds increases as the molecular weight and number of heteroatoms increases. The adsorption of these compounds on the copper surface shows Langmuir adsorption isotherm. They suggested adenine as the best corrosion inhibitor for copper metal in sea water.

Zucchi et al. studied the inhibition effect of various tetrazole compounds on copper in 0.1M sodium chloride solution [214]. The inhibition effect was investigated between pH 4-8 and at 40 and 80°C. The inhibition efficiency was shown between 50 to 99%. These compounds showed better inhibition efficiency with increasing pH value. These compounds inhibit the corrosion of copper metals by chemisorption and physical adsorption.

Tansug et al. synthesized a new inhibitor for copper corrosion protection [215]. The inhibitor consists of azole, thiol and carboxylate functional groups. The thiol group provides better adhesion properties, carboxylate improves molecular interactions and thiol group helps in complex formation with copper ions. The inhibitor showed corrosion inhibition efficiency of 92.50% at 55 °C in 10mM HCl solution.

Benzotriazole is mostly used organic compound for corrosion inhibition of copper metals. The inhibition properties of benzotriazole are investigated in various corrosion environments such as acidic [216], neutral [217], alkaline [218] and chloride containing solutions [219]. Benzotriazole consists of triazole and benzene ring. The nitrogen atoms in benzotriazole helps in complex formation with copper and provides inhibition ability. It can physically adsorb on the copper surface. The orientation of benzotriazole can be vertical or parallel to the surface. The bond strength of the copper-benzotriazole complex depends on the orientation of

benzotriazole molecules. The stronger bond strength was observed when benzotriazole molecules were oriented parallel to the surface of copper metal. This parallel orientation helps in interaction between vacant copper d orbitals and π electrons of benzene [218].

Frignani et al. demonstrated the effect of alkyl chain addition in 1,2,3-benzotriazole on the corrosion inhibition efficiency of this compound in chloride and sulphate solutions [220, 221]. The addition of short alkyl substituents in benzene ring helps in thick film formation on copper surface that provides better barrier properties. The increase in alkyl chain length decreases the solubility of compound but improves its corrosion inhibition ability. The best corrosion protection was obtained with hexyl-benzotriazole compounds. The low concentrations of inhibitor in solution only prevents oxygen reduction reactions. But as we increase the amount of inhibitor in solution it starts to prevent anodic reaction as well.

Ofoegbu et al. compared the corrosion inhibition effect of two triazole compounds having only difference of nitrogen position in triazole ring [222]. 1H-1,2,3-Triazole showed better corrosion inhibition performance because of its ability to form polymeric film with copper ions. In case of 1,2,4-triazole direct adsorption via nitrogen atoms was observed. They concluded that the only structural difference in triazoles effect their inhibition mechanisms.

Wang et al. synthesized dibenzotriazole compounds having more polar heads and alkyl linkers [223]. The aim of their work was to compare the inhibition performance of monobenzotriazole with these newly synthesized dibenzotriazole in sodium chloride solution. The results showed that corrosion inhibition ability of these compounds increased as the amount of benzotriazole molecules and alkyl linkers increases. They investigated the corrosion prevention mechanisms with Langmuir adsorption isotherms.

Villamil et al. investigated the inhibitive effect of sodium dodecylsulfate on copper corrosion in sulphuric acid solutions [224]. They used sodium dodecylsulfate with and without benzotriazole in the solution. Sodium dodecylsulfate showed very weak inhibition effect on copper dissolution. In case of stationary electrode sodium dodecylsulfate with benzotriazole showed cumulative effect on the copper corrosion inhibition. But in case of hydrodynamic system the inhibitive action of benzotriazole

was reduced by the presence of sodium dodecylsulfate. The inhibition properties of benzotriazole can be improved by the addition of some substituent groups in its structure.

H.Ma et al. studied the corrosion inhibition properties of three different Schiff bases in sodium chloride and sodium bromide solutions [225]. Schiff bases are synthesized by the condensation reaction of an amine with aldehyde or a ketone. The Schiff bases used for this work were N,N'-o-phenylene-bis(3-methoxysalicylideneimine), N,N'-p-phenylene-bis(3-methoxysalicylideneimine) and N-[(2-hydroxy-3-methoxyphenyl)methylene]-histidine. The presence of heteroatoms in these compounds helps in complex formation with copper (I) and copper (II) ions. All three Schiff bases suppress cathodic reaction and prevents corrosion of copper. They adsorb easily on copper surface and form a protective layer which helps in reducing copper dissolution. The chelate forming ability of N,N'-o-phenylene-bis(3-methoxysalicylideneimine) makes it better corrosion inhibitor than other two Schiff bases.

Warraky et al. demonstrated the effect of ethylene diamine on corrosion process of copper in HCl solution [226]. The samples were dipped in HCl having Na₂S additive concentrations. Ethylene diamine enhance the copper dissolution reaction without any additive in the solution. The presence of Na₂S in solution helps in forming a thin HS⁻ layer on copper surface. The addition of ethylene diamine to the copper metal having HS⁻ layer helps in forming a complex between ethylene diamine and HS⁻ which protects copper dissolution. Ethylene diamine acts as a corrosion inhibitor in this case.

Baeza et al. demonstrated the protection of copper corrosion by 1,3,4-thiadiazole-2,5-dithiol in HCl solution at room temperature [227]. The inhibition efficiency increases as the amount of increased in the solution. The maximum efficiency value reached was 84.1%. The presence of sulphur atoms helps in chemisorption of 1,3,4-thiadiazole-2,5-dithiol on copper surface. The adsorption of inhibitor followed Langmuir isotherm behavior. The complex formation on copper metal surface helps in corrosion inhibition.

Guo et al. investigated the ability of triethyl phosphate and triphenyl phosphate to protect copper corrosion in salt solution [228]. These phosphates form monolayers

on copper surface. These self-assembled layers of phosphate inhibit copper corrosion. These phosphates are less toxic. Ethanol was used as a solvent for both compounds. The inhibition efficiency increases till a critical immersion time in solution. They concluded that the triphenyl phosphate showed better inhibition properties than triethyl phosphate.

Yang et al. proposed inositol hexaphosphate as green inhibitor to protect metallic corrosion process [229]. Inositol hexaphosphate form monolayers and protect corrosion. This compound reacts with oxides present on copper surface and forms soluble complexes. After self-cleaning of the copper surface inositol hexaphosphate chemically adsorbed to the copper surface. It inhibits the copper corrosion process. The efficiency of this inhibition process is less due to the adsorption of water molecules.

Cheng et al. investigated the inhibiting behavior of Carboxymethylchitosan (CM-chitosan) in acidic solution [230]. Carboxymethylchitosan (CM-chitosan) adsorbed to the substrate surface by a displacement reaction. It removes water molecules from the substrate surface. The adsorption and inhibition efficiency enhanced with increase in concentration of inhibitor. The inhibition efficiency reached 94% at 200mg/L inhibitor concentration.

El-Haddad investigated the corrosion inhibition behavior of chitosan in acidic environment [231]. He immersed copper in acidic solution containing various concentration of chitosan. Chitosan inhibited the copper corrosion process in acidic solution. The inhibition efficiency of copper enhanced with increasing chitosan amount in acidic solution. Chitosan adsorbs to the metal surface and inhibit its dissolution. He concluded from quantum chemical results that oxygen and nitrogen atoms in chitosan structure helped in chitosan adsorption to the metal surface.

Zheludkevich et al. used chitosan as a reservoir for cerium ions [232]. They coated a thin film of chitosan on copper metal surface and checked its anti-corrosion ability with and without cerium ions. The undoped chitosan layer suppressed the corrosion of copper samples. But the cerium ion doped coatings showed better corrosion protection.

Lin Li et al. tried to investigate the adsorption and corrosion protection properties of chitosan derivatives [233]. They synthesized thiocarbohydrazide-modified chitosan

compounds. The electrochemical results showed that thiocarbohydrazide-modified chitosan and chitosan possessed corrosion inhibition ability. They suppressed the copper corrosion in acetate solution. They obtained 88% inhibition efficiency at 30mg/l concentration.

Menaka et al. synthesized chitosan thiophene carboxaldehyde Schiff base. This Schiff is a biocompatible [234]. They investigated its behavior as corrosion inhibitor in acidic solution. This compound showed good adsorption to the substrate surface. This good adsorption ability helps in better inhibition properties. The presence of ions and functional groups helps in suppressing cathodic and anodic reactions. Chitosan thiophene carboxaldehyde Schiff base showed 92% inhibition efficiency at room temperature.

Winnie Ma et al. synthesized nanocomposite coatings containing chitosan nanoparticles as filler materials in epoxy matrix [235]. These coatings were synthesized with various nanochitosan filler loadings. The addition of chitosan in polymeric matrix enhanced the thermal and chemical properties of polymeric matrix. The electrochemical measurements showed the coatings loaded with nanofillers showed better anti-corrosion ability than the neat polymeric coatings. The coatings loaded with 0.5 wt.% nanochitosan showed the best anti-corrosion properties.

Chauhan et al. organically modified chitosan and synthesized Chitosan-Thiosemicarbazide and Chitosan-Thiocarbohydrazide [236]. They evaluated the inhibiting influence of these compounds in 1M hydrochloric acid solutions. Both compounds suppressed anodic and cathodic reactions but predominantly cathodic reaction. The inhibition efficiency of these compounds increased with concentration but decreased with increasing temperature. The molecular dynamics simulation suggested that these inhibitors attached to the substrates surface with parallel or flat orientations.

4.2.6 Electrodeposition of Fe-P alloy thin films

Iron plating is preferred for various applications due to its captivating physical properties, abundance and lower cost. Iron can be deposited as brittle or ductile metal. The properties of deposited metal can be changed by heat treatment or surface modification methods. The properties of pure iron can be improved by alloying it with various other elements. The addition of phosphorus in pure iron can change the

structure of alloy deposit. So, based upon the concentration of phosphorus the iron-phosphorus alloy can be amorphous, crystalline or a mixture of these phases. Amorphous alloys show better properties like corrosion resistance, magnetism, electrical resistivity and good mechanical properties than their crystalline counterparts of similar compositions. The absence of grain boundaries, dislocations and crystalline defects in amorphous alloys enhanced their corrosion resistance [31, 237]. The amorphous structure can be produced by rapid quenching of the alloy melts [238], electrodeposition [239] and chemical deposition [240]. Rapid quenching can be achieved over a wide range of chemical compositions as it is a nonequilibrium process [241]. Electrochemical deposition is better than chemical deposition methods because of its higher deposition rate, lower cost, reproducibility, dense microstructure and easy operation [242]. The use of electrodeposition methods can help in the synthesis of non-equilibrium alloys and also tailoring the phase structure of same alloys by changing its operating parameters [29].

Vitkova et al. investigated the optimum parameter for electrodeposited smooth, uniform and light-colored Fe-P alloys [243]. The amount of phosphorus in the coating is decreased by increasing the pH of electrolyte and current density. They also showed that coating brightening effect can be achieved by adding small amount of Cu^{2+} and Mn^{2+} in electrolyte.

Kamei et al. obtained amorphous Fe-P electrodeposits with increasing phosphorous amount upto 20 at% [244]. They investigated the effects of various electrodeposition parameters on Fe-P alloy microstructures. The thermal stability of these amorphous alloys was also determined.

Dietz et al. produced $\text{Fe}_{1-c}\text{-P}_c$ alloys with three different microstructures [245]. The change in phosphorus content resulted in different morphologies: microcrystalline if $0.01 < c < 0.12$, mixture of amorphous and crystalline if $0.12 < c < 0.15$ and amorphous when $0.15 < c < 0.28$.

Zečević et al. investigated the influence of current density, pH, temperature and chemical composition of chemical bath on the structure and composition of electrodeposited thin films of Fe-P alloy [29]. The results showed that the appearance and morphology of thin Fe-P alloys depends on current density.

Xue et al. fabricated nanowires of Fe-P alloy by electrodeposition technique [246]. The structures of these nanowires were amorphous at phosphorus content of 10.3 wt.%. They investigated the magnetic properties of these amorphous nanowires in aluminum oxide films.

A. Miko et al. deposited amorphous and/or amorphous/nanocrystalline layers of Fe-P layers by pulse electrochemical method [30]. The deposition parameters influenced chemical compositions and structures of deposited layers. The electrochemical properties were influenced by the structural changes. The amorphous surface layers showed positive corrosion potential. As the amount of nanocrystals increased in amorphous layers corrosion potential shifted to negative corrosion potentials.

Huang et al. investigated the inducing effect of aluminum on Fe-P alloys deposited by electroless deposition method [240]. The electrochemical reactions were investigated by changing various parameters like current density, pH, metal salt concentrations and temperature. The deposition rate of Fe-P alloys was determined by current density. The results demonstrated that aluminum induced deposition of Fe-P alloys by decreasing the polarization resistance of electrochemical partial reactions. They further concluded that hydrogen evolution increases the deposition rate of Fe-P alloys.

Mostavan et al. proposed the fabrication of Fe-P alloys by electroforming method [247]. The interaction between structure of electrodeposited material and deposition parameters was investigated. The corrosion potential and structure of alloy is affected by the amount of phosphorus in the electrodeposited alloy.

4.3 Materials, Methods and Techniques

There are two parts in this section. In the first part, the materials and methods that were used in the study of nanocomposite coatings for copper corrosion protection will be introduced. The second part will define the materials and methods that were used to synthesize metallic coatings for corrosion protection.

4.3.1 Anti-corrosion coatings for copper protection

4.3.1.1 Materials

Styrene-Butadiene-Styrene (SBS) triblock copolymer as polymer matrix, which is normally used as additive to enhance mechanical properties of asphalt as well as in the automotive sector and in construction sector. Styrene-Butadiene-Styrene (SBS) triblock copolymer with 30% styrene content and number average molecular weight of 140,000 g/mol was purchased from kraton. Chitosan and polyethylene glycol were chosen as corrosion inhibitors. The chemical structures and molecular weights of these inhibitors are shown in Table 4.1. Chitosan is a polysaccharide and it is derived from chitin, a substance that is found in hard outer shells of lobsters, crabs or shrimps or in cell walls or fungi. Chitosan is soluble in acidic solutions. The presence of nitrogen and oxygen in its structure is responsible for its anti-corrosive properties and probable complex formation with metal atoms [233, 236]. Polyethylene glycol was chosen as corrosion inhibitor because of its ability to adsorb to the metal surface and decrease the cathodic current density [217]. The properties of silica-based fillers used in this study are shown in Table 4.2.

Table 4.1 Properties of corrosion inhibitors used in this work with their specifications.

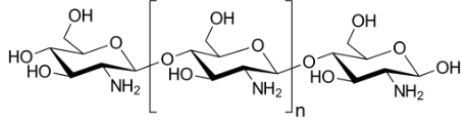
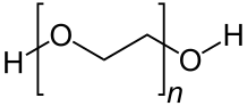
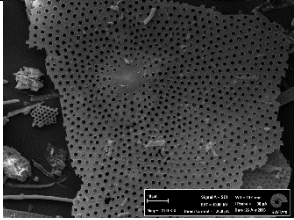
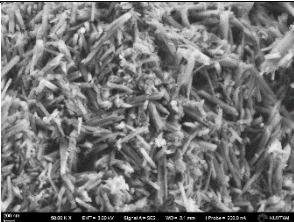
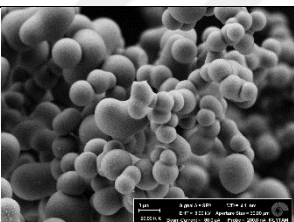
Inhibitor	Molecular weight (g/mol)	Chemical structure	Company
Chitosan	50k-190k		Sigma Aldrich
Polyethylene glycol	10k		Merck

Table 4.2 Properties of silica-based fillers used in this work with their specifications

Fillers	Specific Surface area (m ² /g)	Shape	Company
Diatomaceous earth	35 [134]		Sigma Aldrich
Halloysite nanotubes	65 [142]		Sigma Aldrich
Silica nano/micro particles	428		Synthesized Chapter 2 (Section 2.5.2)

4.3.1.2 Sample preparation

4.3.1.2.1 Filling of pores of silica-based particles with inhibitors

The silica-based porous particles were filled with corrosion inhibitors by dipping them in anti-corrosion agent solution. Polyethylene glycol (10 wt.%) solution was prepared in water. Chitosan was dissolved in 1 vol.% acetic acid and 1 mg/mL solution was prepared. 0.2 g silica-based porous particles were placed in 10 mL solutions of polyethylene glycol (10 wt.% in water) and chitosan (1 mg/mL). These dispersions were sonicated for 30 minutes at room temperature. After sonication, the dispersions were left for one night to obtain thermodynamic equilibrium and then centrifuged. The sediments were dispersed again in the respective solvents and centrifuged immediately to remove the loosely bonded inhibitor. The product was dried in open air.

4.3.1.2.2 Preparation of polymeric composites

SBS stock solution (20 mg/mL) was prepared by dissolving SBS in chloroform. Silica-based porous particles filled with corrosion inhibitors were dispersed in SBS stock solution to obtain 3, 6, 15 and 21 % by mass inhibitor filled silica-based particles in SBS solution. The dispersion and agglomeration of such loaded particles in chloroform were investigated by visual observation. These dispersions are shown in Fig. 4.1. The silica-based fillers which were filled with PEG-10K were homogenously distributed with a smaller number of agglomerates in SBS solution due to solubility of PEG in chloroform. But the ones which were filled with chitosan showed agglomeration. The reason for this agglomeration is the insolubility of chitosan in chloroform. Therefore, PEG helps in better dispersion of particles in chloroform solution, but chitosan enhances the agglomeration of fillers in order to minimize contact with chloroform.

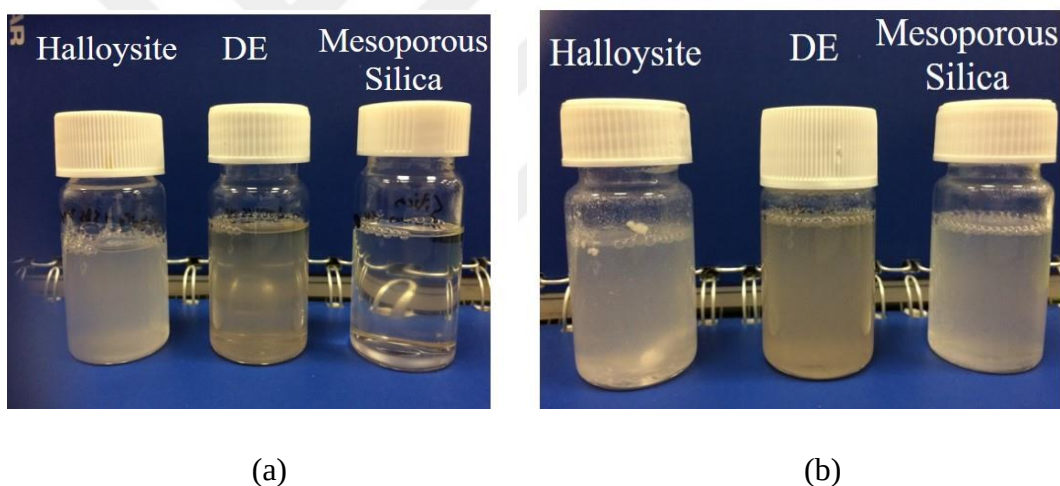


Fig. 4.1. Dispersions of silica-based fillers in chloroform SBS solution, a) PEG loaded silica-based fillers in SBS solution, b) Chitosan loaded silica-based fillers in SBS solution.

4.3.1.2.3 Film formation on copper substrate

Thin films of SBS, SBS/ inhibitor filled halloysite, SBS/inhibitor filled silica and SBS/inhibitor filled diatomaceous earth were prepared by dip coating method. Before dip coating, copper substrates were etched with concentrated sulphuric acid at room temperature to remove the oxides. The etching of copper substrates was followed by rinsing with distilled water. The substrates were dip coated with SBS/inhibitor filled silica-based particles suspensions with the speed of 20-25 mm/s. The dip coated copper substrates were dried in open atmosphere. Fig. 4.2 shows the images of

SBS/inhibitor filled silica-based fillers coated copper substrates. These images showed a smooth homogeneous coating on the copper substrates.

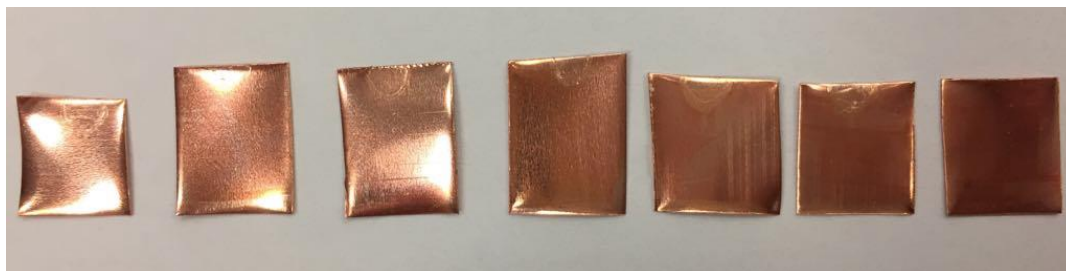


Fig. 4.2 Photographs of SBS/inhibitor filled silica-based particles dip coated on copper substrates. From left to right; only SBS, halloysite loaded with PEG/SBS, silica loaded with PEG/SBS, diatomaceous earth loaded with PEG/SBS, halloysite loaded with chitosan/SBS, silica loaded with chitosan/SBS, diatomaceous earth loaded with chitosan/SBS. The amount of all inhibitor loaded particles is 15 % by mass in SBS.

4.3.2 Characterization

4.3.2.1 Optical Microscope

The surface morphology of coated metallic substrates before and after exposing to corrosive environments was investigated by using Leica DM LM model optical microscope with lowest 5x magnification.

4.3.2.2 Scanning electron Microscope

The morphology of coated metal substrates, dispersion of silica-based fillers in composite films were investigated with field emission scanning electron microscope (Zeiss EVO) coupled with energy dispersive spectroscopy (EDS).

4.3.2.3 Thermogravimetric analysis

The amount of filled inhibitor was investigated by thermogravimetric analysis (TGA). TGA of silica-based particles filled with inhibitors was carried out under air atmosphere with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature up to $700\text{ }^{\circ}\text{C}$.

4.3.2.4 Open circuit potential measurements (OCP)

The open circuit potential is defined as the difference of potential between working electrode and reference electrode when there are no current flows through the system. The first step in most electrochemical experiments is the measurement of open circuit potential (E_{oc}). The cell potential is monitored to understand if the system reached to steady state and the drift of the potential is less than 5 mVs^{-1} . The

stable open circuit potential means that the most reactions in the system have reached to the steady state. The value of current at open circuit potential is called corrosion current (I_{corr}). This measurement was used to investigate the potential of SBS/inhibitor loaded silica particles and their corrosion protection by analyzing this potential with time. These measurements were performed in 0.5 M NaCl solution by using EG&G 272 potentiostat.

4.3.2.5 Cyclic Voltammetry (CV)

Cyclic voltammetry is one of the simplest voltammetric techniques. The electrode potential is swept from a fixed starting point to a fixed upper potential limit and then swept backward to the lower potential limit at constant scan rates. This measurement was carried out in a three-electrode cell system. The cell consists of composite coated copper as working electrode, platinum as auxiliary electrode and Ag/AgCl as reference electrode. The three-electrode system is shown in Fig. 4.3.

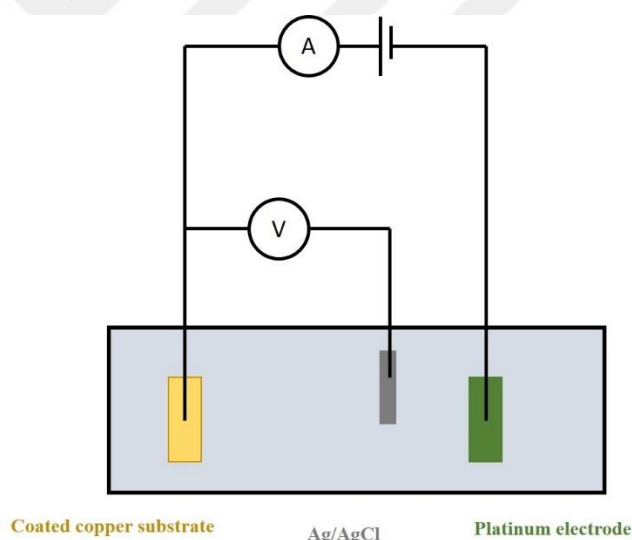


Fig. 4.3 Scheme of three electrode system

In this method the potential changes linearly with time. The potential value is measured between the working copper substrate and Ag/AgCl electrode and the current is measured between copper substrate and platinum electrode. The current at the composite coated copper substrate is plotted versus potential applied to the composite coated substrate to give the cyclic voltammogram. In this study, the polarization curves of voltammograms were obtained by moving +350 mV from open circuit potential at a scan rate of 5 mVs^{-1} . These measurements were performed in 0.5 M NaCl solution by using EG&G 272 Potentiostat.

4.3.1.3.6 Potentiodynamic polarization (Tafel plots)

The corrosion potential and corrosion current densities were determined by Tafel extrapolation technique. This method uses parameters obtained from anodic and cathodic polarization curves. The anodic and cathodic polarization measurements were carried out in three-cell electrode system. The SBS/inhibitor loaded silica-based particles coated copper was used as working electrode, platinum as auxiliary electrode and Ag/AgCl as reference electrode. The current and potential are measured simultaneously. The Tafel plots were obtained by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs⁻¹. The anodic and cathodic polarization curves behave linearly at approximately ± 50 mV from open circuit potential on a semilogarithmic plot. This linear region is called Tafel region. The corrosion potential is determined by extrapolating the Tafel region of anodic and cathodic polarization curves. The rate of oxidation and reduction is equal at corrosion potential. The current density at corrosion potential point shows the corrosion rate of the system. The Tafel extrapolation technique is used to measure extremely low corrosion rates with good accuracy. These measurements were performed in 0.5 M NaCl solution by using EG&G 272 Potentiostat.

4.4.1 Metallic alloys/composite based coatings for corrosion protection

4.4.1.1 Materials

The Fe-P layers and Fe-P based composite coatings were electrodeposited from a phosphate-based solution with and without addition of silica-based fillers as reinforcing agents. The electrolyte contained iron sulphate as Fe source, sodium hypophosphite as P source and ammonium chloride to enhance the conductivity of solution. Iron sulphate, L-ascorbic acid, and boric acid were purchased from Merck. Polyethylene glycol (PEG), Poly-2-ethyl-2-oxazoline (PEOX) were used as additive in electrolyte solution. PEG and PEOX and Chitosan were used as corrosion inhibitors. Halloysite nanotubes and mesoporous silica nano/micro particles were used as nanofillers. Sodium hypophosphite and ammonium chloride were purchased from Sigma Aldrich. PEG ($M_w = 10000$ g/mol) and PEOX ($M_w = 5000$ g/mol, 50000 g/mol) were purchased from Merck. Chitosan ($M_w = 50000$ -1900000 g/mol) and halloysite nanotubes were purchased from Sigma Aldrich. The mesoporous silica

particles were synthesized by combination of hydrolysis and condensation reaction of tetraethyl orthosilicate in the presence of nonionic surfactant Pluronic F127 in acidic aqueous solution as described in Chapter 2.

4.4.1.2 Sample Preparation

4.4.1.2.1 Electrodeposition of Fe-P alloy layers

The Fe-P layers were deposited on various substrates by using direct current electrochemical method from an electrolyte bath at ambient temperature. The exact compositions of electrolytic bath are shown in Table 4.3. Cu wire, Cu sheets and Brass sheets were used as substrates. Prior to the electrodeposition of Fe-P layers, the substrate surfaces were exposed to concentrated H_2SO_4 for 2 seconds for removing the oxide layers, wiped with paper towel, washed with DI water and ethanol respectively and then dried with nitrogen flow. The reagents used for electrochemical deposition were used without any purification process. The electrochemical deposition of Fe-P layers was carried out in a glass cell. Argon gas was used for deaeration of electrolyte bath for 20 minutes before deposition process. The electrolyte bath was constantly agitated at 500 rpm during the deposition process. High purity platinum electrode was used as anode in electrochemical deposition process. After electrochemical deposition of Fe-P layers, the cathode (coated substrates) were removed and rinsed with distilled water and dried with nitrogen flow.

Table 4.3 Composition of electrolyte bath for the electrodeposition of Fe-P layers.

Compound	Amount (g/dm^{-3})
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	300
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	21
H_3BO_3	30
L-Ascorbic Acid	5
NH_4Cl	20

4.4.1.2.2 Filling of pores of silica-based particles with inhibitors

Mesoporous silica particles and halloysite nanotubes were filled with corrosion with the same procedure as described in Section 4.3.1.2.1.

4.4.1.2.3 Electrodeposition of Fe-P matrix reinforced with silica-based fillers

The electrodeposition of Fe-P layers reinforced by silica-based particles was achieved by adding silica-based fillers in electrolyte bath having composition as shown in Table 4.3. The Fe-P layers were reinforced with both unloaded and inhibitor loaded silica-based particles. The concentration of silica-based particles used in electrolytic bath was 0.1 g/L or 2 g/L. The surface tension of the electrolytic bath was reduced by adding PEOX-50K, PEOX-5K or PEG-10K as additives. The concentration of these additives was varied in electrodeposition bath. The deposition bath was stirred with same rate of 500 rpm. All samples were electrodeposited under direct current conditions. Similar experimental conditions were used for the deposition of composite coatings as described in section 4.4.2.1.

4.4.2 Characterization

4.4.2.1 Scanning electron Microscope

The morphology of Fe-P layers and Fe-P/silica-based composite coated metal substrates, dispersion of silica-based fillers in Fe-P matrix were investigated with field emission scanning electron microscope (Zeiss EVO). The energy dispersive spectroscopy (EDS) coupled with SEM was used to investigate the elemental composition of the coated samples.

4.4.2.2 X-ray fluorescence spectroscopy (XRF)

XRF technique is usually used for the investigation of composition and concentration analysis of each element present in Fe-P layers and silica-based fillers containing Fe-P composites. The measurements of Fe-P layers and silica-based loaded Fe-P composites were done with the substrates. In this method, the chemical analysis is done by measuring the fluorescent X-rays emitted by a sample. These X-rays are emitted due to the excitation of the sample by an X-ray source. This is an excellent method for quantitative and qualitative determination of chemical compositions because each element produces a specific set of fluorescent X-rays.

4.4.2.3 X-ray diffraction (XRD)

The structure of Fe-P layers and silica-based fillers containing Fe-P composites was characterized by XRD technique. The measurements of Fe-P layers and silica-based fillers/Fe-P composites were done with the substrates. In this method, the interaction of sample with monochromatic X-rays produces reflected rays. The intensity of

reflected rays depends on the constructive interference of the wavelengths of reflected rays. This constructive interference occurs only when the conditions of Bragg's Law are satisfied. These diffracted rays are then collected, processed and a unique X-ray diffraction pattern is generated. These diffraction patterns are then used to determine the structures of materials.

4.4.2.4 Polarization resistance measurement

Polarization resistance is the measure of resistance of metals against corrosion. The higher polarization resistance value of metals suggests strong resistance towards corrosion process. This measurement was carried out in a three-electrode cell system. The cell consists of electrodeposited sample as working electrode, platinum as auxiliary electrode and Ag/AgCl as reference electrode. For polarization resistance measurement, working electrode was polarized by moving ± 15 mV from open circuit potential. The polarization of the working electrode resulted in current flow between the working and auxiliary electrode. The polarization resistance was measured by taking the inverse of the slope of current versus potential curve. These measurements were performed in 0.1 M NaCl solution by using EG&G 272 potentiostat.

4.5 SBS/silica-based fillers composites for anti-corrosion applications

Corrosion degradation of materials leads to economic losses and environmental damages. Two common approaches are used for protection of materials against corrosion. These approaches include active and passive approach. The active approach works by suppressing the corrosion reactions, while passive approach works by inhibiting the contact between corrosive materials and metal surfaces. The combination of active and passive approach can provide long term corrosion protection to the metallic surfaces [22-24, 186]. Here, we presented comparative studies on silica-based micro- and nano- containers embedded in polymeric matrix. The pores of these silica-based fillers were filled with environment friendly corrosion inhibitors. The silica-based nano- and micro- containers used in this study include silica micro/nano particles, diatomaceous earth particles and halloysite nanotubes. SBS was chosen as a polymeric matrix due to its better strength and wear resistance properties. Chitosan and polyethylene glycol were used as green corrosion inhibitors. Chitosan has been already reported in literature as corrosion inhibitor [231-234]. There are only very few works available on the ability of PEG as corrosion inhibitor [217, 248]. The anti-corrosive ability of these organic compounds depends on their surface adsorption properties. The adsorption of these compounds resulted in effective blocking of active anodic or cathodic sites on the metal surface and resulted in minimizing the corrosion rate of copper substrates. SBS coating itself acted as passive barrier by protecting the metal from dissolution while inhibitor loaded fillers dispersed in SBS matrix enhanced the protective ability of these coatings. These coatings can be simply applied to copper substrates by dip coating method. The anti-corrosion ability of these coatings was investigated by cyclic voltammetry and Potentiodynamic polarization measurements. The results provided a better idea about the proper selection of environment friendly corrosion inhibitors and fillers combination in decreasing the corrosion rate of copper.

4.5.1 Investigation of inhibitor intake capacity of silica-based fillers

Chitosan and polyethylene glycol were used as corrosion inhibitors. The structures of silica-based porous fillers used as carriers for corrosion inhibitors in the composite coatings are shown in Fig. 4.4. Halloysite occurs in shape of hollow nanotubes as

shown in Fig. 4.4 a. These nanotubes had a length of $\sim 1\ \mu\text{m}$ and inner diameter of $\sim 30\ \text{nm}$. Spherical mesoporous silica particles have a diameter of 500-900 nm. These particles are shown in Fig. 4.4 b. DE particles occur in various irregular shapes and sizes as shown in Fig. 4.4 c. The most dominant shape is planar flakes. The size of DE particles ranges from 250 nm to $20\ \mu\text{m}$. The inhibitor intake capacity of these silica-based porous fillers was investigated by TGA.

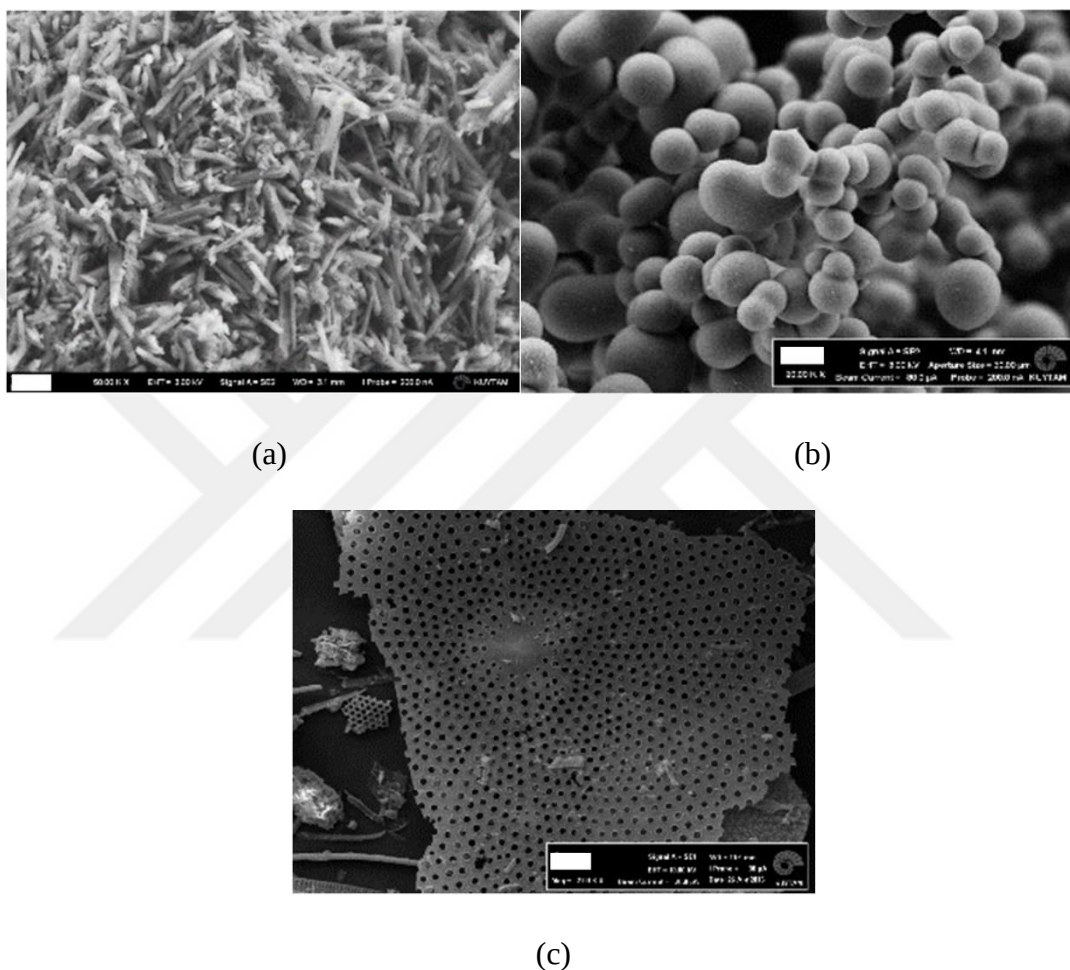


Fig. 4.4 Morphology of silica-based fillers, a) diatomaceous earth, b) halloysite nanotubes and c) mesoporous silica particles. The scale bars shown on the image are a) 1 μm , b) 400 nm and c) 1 μm .

The pores of these silica-based fillers were filled by dipping them in inhibitor solutions. Typically, 0.2 g of silica-based particles were dispersed in 10 mL solution of polyethylene glycol (100 mg/mL) and chitosan (1 mg/mL). These dispersions were sonicated for 30 min at room temperature. After sonication, these dispersions were left for overnight to obtain thermodynamic equilibrium. Then these dispersions were centrifuged. The sediments were washed twice with the respective solvents (DI

water for PEG loaded and acetic acid for chitosan loaded) to remove loosely bounded molecules. The sediments were dried in open air.

The amount of corrosion inhibitor loaded into the pores of silica-based particles is determined by TGA. The thermograms of unreacted silica-based fillers with chitosan loaded fillers are shown in Fig. 4.5. The amount of chitosan loaded into the pores of fillers was calculated by the difference between weight loss of unloaded porous fillers and their respective chitosan loaded mixtures.

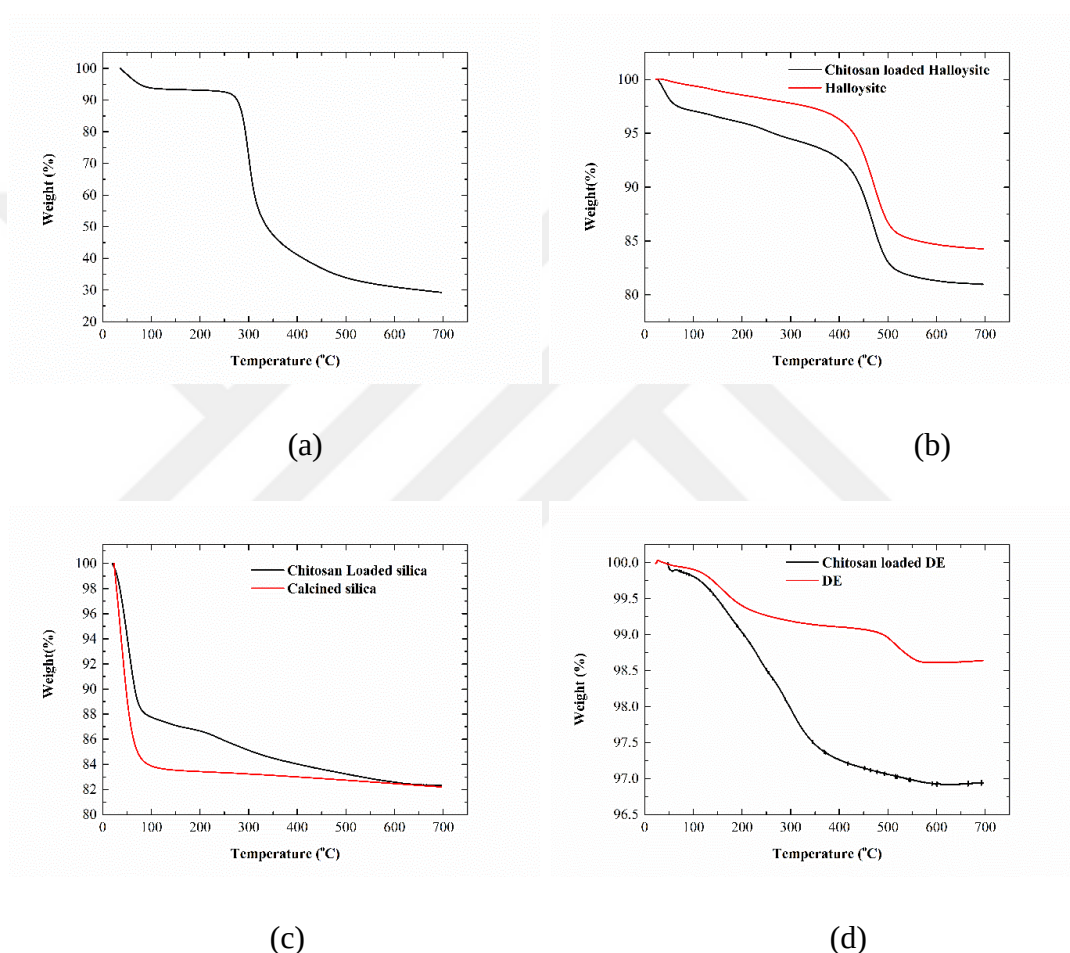


Fig. 4.5 Thermogravimetric analysis plots showing weight losses, (a) untreated chitosan, (b) untreated halloysite (red) and chitosan loaded halloysite (black), (c) untreated silica (red) and chitosan loaded silica (black), (d) untreated DE (red) and chitosan loaded DE (black).

The weight loss curve of chitosan showed two different regions of mass loss. The first weight loss occurred due to the evaporation of moisture content in the temperature range of 35-100 °C. Chitosan molecules have a strong affinity to water molecules in solid state which may result in this moisture content. The second weight loss occurred due to the degradation of chitosan molecules in the temperature

range of 240- 400 °C. The degradation of chitosan molecules continued even beyond 400 °C [249]. The thermogram of untreated halloysite showed a continuous mass loss till 500 °C as shown in Fig. 4.5b. The mass loss of ~15 % is associated with the loss of moisture and dehydroxylation of halloysite matrix [250]. The thermogram of chitosan loaded halloysite showed a total mass loss of ~19%. The degradation temperature of chitosan and halloysite is almost the same. So, the difference between the mass loss of untreated halloysite and chitosan loaded halloysite is ~4%. This ~4% mass loss is attributed to the amount of chitosan loaded into the halloysite nanotubes. The thermogram of untreated silica particles showed a total mass loss of ~16% at 100 °C as shown in Fig. 4.5c. This mass loss is due to the evaporation of water molecules from the silica particles. The thermogram of chitosan loaded silica particles showed total mass loss of ~18% in two different temperature regions. The first mass loss of ~14% is attributed to the evaporation of water molecules. The mass loss of ~4% in temperature range of 230-450 °C is attributed to the degradation of loaded chitosan molecules. The thermogram of untreated DE showed a mass loss of ~1.2%, as shown in Fig. 4.5d. The first mass loss is attributed to the loss of adsorbed moisture content and second mass loss is attributed to the decomposition of some inorganic species [138]. The thermogram of chitosan loaded DE and untreated DE showed a mass loss of ~2.5%. This mass of ~2.5% can be attributed to the amount of chitosan loaded in DE particles. The amount of chitosan loaded in silica and halloysite particles is almost same, but the amount of chitosan loaded in DE is less. The pH of the chitosan solution used for loading was 2.75, chitosan carries positive charge at this pH and silica particles have a negative charge. So, there is an electrostatic interaction between silica-based fillers and chitosan. This electrostatic interaction may have resulted in almost similar loading of chitosan in all these silica-based fillers.

The thermograms of PEG-10K and PEG-10K loaded silica-based fillers are shown in Fig. 4.6. The amount of PEG loaded in silica-based fillers is determined by the difference between the mass loss of untreated fillers and PEG-10K loaded fillers. The thermogram of PEG-10K showed that the decomposition temperature of PEG-10K is 380-400 °C as shown in Fig. 4.6a. The thermogram of PEG loaded DE showed a mass loss of ~15% at decomposition temperature of PEG-10K. The thermogram of PEG loaded halloysite nanotubes showed an initial mass loss of 2% due to the

adsorbed moisture. The mass loss of ~14% at 380 °C is attributed to PEG-10K. The thermogram of PEG loaded silica particles showed a mass loss of 30% at the decomposition temperature of PEG-10K. PEG-10K physically adsorbed to silica-based fillers and usually it fills the pores of the particles (Section 3.4.1). The amount of PEG-10K loaded in the silica particles is more than loaded in DE and halloysite. This difference in PEG-10k amount can be attributed to the difference in specific surface area of silica particles and other fillers. The specific surface area for silica particles is 428 m²/g, but the specific surface area of halloysite and DE is 65 m²/g and 35 m²/g respectively [134, 142].

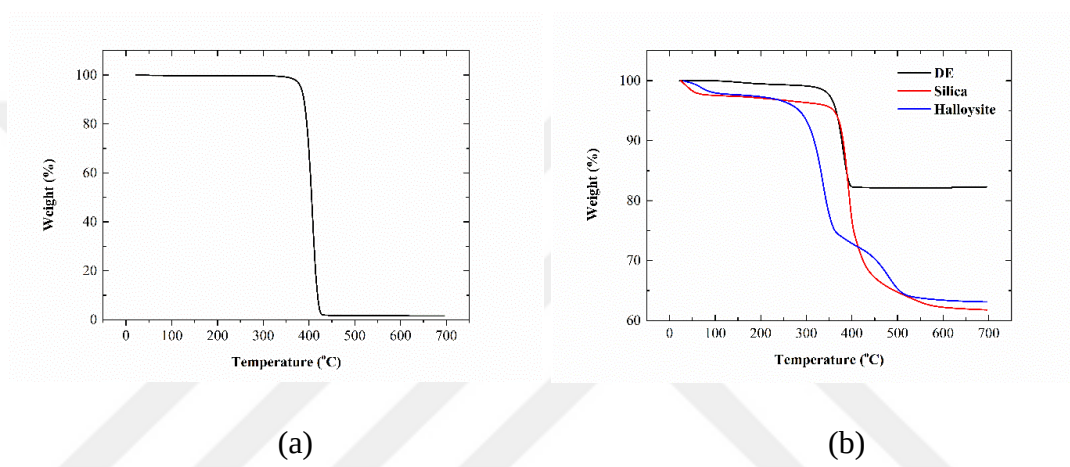


Fig. 4.6 TGA plots showing weight losses (a) untreated PEG10K, (b) DE Particles filled with PEG-10K (black line), halloysite nanotubes filled with PEG-10K (blue line) and silica particles filled with PEG-10k (red line).

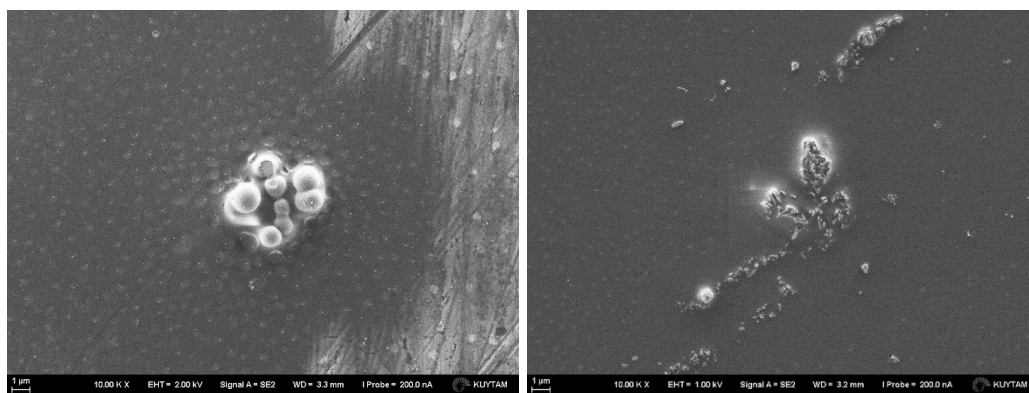
4.5.2 Preparation and investigation of electrochemical properties of inhibitor filled silica-based fillers/SBS composite coated Cu

The preparation of composite coatings consisted of three steps. First, the silica based porous fillers were prefilled with corrosion inhibitors then these prefilled micro- and nano- fillers were dispersed in SBS solution and finally these dispersions were applied to copper surfaces by simple dip coatings method. An array of composite coated samples was prepared by dispersing 15% by mass of prefilled nano- and micro- fillers in SBS solution and then dip coating them on copper surfaces.

4.5.2.1 Incorporation of inhibitor filled silica-based fillers in composite

To prepare a homogeneous composite coating, a dispersion of prefilled silica-based fillers in SBS solution was prepared. For preparing theses dispersions, Silica-based

particles filled with corrosion inhibitors were dispersed in SBS stock solution (20 mg/mL in chloroform) and contained 15% by mass inhibitor filled silica-based particles in SBS solution. The copper samples were dip coated with SBS/silica-based fillers dispersions. The more homogeneous distribution of fillers was obtained by stirring the dispersions at 300 rpm during dip coating process. The copper samples were dried in open atmosphere after dip coating. The incorporation of inhibitor loaded silica-based fillers in SBS matrix was investigated by SEM analysis. The SEM images SBS/silica-based filler composite coated copper substrates are shown in Fig. 4.7. The images of samples coated with SBS/silica-based filler dispersions showed the successful incorporation of inhibitor loaded fillers in SBS matrix. These fillers were observed as individual particles as well as agglomerated particles on the top surface of the copper substrates in all coated samples. The PEG-10k loaded fillers were better dispersed throughout the coatings. The chitosan filled fillers showed agglomerations (Fig. 4.7c-f). Since chitosan is completely insoluble in chloroform (solvent of SBS) it enhanced agglomeration to minimize interaction with chloroform. It was observed that there was a significant amount of inhibitor loaded fillers buried in SBS matrix. These buried fillers can enhance the anti-corrosion ability of the coatings by controlled release of the inhibitors upon physical damages in the coatings. The inhibitor will be released upon contact with corrosive liquid. The higher magnification images taken on SBS coated (Fig. 4.7g) and SBS/silica-based fillers coated showed pores and cracks in the coatings. These inhomogeneities in coatings are associated with the faster evaporation of chloroform.



(a)

(b)

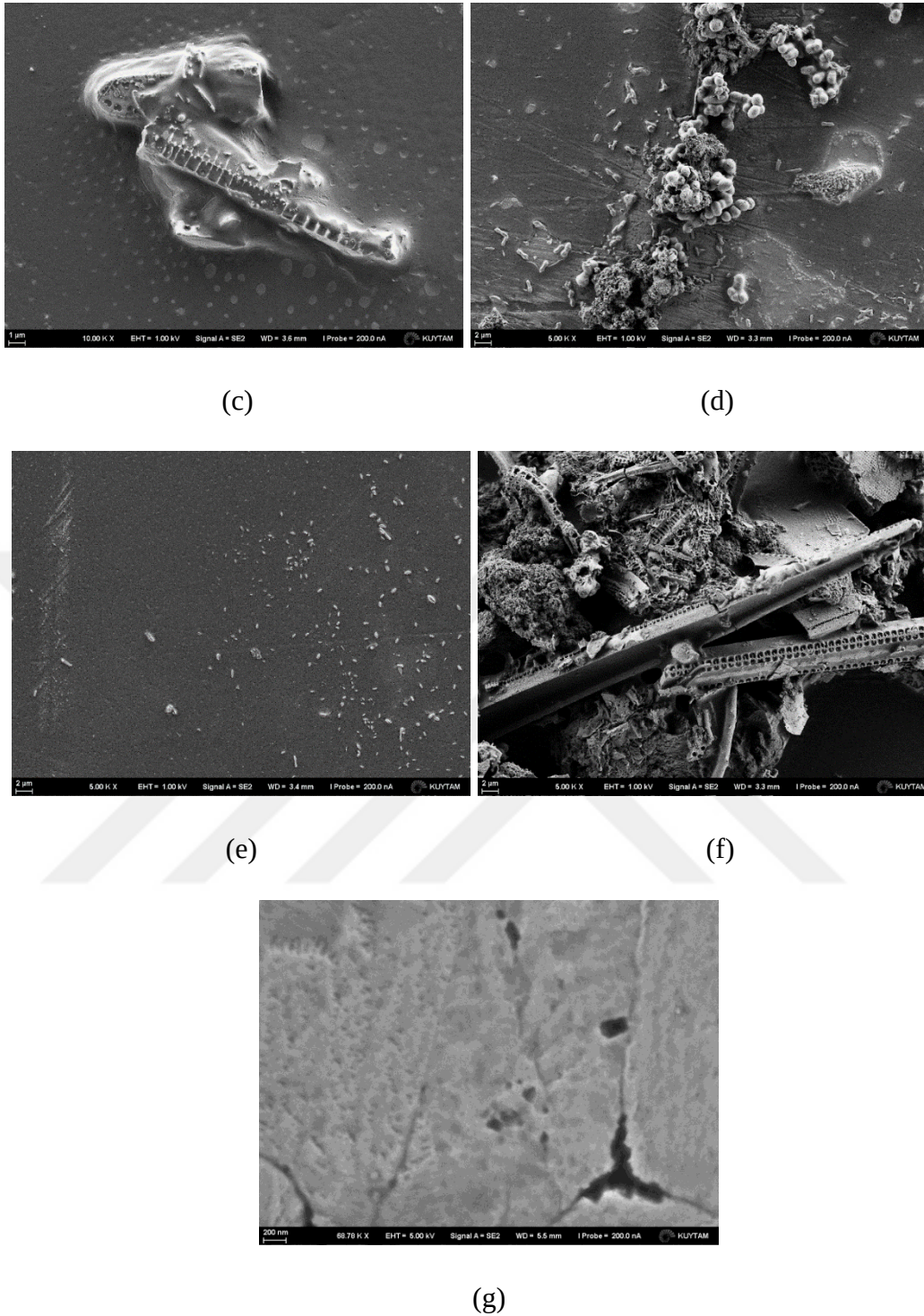


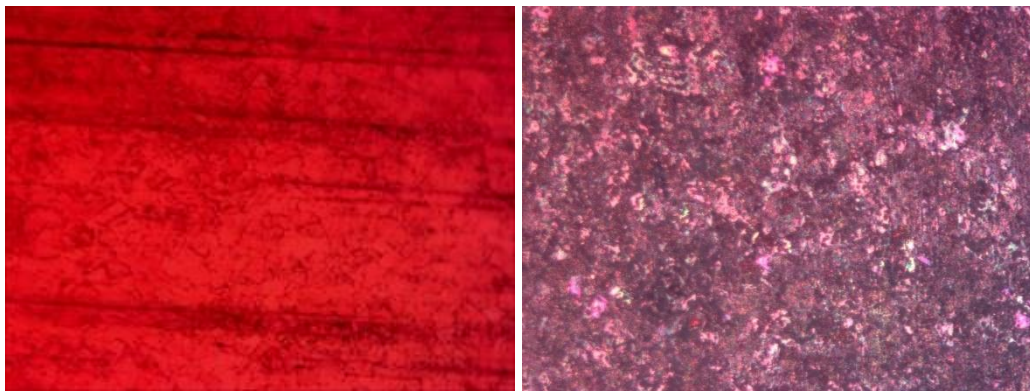
Fig. 4.7 SEM images of composite coated samples synthesized by chitosan/PEG-10K loaded silica-based fillers/SBS dispersions, (a) PEG-10K loaded silica/SBS, (b) PEG-10K loaded halloysite/SBS composites, (c) PEG-10K loaded DE/SBS composites, (d) chitosan loaded silica/SBS composites, (e) chitosan loaded halloysite/SBS composites (f) Chitosan loaded DE/SBS composites and (a) SBS control. The scale bar on images (a-c) is 1 μm , for images (d-f) is 2 μm and for image (g) is 200 nm.

4.5.2.1.1 Investigating the electrochemical properties of silica-based fillers/SBS composite coated Cu samples coated from composite dispersions containing 15% by mass inhibitor filled particles

The electrochemical properties of the inhibitor loaded silica-based filler/SBS composite coated copper samples were investigated in 0.5 M NaCl solution. The concentration of Cl^- ions in this solution is almost the same as in sea water (0.599 M). This higher chloride ions concentrations resulted in faster deterioration of copper metal and could provide us better understanding on the inhibition ability of chitosan and PEG. The surface morphology of the uncoated and composite coated copper samples was investigated by optical microscope. The samples were dipped in 0.5 M NaCl solution for 96 h at room temperature. The surface morphology of the coated copper samples was investigated by removing the corrosion products and composite coating with chloroform. The optical microscope images of composite coated copper samples are shown in Fig 4.8. The bare copper image before exposure to the 0.5 M NaCl solution showed the grain structure of copper metal (Fig. 4.8a). The bare copper sample after exposure to the 0.5 M NaCl solution showed enlarged surface roughness and typical pitting corrosion of copper surface (Fig. 4.8b). The samples coated with SBS and inhibitor loaded composite (Fig. 4.8a c-i) showed pitting corrosion. The extent of pitting corrosion was decreased for the samples coated with inhibitor loaded composite coatings compared to SBS coated sample. The pitting corrosion in all coated copper samples can be attributed to the penetration of liquid solution through the nanodefects in the composite coatings. These images clearly showed that samples coated with chitosan loaded fillers/SBS composite coatings have less pitting corrosion than the PEG loaded filler/SBS composite coated copper samples. The loading of inhibitor loaded silica-based fillers resulted in increased local concentration of chitosan in the composite coatings. So, this increase in amount of inhibitor loaded fillers improved the anti-corrosion performance of these composite coatings.

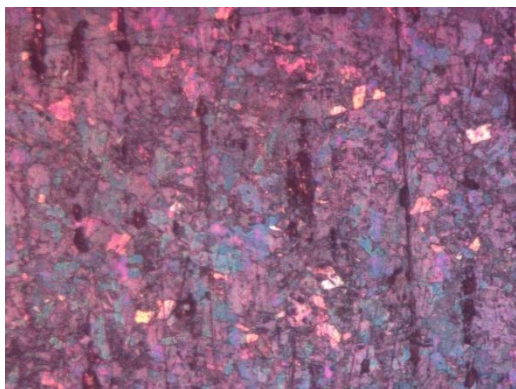
The crystal structure of metals provides information about their properties. Copper have a face centered cubic (FCC) structure. The high strength and ductility of copper metal is attributed to the FCC orientation of copper atoms. The strong interactions between copper atoms in FCC orientation resulted in closed packed structure. This close packing prevents stress corrosion by blocking the diffusion of hydrogen ions

through small spaces. Copper is an excellent electrical conductor due to the free electron cloud in copper lattice. This free electron cloud prevents corrosion of copper metals by forming a protective film on the copper surface. Copper is found in polycrystalline form. It consists of small regions called grains. These grains have well-ordered orientation of copper atoms. The crystal structure orientation of each grain is different. These grains are formed during the solidification process of metals. Between successive grains there are regions of disorder which are called grain boundaries. The disorder in grain boundaries resulted in higher entropy and high surface free energy compared to ordered grain structure. Grain boundaries are also preferred place for the segregation of dislocations and impurities. The difference in electrochemical potential exists between grain boundaries and grain interior due to the presence of impurities. This make grain boundaries more vulnerable to chemical reactions and corrosion. When the metal piece is immersed in corrosive liquid such as 0.5 M NaCl solution, due to the potential difference between grain boundaries and interior of the grains, galvanic couple is formed. The active dissolution of copper metals at grain boundaries starts and these ions reacts with negative ions from the solution. All samples dipped in 0.5 M NaCl solution showed typical pitting corrosion of copper substrates and corrosion started at grain boundaries for all the samples (Fig. 4.8 b-i).

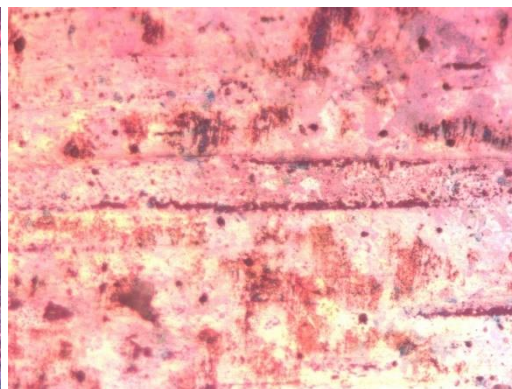


(a)

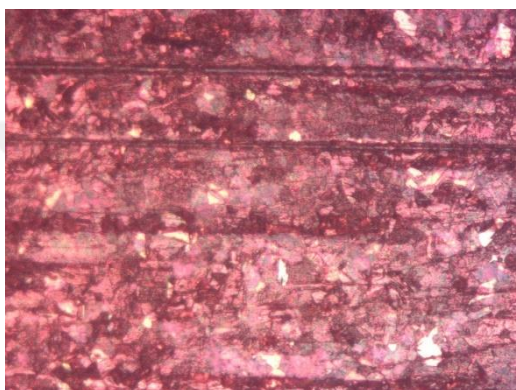
(b)



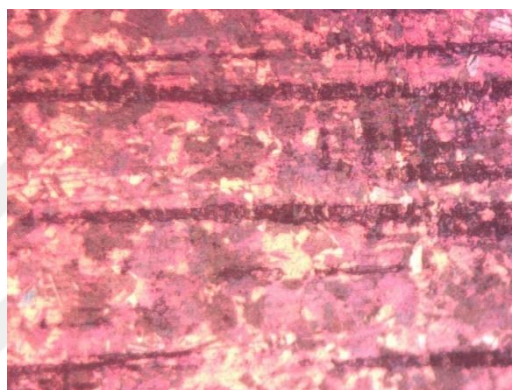
(c)



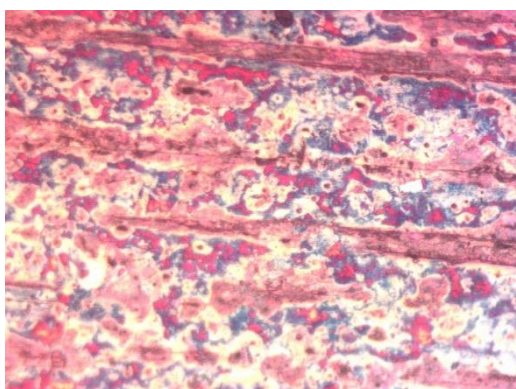
(d)



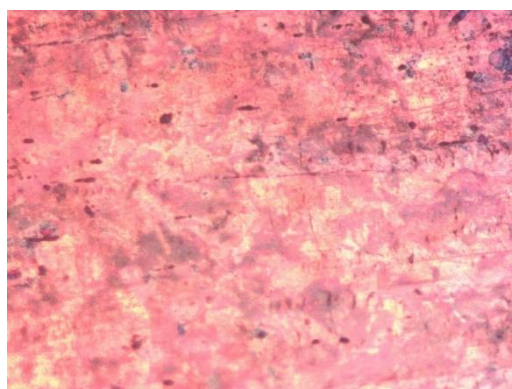
(e)



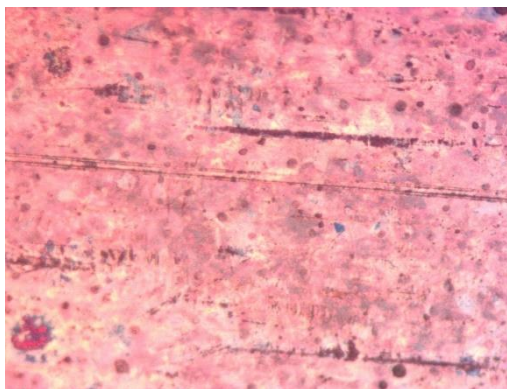
(f)



(g)



(h)



(i)

Fig. 4.8 Optical Microscope images of coated and uncoated copper samples before and after exposure to 0.5 M NaCl solution. (a) bare copper without exposure, (b) bare copper after exposure to 0.5 M NaCl solution, (c) SBS coated copper after exposure, (d) PEG-10K loaded silica particles/SBS coated copper after exposure, (e) PEG-10K loaded halloysite/SBS coated copper after exposure, (f) PEG-10K loaded DE/SBS coated copper after exposure, (g) Chitosan loaded silica particles/SBS coated copper after exposure, (h) Chitosan loaded halloysite/SBS coated copper after exposure and (i) chitosan loaded silica DE/SBS coated copper after exposure. The size of these images is $672\ \mu\text{m} \times 504\ \mu\text{m}$.

The open circuit potentials of bare copper and inhibitor loaded silica-based fillers/SBS composite coated copper samples were determined by exposing them to 0.5 M NaCl solution. Fig. 4.9 shows the open circuit potential of all samples as function of time. The open circuit potentials for all these samples were in the range of -141 to -203 mV. The equilibrium potential values were reached within 75-100 s of immersion time in 0.5 M NaCl solution. These results showed that the open circuit potentials of chitosan loaded silica-based fillers/ SBS composite coated samples were shifted in less noble directions. But the open circuit potentials for PEG-10K loaded fillers/SBS composite coated samples shifted in more noble directions than bare copper metals.

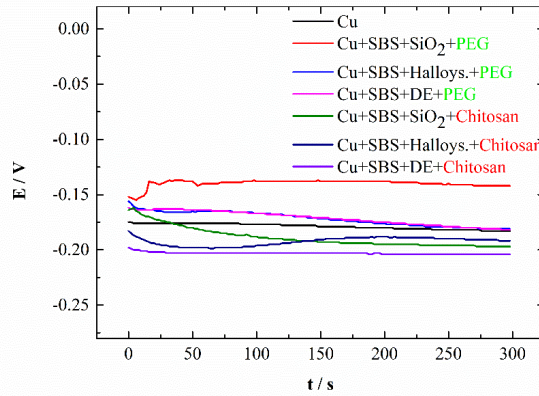


Fig. 4.9 Open circuit potential of bare copper and composite coated copper coatings (15% by mass fillers in dipping dispersions) after exposing to 0.5 M NaCl solution.

The potentiodynamic polarization curves were used to investigate the corrosion current density, corrosion potential, corrosion mechanism and corrosion inhibition efficiency of various inhibitors. The polarization curves for bare copper and composite coated copper samples were obtained by dipping them in 0.5 M NaCl solution. The Tafel plots were obtained for samples coated with composite dispersions containing 15% by mass inhibitor filled particles by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs⁻¹. The Tafel plots are shown in Fig. 4.10. The polarization parameters calculated from Tafel curves of these composite coated copper samples are shown in Table 4.4. These parameters included corrosion potential (E_{corr}), corrosion current density (I_{corr}) obtained by extrapolating the Tafel lines to corrosion potential, surface coverage (θ) and inhibition efficiency (π). The surface coverage is calculated by using the following equation [231]. The I_{corr}^0 in equation is the corrosion current density without any corrosion inhibitor in the system (I_{corr} of Cu). The inhibition efficiency is determined by multiplying the surface coverage values with 100.

$$\theta = 1 - \frac{I_{\text{corr}}}{I_{\text{corr}}^0}$$

The corrosion potential changes from -248 mV to -209 mV by just coating the copper surface with SBS. The addition of inhibitor loaded particles further decreased this potential to -188 mV. This shift in corrosion potential values towards more noble potentials showed that anodic reaction of the metal was suppressed by the protective composite coated layer on the copper surface.

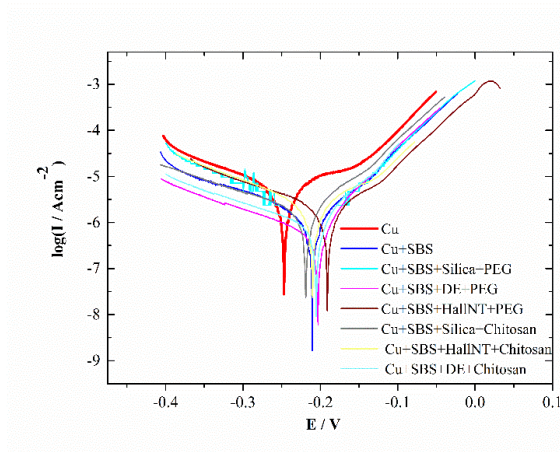


Fig. 4.10 Tafel curves for the bare and composite coated copper (containing 15% inhibitor loaded silica-based fillers in dipping dispersions) in 0.5 M NaCl at room temperature.

Table 4.4 Electrochemical parameters acquired from Tafel curves for bare copper and composite coated copper samples (containing 15% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	E_{corr} / mV	$I_{corr} / \mu\text{Acm}^{-2}$	Θ	$\Pi \%$
Bare Cu	-248	6.78	0	0
Cu+SBS	-209	1.56	0.769	76.9
Cu+SBS+SiNP+PEG	-199	1.156	0.829	82.9
Cu+SBS+HalNT+PEG	-188	1.999	0.705	70.5
Cu+SBS+DE+PEG	-203	0.516	0.923	92.3
Cu+SBS+SiNP+Chitosan	-219	1.69	0.751	75.1
Cu+SBS+HalNT+Chitosan	-210	2.25	0.668	66.8
Cu+SBS+DE+Chitosan	-205	0.804	0.881	88.1

The inhibition efficiency results revealed that the SBS coating itself performed as a good inhibiting agent. The inhibition efficiency was further increased by the addition of inhibitor filled particles in SBS matrix. The maximum inhibition efficiency of 92.3% was achieved for the coatings containing DE particles filled with PEG. But, in case of chitosan loaded silica-based fillers the maximum corrosion inhibition efficiency of 88.1% was achieved for the composite coatings containing DE loaded

chitosan particles. The inhibition efficiency of inhibitor filled halloysite sample was less compared to SBS coated samples. This decrease in inhibition efficiency can be attributed to the presence of inhomogeneities in composite coatings due to the agglomerated particles. These inhomogeneities may have served as the sites for penetration of chloride ions into the coatings which resulted in pitting corrosion of Cu samples. The corrosion inhibition efficiency can be further improved by changing the concentration of inhibitor loaded particles in composite films or by increasing the thickness of SBS coatings.

The electrochemical properties of the copper samples coated with inhibitor loaded silica-based fillers/SBS composite coatings (containing 15% by mass fillers in dipping solutions) were further investigated by dipping these coatings in 0.5 M NaCl solution. The comparison of cyclic voltammograms of all these composite coated samples with bare copper is shown in Fig. 4.11. These curves were obtained by scanning towards positive potential from OCP with a scan rate of 5mV/s. The typical active-passive behavior was shown by copper sample. The current density increases slowly till 20 mV from OCP then it suddenly increases till 109 mV. This sudden increase in current density is attributed to the change in dissolution mechanism of copper metal. When the positive potential was increased further after reaching the passivation potential (109 mV) the current density dropped. The constant current density of 3.98 mA/cm^{-2} was determined from 153 mV onwards in passive region. As the applied potential was reversed, the observed value of current density was lower than the value measured during the forward scan. This decrease in current density value is attributed to the passive layer formed on the copper sample. This passive layer reduced the active dissolution of copper metal. However, chloride ions can penetrate through the defects in the coatings (Fig. 4.7g) and cause localized corrosion of copper metal. The symmetric reduction peak was observed between the potential range of -58 to -184 mV. This reduction peak resulted due to the reduction of passive layer from the copper surface.

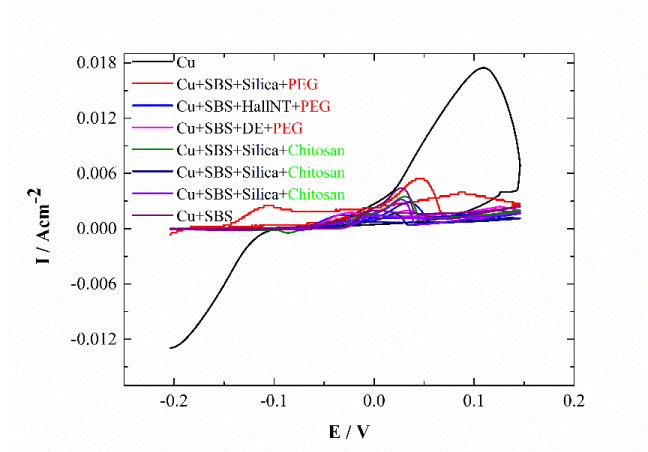


Fig. 4.11 Cyclic voltammograms for investigation of electrochemical behavior of composite coated copper samples dipped in 0.5 M NaCl solutions, (a) comparison of bare copper with composites coated copper samples.

The cyclic voltammograms of SBS and composite coated samples showed significant decrease in current densities compared to the bare copper sample in the same potential range. These voltammograms showed that SBS itself protects the copper surface against corrosion process. The thickness of SBS and composite coatings on copper samples was $\sim 5 \mu\text{m}$. The shapes of cyclic voltammograms changed after coating them with SBS or composites. The shape of voltammograms is same for all coated samples. The cyclic voltammogram of SBS coated sample is shown in Fig. 4.12. The current density of SBS coated copper sample increased by increasing the potential towards more positive values with a scan rate of 5 mV/s. The increase in current density is resulted due to the active dissolution of copper samples through various nanodefects in SBS coating. The passivation potential for SBS coated sample was 80 mV less than copper samples. The maximum current density measured for SBS coated sample at passivation potential was 4.4 mA/cm^2 . The current density was then decreased after increasing potential further towards positive values. A small shoulder was observed at 41.19 mV. This shoulder could be due to an oxide layer having dual composition. This dual composition could be made of both cuprous and cupric oxides. This shoulder was only observed for SBS coated samples. The transpassive dissolution of the SBS coated sample was observed at 72 mV potential value. This transpassive dissolution resulted in breakdown of protective copper layer and increased current density as potential was further increased towards more positive direction. The removal of protective layer during the forward scan resulted

in less pronounced reduction peaks during backward scan. This decrease in reduction peak was observed for all coated samples. The higher current density till 41.19 mV potential resulted in additional loops during backward scan of potential. This potential (41.19 mV) is called repassivation potential (E_{rp}). The shape of the curve and higher current density during backward scan indicates the presence of pitting corrosion. These results are confirmed by the samples dipped in 0.5 M NaCl solution. The optical images of those samples confirmed the pitting corrosion of copper substrates. The repassivation potential resulted in a decrease in current density value compared to the current density value during forward scan. This lower current density value showed the slower dissolution of copper during backward scan.

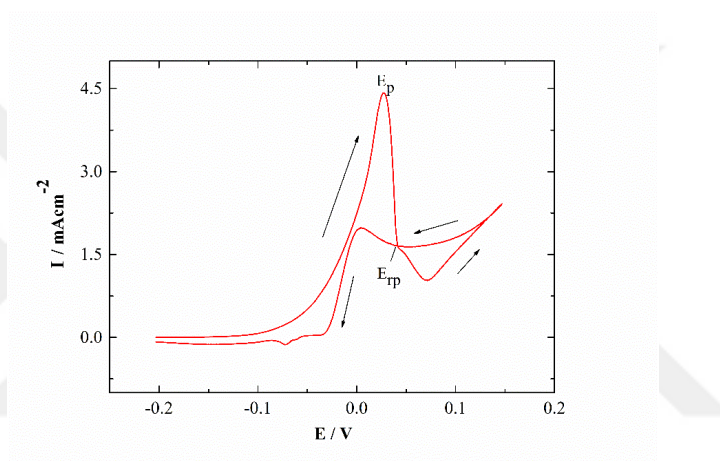


Fig. 4.12 Cyclic voltammogram of SBS coated copper sample dipped in 0.5 M NaCl solution. The arrows represent the direction of scan.

The passivation potential (E_p), passive current density (I_p), repassivation potential (E_{rp}) and charge during the forward scan (Q) for all composite coated samples are shown in Table 4.5. This table shows that introducing inhibitor loaded silica-based fillers into SBS coatings decreased the active dissolution of copper samples. Chitosan loaded filler containing samples showed lower passive current densities as compared to PEG loaded filler containing samples. These results are in line with the charge measured during forward scan due to active and passive dissolution of Cu. These results were confirmed by the optical microscope images of chitosan loaded composite coatings exposed to 0.5 M NaCl solution for 96 h (Fig. 4.8). This chitosan loaded samples showed less pitting corrosion than PEG filled samples. The presence of more heteroatoms in chitosan helped to improve its corrosion inhibition ability than PEG. The presence of nitrogen and oxygen resulted in better adsorption of

chitosan on the copper surface than PEG which only contains oxygen [231]. The lowest passive current density was measured on samples containing halloysite loaded with chitosan and DE loaded with PEG. The values of charge during the forward scan due to active and transpassive dissolution of copper further confirmed that chitosan loaded halloysite and PEG loaded DE samples performed better anti-corrosive ability. Overall, the results of electrochemical measurements showed that composite samples containing chitosan loaded halloysite or PEG loaded DE samples minimized the corrosion of Cu substrates.

Table 4.5 Electrochemical parameters acquired from cyclic voltammograms for bare copper and composite coated copper samples (containing 15% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Bare Cu	17.5	$1.81 \cdot 10^{-3}$	109.36	-
Cu+SBS	4.4	$3.80 \cdot 10^{-4}$	27.62	41.19
Cu+SBS+SiNP+PEG	5.3	$7.06 \cdot 10^{-4}$	45.80	66.20
Cu+SBS+HalNT+PEG	2.8	$2.86 \cdot 10^{-4}$	35.10	52.33
Cu+SBS+DE+PEG	1.9	$2.59 \cdot 10^{-4}$	34.32	47.14
Cu+SBS+SiNP+Chitosan	3.4	$2.99 \cdot 10^{-4}$	30.91	43.62
Cu+SBS+HalNT+Chitosan	1.6	$1.65 \cdot 10^{-4}$	19.93	30.53
Cu+SBS+DE+Chitosan	3.1	$2.61 \cdot 10^{-4}$	27.30	38.64

4.5.3 Effect of the concentration of inhibitor loaded silica-based fillers in dipping dispersions on electrochemical properties of composite coated Cu samples

The copper samples coated with composite coatings containing chitosan loaded halloysite or PEG loaded DE particles showed better corrosion inhibition ability than their counterparts at 15% by mass concentrations of inhibitor loaded silica-based fillers in dipping solution. The anti-corrosion ability of these best samples was

further investigated by changing their concentration to 3, 6 and 21% by mass in dipping dispersions.

4.5.3.1 Investigation of electrochemical properties of sample containing 3% by mass inhibitor loaded particles in dipping solution

The anti-corrosion ability of composite coated samples containing chitosan loaded halloysite or PEG loaded DE particles was investigated by decreasing the concentration of chitosan loaded halloysite and PEG loaded diatomaceous earth particles in dipping dispersions. The composite dispersions were prepared by dispersing chitosan filled halloysite nanotubes and PEG filled DE particles separately in SBS stock solution (20 mg/mL) to obtain 3% by mass composite dispersions. The copper samples were dip coated with these dispersions. The more homogeneous distribution of silica-based fillers was obtained by stirring the dispersions at 300 rpm during dip coating process. The copper samples were dried in open atmosphere after dip coating. The electrochemical properties of these chitosan loaded halloysite/SBS and PEG filled DE /SBS composite coated copper samples were investigated in 0.5 M NaCl solution. The surface morphology of these composite coated copper samples was investigated by optical microscope. The samples were dipped in 0.5 M NaCl solution for 96 h at room temperature. The surface morphology of the coated copper samples was investigated by removing the corrosion products and composite coating with chloroform. The optical microscope images of composite coated copper samples are shown in Fig 4.13. These composite coated samples (Fig. 4.13a-b) showed pitting corrosion. The extent of the pitting corrosion was less than the samples coated with pure SBS (Fig. 4.8c). These images showed that copper samples coated with PEG filled DE/SBS and chitosan loaded halloysite/SBS composites showed almost same extent of pitting. The extent of pitting corrosion for these composite coated samples was almost similar to their counterparts coated with dispersions containing 15% by mass inhibitor loaded silica-based fillers (Fig. 4.8 f, Fig. 4.8 h). This better corrosion inhibition ability at such low concentration can be attributed to the homogeneous distribution or less agglomeration of inhibitor loaded particles in dipping solutions and eventually in composite coatings. The open circuit potentials of bare copper, PEG filled DE/SBS composite coated copper and chitosan filled halloysite/SBS coated copper samples with filler loading of 3% by mass in dipping dispersions were determined by exposing them to 0.5 M NaCl solution. Fig. 4.14 shows the open

circuit potential of all samples as function of time. The open circuit potentials for all these samples were in the range of -183 to -193 mV. The equilibrium potential values were reached within 200-225 s of immersion time in 0.5 M NaCl solution. These results showed that the open circuit potentials of PEG filled DE/ SBS and chitosan filled halloysite/SBS composite coated sample was shifted in less noble directions than bare copper.

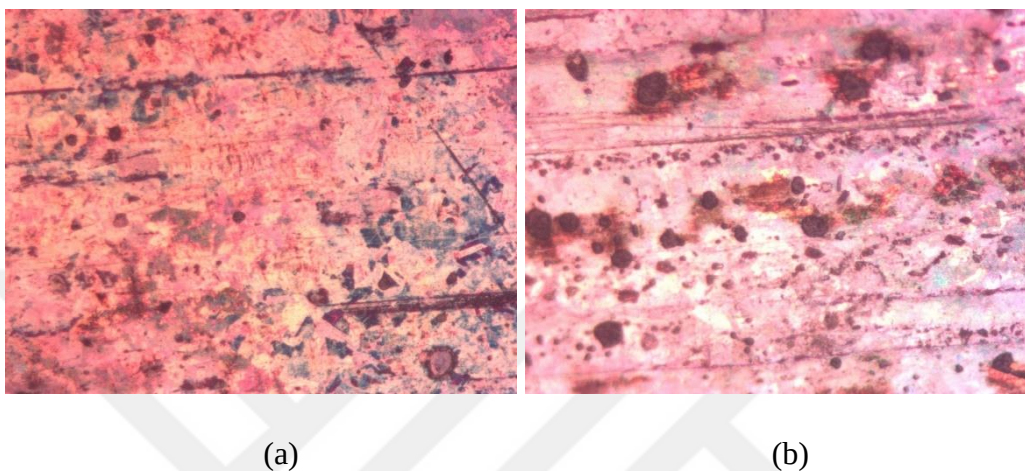


Fig. 4.13 Optical Microscope images of coated copper samples after exposure to 0.5 M NaCl solution, a) PEG-10K loaded DE/SBS composites and b) chitosan loaded halloysite/SBS composites. The size of these images is 672 μm x 504 μm .

The polarization curves for copper samples coated with composite dispersions containing 3% chitosan loaded halloysite nanotube or PEG filled DE particles were obtained by dipping them in 0.5 M NaCl solution. Similar to previous composite coated samples, the Tafel plots for these samples were obtained by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs^{-1} . The polarization parameters calculated from the Tafel curves of these composite coated copper samples are shown in Table 4.6. These parameters included corrosion potential (E_{corr}), corrosion current density (I_{corr}) obtained by extrapolating the Tafel lines to corrosion potential, surface coverage (Θ) and inhibition efficiency (π). The corrosion potential for composite coated samples is shifted towards more positive side than bare copper samples. The corrosion potential changed from -248 mV for bare Cu to -202 mV for composite coated copper samples containing DE filled PEG and -195 mV for composite coated copper containing chitosan loaded halloysite nanotubes. This shift in corrosion potential values towards more noble potentials than bare copper sample showed that anodic reaction of the metal was suppressed by

the protective composite coated layer containing inhibitor loaded silica-based fillers on the copper surface. The corrosion inhibition efficiency of composite containing chitosan loaded halloysite was 82.3% and for composites containing PEG loaded DE particles was 83.9%. The corrosion inhibition efficiency of both the composite coated samples is comparable. The nanodefects in composite coatings have resulted in lower corrosion inhibition efficiency of the composite coated copper samples as well. These defects served as the sites for penetration of aggressive liquids into the coatings which resulted in pitting corrosion of Cu samples.

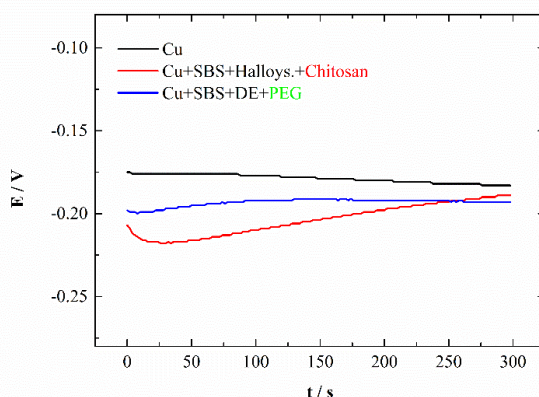


Fig. 4.14 Open circuit potential of bare copper, PEG filled DE/ SBS composite and chitosan filled halloysite/SBS composite coated copper coatings (3% by mass silica-based fillers in dipping solution) after exposing to 0.5 M NaCl solution.

Table 4.6 Electrochemical parameters acquired from Tafel curves for composite coated copper samples (containing 3% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	$E_{\text{corr}} / \text{mV}$	$I_{\text{corr}} / \mu\text{Acm}^{-2}$	Θ	$\Pi \%$
Cu+SBS+HalNT+Chitosan	-195	1.2	0.823	82.3
Cu+SBS+DE+PEG	-202	1.09	0.839	83.9

The electrochemical properties of chitosan filled halloysite/SBS composite coated copper and PEG filled DE/SBS composite coated copper samples (containing 3% by mass filler loading in dipping solutions) were further investigated in 0.5 M NaCl solution. The cyclic voltammograms of these coated samples are shown in Fig 4.15.

These voltammograms were obtained by scanning towards positive potential from OCP with a scan rate of 5mV/s. These samples like their counterparts also showed active-passive behavior. The similar shape and behavior were observed for both composite coated samples. The current density increases from the OCP by moving towards more positive potential for both the samples. This increase in current density is attributed to the active dissolution of copper samples through nanodefects in the composite coatings. The passivation potential of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 16.5 mV and 29.6 mV respectively. These passivation potential values are lower than bare copper (109 mV). The passive current density of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 1.24 mAcm⁻² and 4.71 mAcm⁻² respectively. The passive current density of both composite coated samples was also lower than bare copper (17.5 mAcm⁻²). The current density swiftly dropped after reaching the passivation potential for all coated samples upon further increase in positive potential. The transpassive dissolution of chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 31.3 mV and 49.3 mV respectively. The chitosan filled halloysite/SBS composite coated samples having less passivation potential and current density showed transpassive dissolution at lower potentials. During the transpassive dissolution protective film was broken down which resulted in active dissolution of copper samples and increased current density. The sudden increase in current density during backward potential scan is observed till repassivation potential. The repassivation potential values for the chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 23.90 mV and 42.80 mV respectively. The higher current densities during backward scan and shapes of the voltammograms indicated pitting corrosion effect in the composite coated copper samples. The higher current density during backward scan till repassivation potential resulted in significant pitting corrosion of copper samples (Fig. 4.15). The extent of pitting corrosion was well pronounced in both chitosan loaded and PEG loaded samples (Fig. 4.13). The cyclic voltammograms showed that the decrease in current density after repassivation potential which indicated that the rate of copper dissolution is slower during the backward scan than the forward scan. The passive current density (I_p), passivation potential (E_p), repassivation potential (E_{rp}) and charge during the forward scan (Q) are shown in Table 4.7. This table shows that the halloysite loaded with chitosan/SBS coated Cu

samples showed lower passivation current density than diatomaceous earth loaded with PEG/SBS coated Cu samples. The values of charge during forward scan due to active and transpassive dissolution of copper also showed that chitosan loaded samples performed better anti-corrosive ability than PEG loaded samples. The optical microscope images of chitosan loaded halloysite/SBS composite coated and PEG filled DE/SBS composite coated samples exposed to 0.5 M NaCl solution for 96 h (Fig. 4.13) showed almost same extent of pitting corrosion. The better corrosion inhibition ability of chitosan loaded halloysite/SBS coated Cu samples at this low concentration is attributed to the homogenous distribution of inhibitor loaded fillers in SBS matrix and their better adsorption ability.

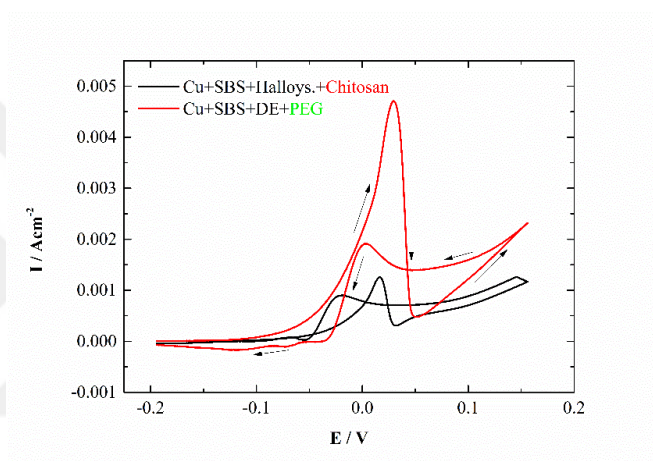


Fig. 4.15 Cyclic voltammograms for investigation of electrochemical behavior of composite coated copper samples dipped in 0.5 M NaCl solutions. The arrows showed the directions of potential scans. The scan rate used was 5 mV/s.

Table 4.7 Electrochemical parameters acquired from cyclic voltammograms for composite coated copper samples (containing 3% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Cu+SBS+HalNT+Chitosan	1.24	$1.35 \cdot 10^{-4}$	16.50	23.97
Cu+SBS+DE+PEG	4.71	$3.59 \cdot 10^{-4}$	29.68	42.86

4.5.3.2 Investigation of electrochemical properties of sample containing 6% by mass inhibitor loaded particles in dipping solution

The anti-corrosion ability of composite coated samples containing chitosan loaded halloysite or PEG loaded DE particles was investigated by increasing the concentration from 3% to 6% by mass of chitosan loaded halloysite and PEG loaded diatomaceous earth particles in dipping dispersions. The copper samples were dip coated with these dispersions. The copper samples were dried in open atmosphere after dip coating. The surface morphology of these composite coated copper samples was investigated by optical microscope. The samples were dipped in 0.5 M NaCl solution for 96 h at room temperature. The surface morphology of the coated copper samples was investigated by removing the corrosion products and composite coating with chloroform. The optical microscope images of composite coated copper samples are shown in Fig 4.16.

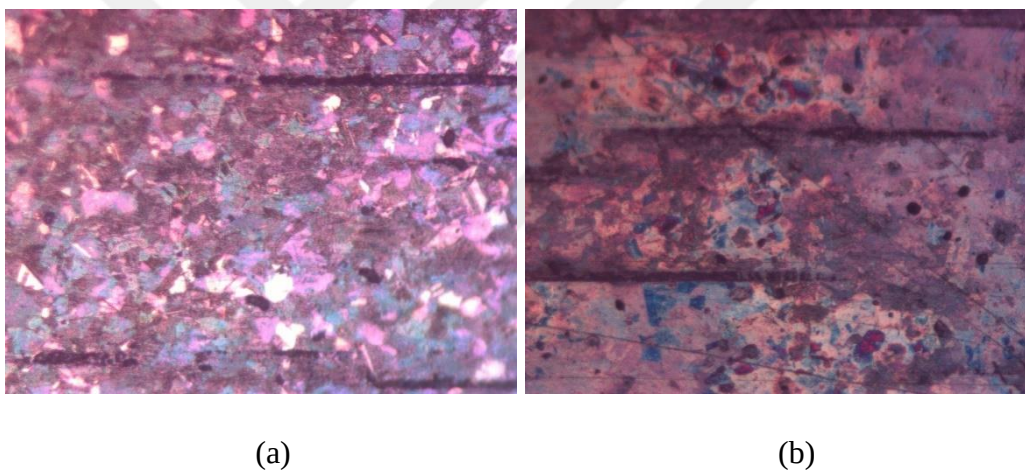


Fig. 4.16 Optical Microscope images of composite coated copper samples after exposure to 0.5 M NaCl solution, a) PEG-10K loaded DE/SBS composites and b) chitosan loaded halloysite/SBS composites. The size of these images is 672 μm x 504 μm .

These images showed that the composite coated samples showed pitting corrosion. These images clearly showed that copper samples coated with PEG filled DE/SBS composites showed less pitting corrosion than chitosan loaded halloysite/SBS composite coated copper samples. The difference in extent of severe pit formation in chitosan loaded samples as compared to PEG loaded samples is attributed to agglomeration of chitosan loaded particles in composite films. The better distribution of PEG loaded particles resulted in less pitting corrosion of sample containing PEG loaded DE particles. The extent of pitting corrosion for these composite coated

samples was significantly higher than their counterparts coated with dispersions containing 3% and 15% by mass inhibitor loaded silica-based fillers (Fig. 4.13, Fig. 4.8). This higher pitting corrosion can be attributed to more agglomerations of inhibitor loaded particles in dipping solutions and eventually in composite coatings. These agglomerates may have resulted in more inhomogeneities in composite coated copper samples which served as sites for chloride ions penetrations.

The open circuit potentials of PEG filled DE/SBS composite coated copper and chitosan filled halloysite/SBS coated copper samples with filler loading of 6% by mass in dipping dispersions were determined by exposing them to 0.5 M NaCl solution. Fig. 4.17 shows the open circuit potential of all samples as function of time. The open circuit potentials for PEG filled DE/SBS composite coated copper and chitosan filled halloysite/SBS coated copper samples were -192 mV and -172 mV respectively. The equilibrium potential values were reached within 200-225 s of immersion time in 0.5 M NaCl solution. These results showed that the open circuit potentials of PEG filled DE/ SBS composite coated sample was shifted in less noble directions than bare Cu, but the open circuit potential of chitosan filled halloysite/SBS composite coated sample was shifted in more noble direction than bare Cu.

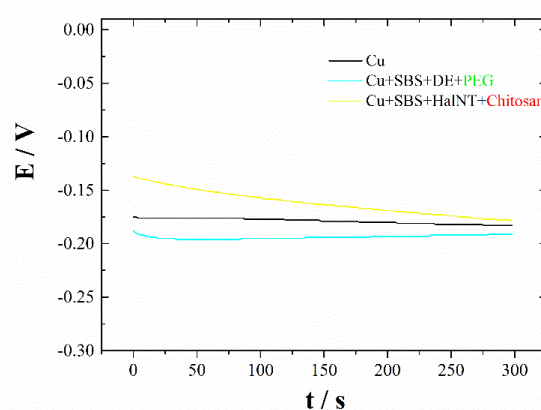


Fig. 4.17 Open circuit potential of bare copper, PEG filled DE/ SBS composite and chitosan filled halloysite/SBS composite coated copper coatings (6% by mass silica-based fillers in dipping solution) after exposing to 0.5 M NaCl solution.

The polarization curves for copper samples coated with composite dispersions containing 6% by mass chitosan loaded halloysite nanotube or PEG filled DE particles were obtained by dipping them in 0.5 M NaCl solution. Similar to previous

composite coated samples, the Tafel plots for these samples were obtained by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs^{-1} . The polarization parameters calculated from the Tafel curves of these composite coated copper samples are shown in Table 4.8. The corrosion potential for composite coated samples is shifted towards more positive side than bare copper samples. The corrosion potential changed from -248 mV for bare Cu to -201 mV for composite coated copper samples containing DE filled PEG and -239 mV for composite coated copper containing chitosan loaded halloysite nanotubes. This shift in corrosion potential values towards more noble potentials than bare copper sample showed that anodic reaction of the metal was suppressed by the protective composite coated layer containing inhibitor loaded silica-based fillers on the copper surface. The Tafel plots are used to determine E_{corr} and I_{corr} values only when the polarization curves are under charge control mechanism. In case of DE filled PEG loaded samples, the polarization curves showed diffusion-controlled part as well. So, the extrapolation of these curves is not useful in calculating I_{corr} values. The E_{corr} value was estimated by the extrapolation of only cathodic polarization curve of that sample. Since we could not measure the value of I_{corr} for DE filled PEG samples, the corrosion inhibition efficiency of that sample could not be calculated. The corrosion inhibition efficiency for composites coated Cu containing chitosan loaded halloysite was 60.9%. The nanodefects in composite coatings due to the agglomerated particles and faster evaporation of solvent may have resulted in lower corrosion inhibition efficiency of the chitosan containing samples. These defects served as the sites for penetration of aggressive liquids into the coatings which resulted in pitting corrosion of Cu samples. These results of higher pitting corrosion in sample containing chitosan loaded halloysite are consistent with the results shown in Fig. 4.17.

Table 4.8 Electrochemical parameters acquired from Tafel curves for composite coated copper samples (containing 6% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	$E_{\text{corr}} / \text{mV}$	$I_{\text{corr}} / \mu\text{Acm}^{-2}$	Θ	$\Pi \%$
Cu+SBS+HalNT+Chitosan	-234	2.65	0.609	60.9
Cu+SBS+DE+PEG	-201	-	-	-

The electrochemical properties of chitosan filled halloysite/SBS composite coated copper and PEG filled DE/SBS composite coated copper samples (containing 6% by mass filler loading in dipping solutions) were further investigated by cyclic voltammetry measurements. The cyclic voltammograms of these coated samples are shown in Fig 4.18. These voltammograms were obtained by scanning towards positive potential from OCP with a scan rate of 5mV/s. Both the composite coated samples showed similar active-passive behavior. The current density increases from the OCP by moving towards more positive potential due to the active dissolution of copper samples through nanodefects in the composite coatings. The passivation potential of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 33.67 mV and 38.48 mV respectively. These passivation potential values are lower than bare copper (109 mV). The passive current density of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 2.9 mAcm^{-2} and 3.6 mAcm^{-2} respectively. The passive current density of both composite coated samples was also lower than bare copper (17.5 mAcm^{-2}). The current density swiftly dropped after reaching the passivation potential for all coated samples upon further increase in positive potential. The transpassive dissolution of chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 55.8 mV and 56.6 mV respectively. The chitosan filled halloysite/SBS composite coated samples having less passivation potential and current density showed transpassive dissolution at lower potentials. During the transpassive dissolution protective film was broken down which resulted in active dissolution of copper samples and increased current density. The chitosan filled halloysite containing composite coated sample showed lower increase in current density which resulted in more pronounced reduction peak during the backward scan. The increase in current density during backward potential scan is observed till repassivation potential. The repassivation potential values for the chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 50.74 mV and 52.06 mV respectively. The higher current densities during backward scan and shapes of the voltammograms indicated pitting corrosion effect in the composite coated copper samples. The extent of pitting corrosion was well pronounced in both chitosan loaded and PEG loaded samples (Fig. 4.16). The decrease in current density after repassivation potential indicated that the rate of copper dissolution is slower during the backward scan than the forward scan.

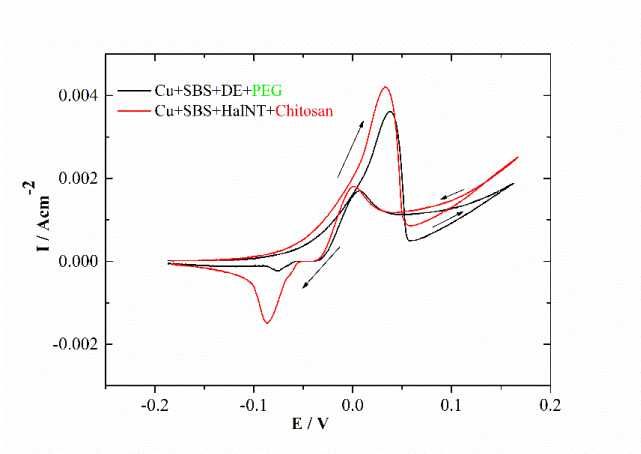


Fig. 4.18 Cyclic voltammograms for investigation of electrochemical behavior of composite coated copper samples dipped in 0.5 M NaCl solutions. The arrows showed the directions of potential scans. The scan rate used was 5 mV/s.

Table 4.9 Electrochemical parameters acquired from cyclic voltammograms for composite coated copper samples (containing 6% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Cu+SBS+HalNT+Chitosan	4.2	$4.10 \cdot 10^{-4}$	33.67	50.74
Cu+SBS+DE+PEG	3.6	$3.15 \cdot 10^{-4}$	38.48	52.06

The passive current density (I_p), passivation potential (E_p), repassivation potential (E_{rp}) and charge during the forward scan (Q) are shown in Table 4.9. This table shows that the halloysite loaded with chitosan/SBS coated Cu samples showed higher passivation current density than diatomaceous earth loaded with PEG/SBS coated Cu samples. The values of charge during forward scan due to active and transpassive dissolution of copper showed results were consistent with these passive current density results. The charge value during forward scan showed that PEG loaded samples performed better anti-corrosive ability than chitosan loaded samples. These results of optical microscope images of chitosan loaded halloysite/SBS composite coated and PEG filled DE/SBS composite coated samples exposed to 0.5 M NaCl solution for 96 h (Fig. 4.16) confirmed these current density and charge results. The samples containing PEG loaded DE showed less pitting corrosion due to lower active dissolution of copper than chitosan loaded halloysite samples. The

better performance can be attributed to the higher loading concentration of PEG. This higher loading may have resulted in more available concentration of PEG for surface adsorption at this concentration of composite coated samples.

4.5.3.3 Investigation of electrochemical properties of sample containing 21% by mass inhibitor loaded particles in dipping solution

The anti-corrosion ability of composite coated samples containing chitosan loaded halloysite or PEG loaded DE particles was investigated by increasing the concentration to 21% by mass of chitosan loaded halloysite and PEG loaded diatomaceous earth particles in dipping dispersions. The copper samples were dip coated with these dispersions. The surface morphology of these composite coated copper samples was investigated by optical microscope. The samples were dipped in 0.5 M NaCl solution for 96 h at room temperature. The surface morphology of the coated copper samples was investigated by removing the corrosion products and composite coatings with chloroform. The optical microscope images of composite coated copper samples are shown in Fig. 4.19. These composite coated samples (Fig. 4.19a-b) showed pitting corrosion. The extent of pitting corrosion was decreased for the copper sample coated with PEG filled DE/SBS composite as compared to bare copper sample (Fig. 4.8b) and sample coated with (6% and 15% by mass) PEG filled DE in SBS matrix (Fig. 4.16a, Fig. 4.8f). Similarly, the extent of corrosion was decreased for the copper samples coated with chitosan loaded halloysite nanotubes as compared to bare copper and sample coated with 6% and 15% by mass chitosan loaded halloysite nanotubes containing composite dispersions. But, in case of chitosan loaded halloysite nanotubes (Fig. 4.19b), severe pitting corrosion was observed on selective sites as compared to sample coated with 15% by mass chitosan loaded halloysite in SBS matrix (4.10e). These images clearly showed that copper samples coated with PEG filled DE/SBS composites showed less pitting corrosion than chitosan loaded halloysite/SBS composite coated copper samples. The difference in extent of severe pit formation in chitosan loaded samples as compared to PEG loaded samples could be attributed to the agglomeration of chitosan loaded particles in composite films. These agglomerates resulted in localized increase in chitosan concentration but the areas without chitosan could be the preferential anodic sites for copper dissolution and severe pitting corrosion can occur. The increase in

amount of inhibitor loaded silica-based fillers improved the anti-corrosion performance of these composite coatings. The open circuit potentials of bare copper, PEG filled DE/SBS composite coated copper and chitosan filled halloysite/SBS coated copper samples with higher filler loading (21% by mass) in dipping dispersions were determined by exposing them to 0.5 M NaCl solution.

The open circuit potential of these samples as function of time are shown in Fig. 4.20. The open circuit potentials of chitosan loaded halloysite and PEG loaded DE samples were -166 mV and -183.8 mV respectively. The equilibrium potential values were reached within 50 s to 75 s of immersion time in 0.5 M NaCl solution. These results showed that the open circuit potentials of PEG filled DE/ SBS composite coated sample was shifted in less noble directions than bare copper. But the open circuit potentials for chitosan filled halloysite/SBS composite coated sample was shifted in more noble directions than bare copper.

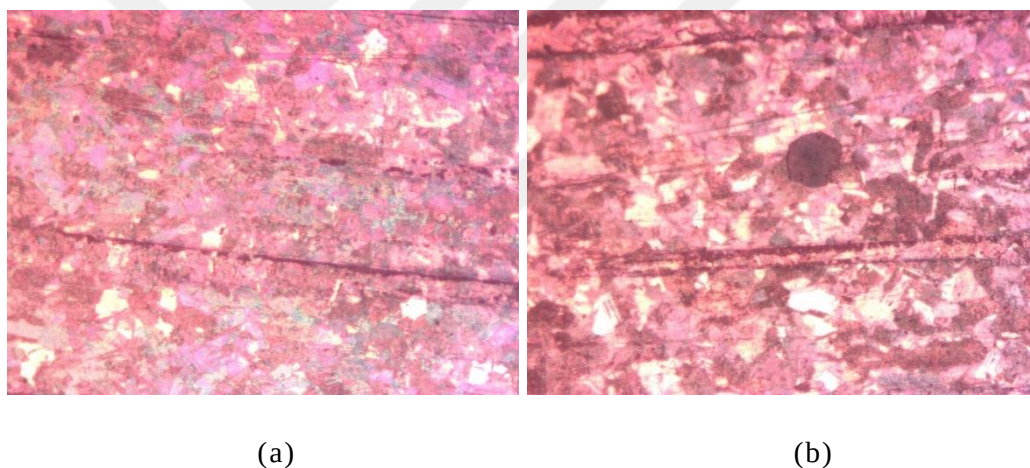


Fig. 4.19 Optical Microscope images of coated copper samples after exposure to 0.5 M NaCl solution, a) PEG-10K loaded DE/SBS composites and b) chitosan loaded halloysite/SBS composites. The size of these images is 672 μm x 504 μm .

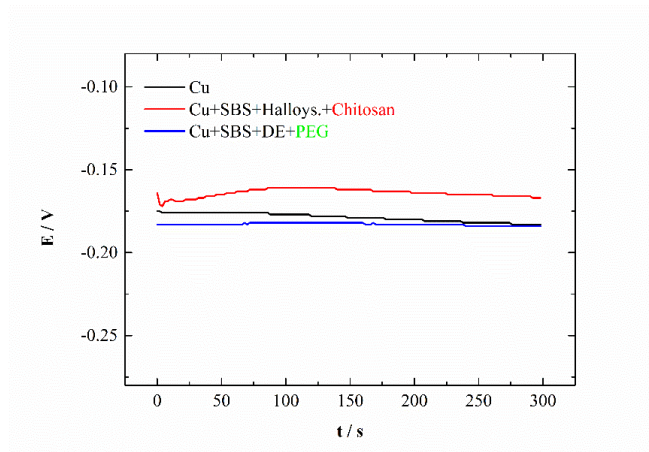


Fig. 4.20 Open circuit potential of bare copper, PEG filled DE/ SBS composite and chitosan filled halloysite/SBS composite coated copper coatings (21% by mass silica-based fillers in dipping dispersions) after exposing to 0.5 M NaCl solution.

The polarization curves for copper samples coated with composite dispersions containing 21% chitosan loaded halloysite nanotube or PEG filled DE particles were obtained by dipping them in 0.5 M NaCl solution. Similar to previous composite coated samples, the Tafel plots for these samples were obtained by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs^{-1} . The polarization parameters calculated from the Tafel curves of these composite coated copper samples are shown in Table 4.10. The corrosion potential for composite coated samples is shifted towards more positive side than bare copper samples. The corrosion potential changed from -248 mV for bare Cu to -200 mV for composite coated copper samples containing DE filled PEG and -178 mV for composite coated copper containing chitosan loaded halloysite nanotubes. This shift in corrosion potential values towards more noble potentials showed that anodic reaction of the metal was suppressed by the protective composite coated layer containing inhibitor loaded silica-based fillers on the copper surface. The inhibition efficiency results showed that the corrosion inhibition efficiency of composite coatings containing chitosan loaded halloysite nanotubes increased by increasing the concentration of inhibitor filled particles from 15% to 21% by mass in dipping solution. The maximum inhibition efficiency of 91.1% was achieved for the coatings containing chitosan loaded halloysite nanotubes. This improvement in efficiency can be attributed to the presence of higher chitosan loaded silica fillers in composite coatings. The local concentration of chitosan loaded fillers may have increased in

composite coated samples which have resulted in improved corrosion inhibition efficiency. In case of composite coated samples containing PEG loaded DE particles the maximum corrosion inhibition efficiency of 86.3% was achieved. Furthermore, the nanodefects in composite coatings have affected the corrosion inhibition efficiency of the composite coated copper samples. These defects served as the sites for penetration of aggressive chloride ions into the coatings which resulted in pitting corrosion of Cu samples.

Table 4.10 Electrochemical parameters acquired from Tafel curves for composite coated copper samples (containing 21% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	$E_{\text{corr}} / \text{mV}$	$I_{\text{corr}} / \mu\text{Acm}^{-2}$	Θ	$\Pi \%$
Cu+SBS+HalNT+Chitosan	-178	0.603	0.911	91.1
Cu+SBS+DE+PEG	-200	0.923	0.863	86.3

The electrochemical properties of chitosan filled halloysite/SBS composite coated copper and PEG filled DE/SBS composite coated copper samples (containing 21% by mass filler loading in dipping solution) were further investigated by cyclic voltammetry measurements. The cyclic voltammograms of these coated samples are shown in Fig 4.21. These voltammograms were obtained by scanning towards positive potential from OCP with a scan rate of 5mV/s. These composite coated samples showed similar active-passive behavior. The current density increases from the OCP by moving towards more positive potential for both the samples. This increase in current density is attributed to the active dissolution of copper samples through nanodefects in the composite coatings. The passivation potential of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 13 mV and 39 mV respectively. These passivation potential values are lower than bare copper (109 mV). The passive current density of chitosan filled halloysite/SBS coated and PEG filled DE/SBS composite coated copper samples was 0.69 mAcm⁻² and 1.2 mAcm⁻² respectively. The passive current density of both composite coated samples was also lower than bare copper (17.5 mAcm⁻²). The current density swiftly dropped after reaching the passivation potential for all coated samples upon further increase in positive potential. The transpassive dissolution of

chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 44 mV and 59 mV respectively. The chitosan filled halloysite/SBS composite coated samples having less passivation potential and current density showed transpassive dissolution at lower potentials. During the transpassive dissolution protective film was broken down which resulted in active dissolution of copper samples and increased current density. The backward scan of potential resulted in sudden increase in current density for chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples at 155 mV. This sudden increase in current density was more for chitosan loaded samples compared to PEG loaded samples. This sudden increase indicated the change in dissolution mechanism of coated copper samples. This sudden increase in current density is followed by a slight decrease till repassivation potential. The repassivation potential values for the chitosan filled halloysite/SBS coated and PEG filled DE/SBS coated copper samples was 18.80 mV and 51.82 mV respectively. The higher current densities during backward scan and shapes of the voltammograms indicated pitting corrosion effect in the composite coated copper samples. The extent of severe pitting corrosion on selective sites was well pronounced in chitosan loaded samples than PEG loaded samples (Fig. 4.19) which can be attributed to higher intensity of current density during backward scan of potential in chitosan loaded samples. The cyclic voltammograms showed that the decrease in current density after repassivation potential which indicated that the rate of copper dissolution is slower during the backward scan than the forward scan.

The passive current density (I_p), passivation potential (E_p), repassivation potential (E_{rp}) and charge during the forward scan (Q) are shown in Table 4.11. This table showed that the halloysite loaded with chitosan/SBS coated Cu samples showed better corrosion resistance than diatomaceous earth loaded with PEG/SBS coated Cu samples. The values of charge during forward scan due to active and transpassive dissolution of copper showed that chitosan loaded samples performed better anti-corrosive ability than PEG loaded samples. These results were confirmed by the optical microscope images of chitosan loaded composite coatings exposed to 0.5 M NaCl solution for 96 h (Fig. 4.19). The chitosan loaded samples showed less pitting corrosion than PEG filled samples except few selected pits. The current density of both composite coated samples was reduced quite significantly as compared to their counterparts of lower concentrations (3-15% by mass). The higher loading of

inhibitor filled silica-based fillers in SBS matrix improved the corrosion inhibition ability of these composite coatings.

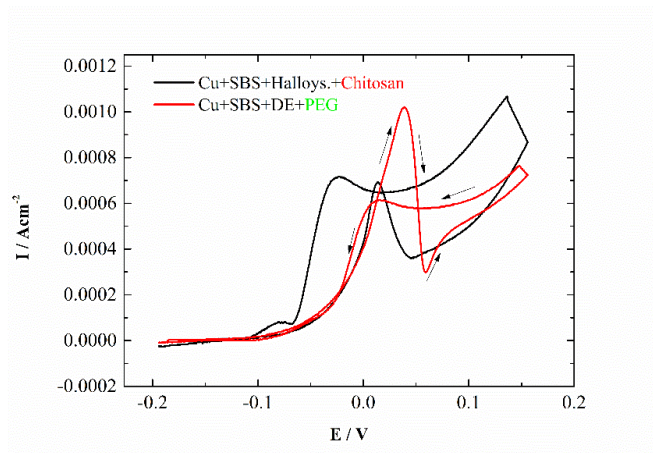


Fig. 4.21 Cyclic voltammograms for investigation of electrochemical behavior of composite coated copper samples dipped in 0.5 M NaCl solutions. The arrows showed the directions of potential scans. The scan rate used was 5 mV/s.

Table 4.11 Electrochemical parameters acquired from cyclic voltammograms for composite coated copper samples (containing 21% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Cu+SBS+DE+PEG	1.02	$1.089 \cdot 10^{-4}$	39.05	51.82
Cu+SBS+HalNT+Chitosan	0.69	$9.63 \cdot 10^{-5}$	13.90	18.83

4.5.3.4 Comparison of the effect of the concentration of inhibitor loaded silica-based fillers on electrochemical properties of composite coated copper

The effect of concentration of inhibitor filled particles in dipping dispersions on electrochemical properties was investigated for composite coated samples containing chitosan loaded halloysite nanotubes or PEG loaded DE particles in them. This combination of fillers and inhibitor was selected due to their better corrosion inhibition efficiency than their counterparts at 15% by mass concentrations in dipping solution. The effect of the concentration of chitosan loaded halloysite or PEG loaded DE particles on the passive current density and corrosion current density

of composite coated copper samples is shown in Fig. 4.22. Overall, the corrosion current density decreased with increasing the concentration of inhibitor loaded silica-based fillers in dipping dispersion. In case of composite coated samples containing chitosan loaded halloysite nanotubes, the corrosion current density is lower at lower concentrations followed by an increase and gradual decrease at higher concentrations. The lower corrosion current density at lower inhibitor loaded filler concentrations can be attributed to the better distribution of chitosan loaded particles in composite coatings or to the less agglomerates of these particles in composite coatings. The decrease in corrosion current density at higher particle concentrations in dipping solution can be due to the higher number of individual and agglomerated inhibitor loaded particles in coatings which may affected the local concentration of chitosan in composite coatings. But in case of composite coated samples containing PEG filled DE particles the corrosion current density decreased by increasing the concentration of PEG filled DE in dipping dispersions. Fig. 4.22b shows the effect of concentration of inhibitor loaded particles in dipping dispersions on passive current density of composite coated samples. The effect of inhibitor concentration in dipping dispersions on the passive current density of composite coated samples is similar to their effect on corrosion current density of these composite coated samples. The passive current density of composite coated samples containing PEG loaded DE particles decreased by increasing the concentration of inhibitor filled particles in dipping dispersions. But in case of chitosan loaded halloysite nanotubes containing composite coated samples, the lower passive current density at lower concentration can be attributed to the homogeneous distribution of chitosan loaded halloysite nanotubes in composite coatings. In conclusion the corrosion current density and passive current density of composite coated copper samples can be decreased by increasing the concentration of inhibitor loaded particles in dipping solution and by homogeneously distributing these particles in composite coatings. It was further observed that the corrosion current density and passivation current density values for PEG loaded and chitosan loaded samples were comparable in investigated compositional range. These results indicated that PEG can also be used as corrosion inhibitor for copper samples.

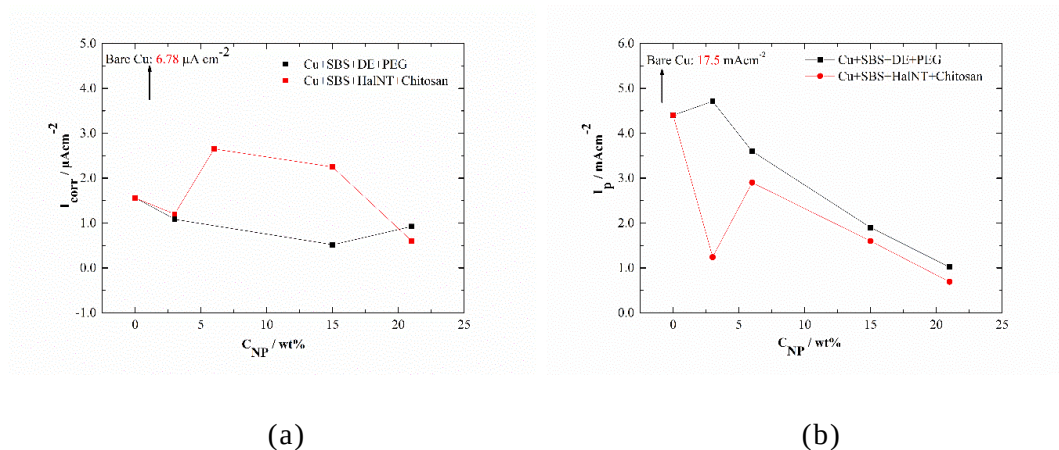


Fig. 4.22 Effect of concentration of inhibitor loaded particles on electrochemical properties of composite coated copper samples, (a) effect on corrosion current density, (b) effect on passive current density.

4.5.4 Investigation of the electrochemical properties of commercial inhibitor loaded silica-based fillers/SBS composite coated Cu samples

Azoles are commercially used as corrosion inhibitors for copper metal. These compounds contain nitrogen atoms having free electron pairs that act as potential sites for binding with Cu metal. 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) is the most commonly used derivative of azoles. This compound proved to be a good corrosion inhibitor for copper with corrosion inhibition efficiency increases with concentration, oxygen content and exposure time [208]. AETDA is used as a reference inhibitor. The pores of these silica-based fillers were filled by dipping them in inhibitor solutions. Typically, 0.2 g of silica-based particles were dispersed in 10 mL solution of AETDA (1 mg/mL). These dispersions were sonicated for 30 min at room temperature. After sonication, these dispersions were left for overnight to obtain thermodynamic equilibrium. Then these dispersions were centrifuged. The sediments were washed twice with the respective solvents to remove loosely bounded molecules. The sediments were dried in open air. Silica-based particles filled with AETDA were dispersed in SBS stock solution (20 mg/mL) to obtain 15% by mass inhibitor filled silica-based particles in SBS solution. The copper samples were dip coated with AETDA loaded silica-based fillers/SBS dispersions. The more homogeneous distribution of fillers was obtained by stirring the dispersions at 300

rpm during dip coating process. The copper samples were dried in open atmosphere after dip coating.

The electrochemical properties of AETDA loaded silica-based fillers/SBS composite coated samples were investigated by dipping them in 0.5 M NaCl solution. The open circuit potentials of bare copper, AETDA loaded silica-based fillers/SBS coated copper samples with higher filler loading (15% by mass) in dipping solutions were determined by exposing them to 0.5 M NaCl solution. Fig. 4.23 shows the open circuit potential of all samples as function of time. The open circuit potentials for all these samples were in the range of -0.183 to -0.229 V. The equilibrium potential values were reached within 50-100 s of immersion time in 0.5 M NaCl solution. These results showed that the open circuit potentials of AETDA filled halloysite/SBS composite coated sample was shifted in less noble directions than bare copper sample.

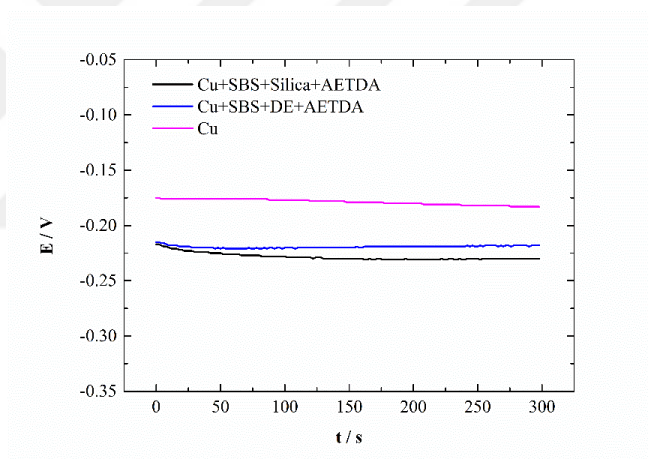


Fig. 4.23 Open circuit potential of bare copper, AETDA filled silica-based fillers/SBS composite coated copper coatings (containing 15% by mass fillers in dipping solution) after exposing to 0.5 M NaCl solution.

The polarization curves for copper samples coated with composite dispersions containing 15% AETDA loaded silica-based fillers were obtained by dipping them in 0.5 M NaCl solution. The Tafel plots for these samples were obtained by scanning from -200 mV to +200 mV through open circuit potential with a scan rate of 1 mVs⁻¹. The polarization parameters calculated from the Tafel curves of these composite coated copper samples are shown in Table 4.12. The corrosion potential for composite coated samples is shifted towards more positive side than bare copper samples. The corrosion potential of the bare copper changed from -248 mV to -201

mV by coating the copper samples with composite coatings containing AETDA filled silica-based fillers. This shift in corrosion potential values towards more noble potentials than bare copper sample showed that anodic reaction of the metal was suppressed by the protective composite coated layer containing AETDA loaded silica-based fillers on the copper surface. The corrosion inhibition efficiency for all copper samples coated with composites containing AETDA filled silica-based fillers was above 90%. This higher corrosion inhibition efficiency for all these samples can be attributed to the better inhibiting action of AETDA. The presence of heteroatoms such as nitrogen, oxygen and sulphur resulted in its better inhibiting ability. The free electron in these compounds resulted in complex formation with copper and enabled the chemisorption of AETDA on substrate surface [208, 210] This enhancement in corrosion inhibition efficiency for copper samples coated with dipping solution containing lower concentrations of inhibitor loaded particles can be also attributed to the homogeneous distribution of AETDA loaded particles in composite coatings. The nanodefects in composite coatings have resulted in lowering the corrosion inhibition efficiency of the composite coated copper samples as well. These defects served as the sites for penetration of chloride ions into the coatings which resulted in pitting corrosion of Cu samples.

Table 4.12 Electrochemical parameters acquired from Tafel curves for composite coated copper samples (containing 15% by mass silica-based fillers in dipping dispersions) dipped in 0.5 M NaCl solution.

Sample	$E_{\text{corr}} / \text{mV}$	$I_{\text{corr}} / \mu\text{Acm}^{-2}$	Θ	$\Pi \%$
Cu+SBS+HalNT+AETDA	-208	0.49	0.927	92.7
Cu+SBS+DE+AETDA	-201	0.65	0.904	90.4
Cu+SBS+Silica+AETDA	-222	0.22	0.967	96.7

The cyclic voltammograms of these coated samples are shown in Fig 4.24. These voltammograms were obtained by scanning towards positive potential from OCP with a scan rate of 5mV/s. These samples also showed active-passive behavior like the samples coated with chitosan/PEG loaded silica-based fillers/SBS composites. The similar shape and behavior were observed for all composite coated samples. The current density increased from the OCP by moving towards positive potential for the samples. This increase in current density is attributed to the active dissolution of

copper samples through nanodefects in the composite coatings. The passivation potential of AETDA filled silica/SBS, AETDA filled halloysite/SBS and AETDA filled DE/SBS composite coated copper samples was 22.0 mV, 16.7 mV and 22.7 mV respectively. These passivation potential values are lower than bare copper (109 mV). The passive current density of AETDA loaded silica-fillers/SBS composite coated samples was also lower than bare copper (17.5 mAcm^{-2}) as shown in Table 4.13. The current density swiftly dropped after reaching the passivation potential for all coated samples upon further increase in positive potential. The transpassive dissolution of all composite coated samples resulted in breakdown of passive protective film. The AETDA filled halloysite/SBS composite coated samples having less passivation potential and current density showed transpassive dissolution at lower potentials as compared to other AETDA loaded filler coated samples. The backward scan of potential resulted in sudden increase in current density for all AETDA loaded silica-based fillers/SBS composite coated copper samples. This sudden increase in current density was more for AETDA loaded DE/SBS composite coated samples other counterparts. This sudden increase indicated the change in dissolution mechanism of coated copper samples. This sudden increase in current density during backward scan indicated the damage caused by the pitting corrosion of copper substrates. The cyclic voltammograms also showed the decrease in current density after repassivation potential which indicated that the rate of copper dissolution is slower during the backward scan than the forward scan.

The passive current density (I_p), passivation potential (E_p), repassivation potential (E_{rp}) and charge during the forward scan (Q) are shown in Table 4.14. This table shows that the AETDA loaded halloysite/SBS coated Cu samples showed better corrosion resistance than other two AETDA loaded silica fillers/SBS composite coated samples. The values of charge during forward scan due to active and transpassive dissolution of copper showed that AETDA loaded halloysite/SBS composite coated samples showed better anti-corrosive ability than their counterparts.

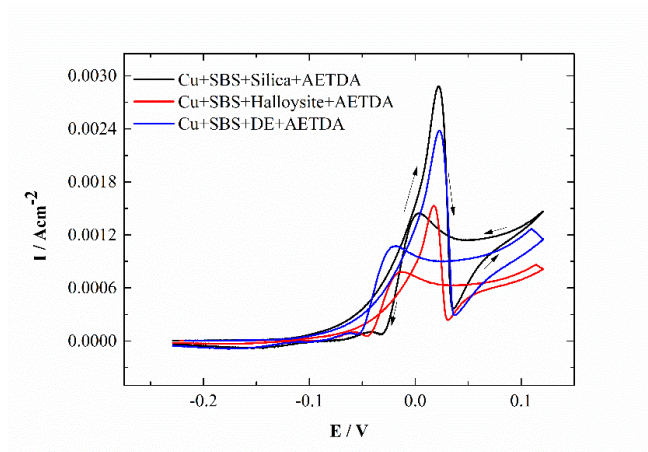


Fig. 4.24 Cyclic voltammograms for investigation of electrochemical behavior of composite coated copper samples dipped in 0.5 M NaCl solutions. The arrows showed the directions of potential scans. The scan rate used was 5 mV/s.

Table 4.13 Electrochemical parameters acquired from cyclic voltammograms for composite coated copper samples (containing 15% by mass silica-based fillers) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Cu+SBS+HalNT+AETDA	1.53	$1.13 \cdot 10^{-4}$	16.70	25.71
Cu+SBS+DE+AETDA	2.4	$1.70 \cdot 10^{-4}$	22.68	31.79
Cu+SBS+Silica+AETDA	2.8	$2.10 \cdot 10^{-4}$	22.02	31.01

4.5.5 Comparison of inhibiting action of AETDA with Chitosan and PEG

In this part, the corrosion inhibition ability of green corrosion inhibitors (PEG and Chitosan) was compared with commercially used inhibitor (AETDA). For that purpose, the electrochemical properties of copper samples coated with composites containing chitosan filled with halloysite nanotubes or PEG filled DE particles were compared with copper samples coated with AETDA filled halloysite nanotubes. The copper samples were coated with composite dispersions containing 15% by mass inhibitor loaded particles. Fig. 4.25 shows the Tafel curves for these composite coated samples and bare copper sample. The corrosion potential for all composite coated samples is shifted towards less negative potential than the bare copper

samples. This potential shift showed that these inhibitors acted as anodic inhibitors by suppressing the oxidation of copper substrates. The maximum corrosion inhibition efficiency of 92.7% was achieved for copper samples coated with composites containing AETDA loaded halloysite nanotubes. But the corrosion inhibition efficiency for the samples coated with composites containing PEG filled DE particles or chitosan loaded halloysite nanotubes was 92.3% and 67% respectively. These curves clearly showed that the corrosion inhibition ability of AETDA and PEG was almost same. The lower corrosion inhibition efficiency of chitosan loaded halloysite nanotubes was attributed to the insolubility of chitosan in organic solvents which resulted in agglomerations of chitosan loaded halloysite nanotubes. These agglomerated particles may have resulted in inhomogeneities in composite coatings. These inhomogeneities could serve as sites for the penetration of corrosive liquids and ultimately active dissolution of copper samples.

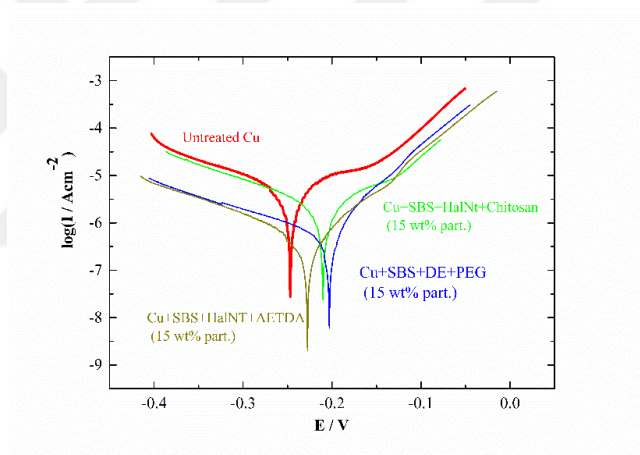


Fig. 4.25 Comparison of Tafel curves for the bare and composite coated copper (containing 15% inhibitor loaded fillers in dipping dispersions) in 0.5 M NaCl at room temperature.

The cyclic voltammograms of these samples were compared and the forward scan of those voltammograms is shown in Fig. 4.26. Similar shape and behavior were observed for all composite coated samples. These cyclic voltammograms were used to calculate the passive current density, passive potential and charge during forward scan. The values of all these calculated parameters are shown in Table. 4.14. The passive current density of composite coatings containing AETDA filled halloysite nanotubes or chitosan loaded halloysite nanotubes were almost same. The charge during the forward scan due to active and passive dissolution of copper substrates further proved that both AETDA and chitosan have similar ability to inhibit copper

corrosion. The passive current density value of composite coatings containing PEG filled DE is also not that far from the other two inhibitor loaded particles composite coatings. These electrochemical results clearly showed that both chitosan and PEG can be used as corrosion inhibitors for copper. Chitosan and PEG showed the inhibition efficiency comparable to the commercially used corrosion inhibitor. PEG and chitosan are green inhibitors, and this makes them better choice for corrosion inhibition of copper.

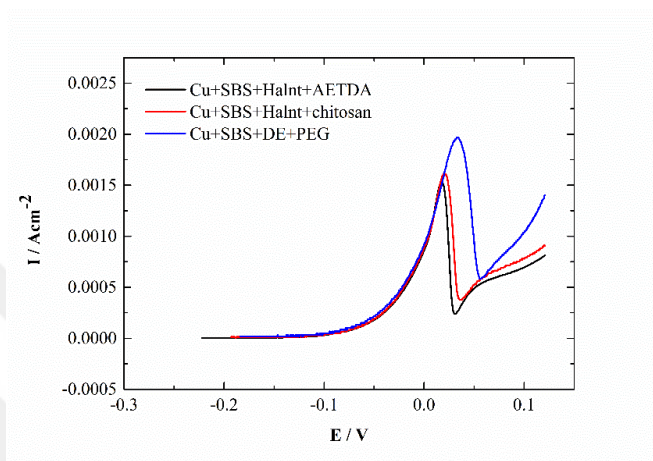


Fig. 4.26 Comparison of cyclic voltammograms (only forward scan) for the composite coated copper samples dipped in 0.5 M NaCl solutions.

Table 4.14 Electrochemical parameters acquired from cyclic voltammograms for composite coated copper samples (containing 15% by mass silica-based fillers) dipped in 0.5 M NaCl solution.

Sample	I_p / mAcm^{-2}	Q / C	E_p / mV	E_{rp} / mV
Cu+SBS+HalNT+AETDA	1.53	$1.135 \cdot 10^{-4}$	16.7	25.7
Cu+SBS+HalNT+Chitosan	1.6	$1.65 \cdot 10^{-4}$	19.9	30.5
Cu+SBS+DE+PEG	1.9	$2.59 \cdot 10^{-4}$	34.3	47.1

4.6 Electrochemical deposition of Fe-P thin films reinforced by inhibitor loaded/unloaded silica micro-and nano-particles

Iron plating is widely used due to its enticing physical properties and lower cost. The properties of pure iron can be altered by alloying it with metals (nickel, cobalt, zinc) and semimetals (like phosphorus). So, based upon the concentration of phosphorus the iron -phosphorus alloy can be amorphous, crystalline or a mixture of these phases. Amorphous alloys show different properties in corrosion resistance, magnetism, electrical resistivity than their crystalline counterparts of similar compositions. The better corrosion resistance of amorphous Fe-P alloys is due to the absence of grain boundaries, crystalline defects and dislocations in them [102]. In this work, thin Fe-P/silica-based fillers composite films were electrodeposited on metallic substrates from sulphate solutions with/without additive. The influence of current density on the structure and composition of deposited composite films was investigated. PEOX-5K, PEOX-50K and PEG-10K were used as additives to decrease the surface tension of the solution bath. Mesoporous silica and halloysite nanotubes were used as corrosion inhibitor carriers. Chitosan, PEG-10K and PEOX-5K were used as corrosion inhibitors. Porous silica-based particles filled with PEOX-5K, chitosan and PEG-10K were reinforced in Fe-P films. Standard electrochemical methods, scanning electron microscopy, X-ray fluorescence and X-ray diffraction spectroscopy were used to evaluate the samples. The morphology and chemical compositions of the composite films were found to depend on the current density. The crystallinity of the composite films was verified by X-ray diffraction technique. Similar to anti-icing and anti-corrosive composite coatings explained in Chapter 3 and Chapter 4 respectively, these composite coatings also have the great advantage of keeping the inhibitor in the micro- and nano- containers and releasing it locally in damaged or scratched regions.

4.6.1 Investigation of chemical composition of electrodeposited films

4.6.1.1 Co-deposition of Fe-P binary alloy films

The electrodeposition of phosphorous alone from aqueous solution is not possible. However, it can be easily co-deposited from aqueous baths containing elements from the iron group. This co-deposition phenomenon is known as induced

electrodeposition. The polarization energy of iron group elements provides required activation energy for the deposition. The activation energy of deposition of phosphorous is provided by the polarization energy of iron group elements. Hydrogen can also induce the co-deposition of phosphorous in the presence of iron group elements [239, 251]. The proposed reactions for co-deposition of P in Fe-P layers are shown below. The reduction of hypophosphite ions, disproportionation of hypophosphite ions and redox reaction between iron and phosphine can be the proposed methods for co-deposition of P in Fe-P layers [252]. Due to the low pH of electrolyte bath, the reduction of hypophosphite ion and disproportionation of hypophosphite ions can be the most probable methods for the deposition of P in Fe-P layers deposited in this work.

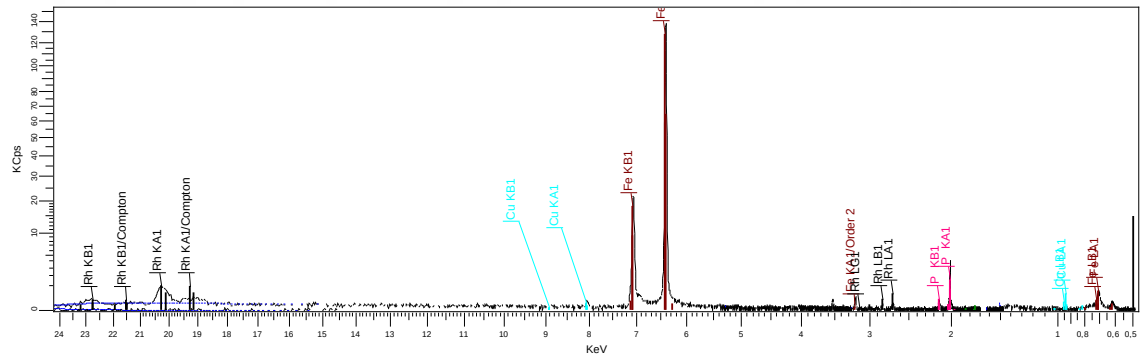
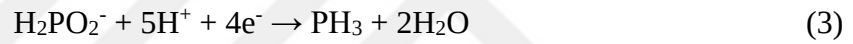
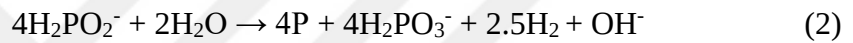


Fig. 4.27 XRF spectrum of Fe-P binary films deposited on copper substrate by using the current density of 10 mA/cm^2 .

The co-deposition of phosphorous with iron as binary alloy was confirmed by XRF analysis. The XRF pattern of electrodeposited Fe-P film on copper substrate is shown in Fig. 4.27. The presence of Fe and P peaks in XRF spectrum confirmed the incorporation of P in Fe matrix. The appearance of Cu peaks can be attributed to the underlying substrate because the XRF spectrum was measured on most of the samples together with the substrate. The additional peaks of Rh are coming from the

X-ray source material. This is a typical XRF spectrum shown by all the samples investigated in this study. The chemical composition of electrodeposited Fe-P binary alloy films is affected by many parameters which will be discussed in next sections.

4.6.1.2 Effect of current density on composition of electrodeposited Fe-P films

Thin Fe-P layers with and without silica particles were deposited on various substrates by using direct current electrochemical method from an electrolyte bath at ambient temperature. The current densities used for the electrodeposition of Fe-P binary alloy were 10, 30, 50, 70, 100 mA/cm² and the electrodeposition time for these current densities was 100, 33, 20, 14 and 10 min respectively. The Fe-P layers with and without silica particles were deposited on Cu wires. The amount of porous and PEOX-5K filled silica particles used in electrolytic bath was 0.1 g/L. The combine effect of current densities and PEOX-5K/mesoporous silica as additive on chemical composition of Fe-P layers was also investigated. The effect of current density on the chemical composition of electrodeposited Fe-P alloys with and without silica content was investigated by XRF analysis. The reference qualitative spectrum of XRF analysis was shown in Fig. 4.27. The quantitative data was obtained from XRF spectrums. This quantitative data of the electrodeposited Fe-P binary alloy layers was analyzed to determine the effect of current density on the chemical composition of these layers. Fig. 4.28 shows the effect of current density and combine effect of current density and additives on the chemical composition of Fe-P layers deposited on copper wires. The results clearly showed that the Fe content in the electrodeposited films increased from 74.7 wt% at 10 mA/cm² to 91.9 wt% at 100 mA/cm². The increase in Fe content with increasing current density is similar to that already reported in literature [251, 252]. The increase in current density may have enhanced the precipitation of iron hydroxide at the cathode surface which resulted in higher iron content in the Fe-P deposited layers [251]. The addition of unloaded and PEOX-5K loaded silica particles in electrolytic bath enhanced the Fe content for all the current densities. The maximum iron amount of 95.9 wt% at 100 mA/cm² was obtained for the samples electrodeposited from the solution containing PEOX-5K filled silica particles. The effect of additives on the composition will be further elaborated in next section. A general trend can be observed when the investigating the Fe composition as a function of current density, the amount of Fe

increases with increasing the current density for all the electrodeposited samples obtained from electrolytic solution with or without additives (silica/PEOX-5k). Therefore, the P content decreases from 25.3 wt% at 10 mA/cm² to 8.1 wt% at 100 mA/cm² for Fe-P layers deposited from solution without any additives. This decrease in P content can be attributed to the increase in hydrogen evolution reaction. The co-deposition of P is directly proportional to the amount of hydrogen ions in solution as shown in reaction 1. The increase in hydrogen evolution will decrease the concentration of hydrogen ions that resulted in lowering the P content in Fe-P layers [251, 252]. The addition of additive in electrolytic bath resulted in further decrease in phosphorous content in electrodeposited Fe-P layers.

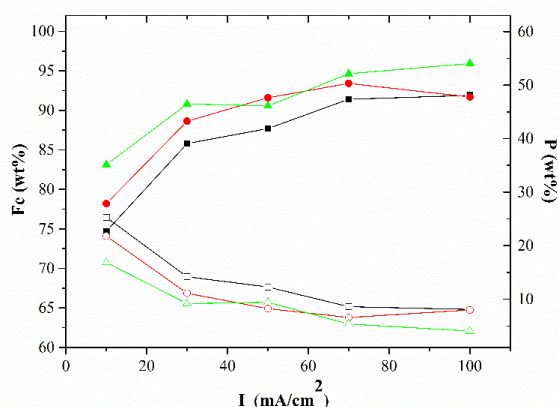


Fig. 4.28 Effect of current density and additives (PEOX-5k and SiO₂ particles) on the composition of the electrodeposited Fe-P layers, Fe content without any additive in bath (filled black squares), Fe content with porous SiO₂ in bath (filled red circles), Fe content with PEOX-5K filled SiO₂ in bath (filled green triangles), P content without any additive in bath (hollow black squares), P content with porous SiO₂ in bath (hollow red circles), P content with PEOX-5K filled SiO₂ in bath (hollow green triangles).

Furthermore, the effect of different substrates on the chemical composition of Fe-P layers was investigated. The results showed that the content of Fe deposited on Cu wire was 74.7 wt% at current density of 10 mA/cm² and increased to 91.9 wt% at current density of 100 mA/cm². When the Fe-P layers were deposited on brass sheets, the content of iron was increased to 89.3 wt% and 93 wt% at current density of 10 and 100 mA/cm² respectively. This increase in iron content can be attributed to the bigger size of brass sheets compared to Cu wires. In addition to this the smaller size of Cu wires can affect the precision of the results obtained by XRF analysis. The

electrodeposition current densities have a significant effect on the surface morphology of deposited Fe-P layers. The surface morphology of electrodeposited Fe-P layers was investigated by SEM analysis. Fig. 4.29 shows the SEM images of Fe-P layers deposited on Cu wires by varying the current densities. The deposition solution did not contain any additive in it. The surface morphology of the Fe-P layers gradually changed from flat and uniform surfaces to globular structures. The morphology of Fe-P layers obtained at 10-30 mA/cm² was smooth. The morphology obtained at 50 mA/cm² consisted of smaller globules. The morphology of Fe-P layers obtained at 70-100 mA/cm² contained bigger globules and some cracks were evident on the surface. These cracks can be attributed to the stress induced into the Fe-P due to higher current densities. The increase in current density resulted in enhanced hydrogen evolution reaction and faster nucleation of Fe-P layers. The concentration gradient resulted in introduction of hydrogen atoms in Fe-P layers and these hydrogen atoms combine to form H₂ molecules that ultimately resulted in hydrogen embrittlement. The transition from flat to globular structure could be due to the hydrogen embrittlement. In addition to this the decrease in P content with increasing current density can affect the surface morphology of Fe-P layers. The increase in P content with decreasing current density resulted in less uneven and flat structure [253]. The increase in current density resulted in enhanced hydrogen evolution reaction that resulted in local pH change in electrolytic solution which also may have affected the surface morphology. The white aggregates of iron hydroxide were evident on the surface of the Fe-P layers deposited at higher current densities. The local change in pH at higher current densities could result in deposition of iron hydroxide on the surface of Fe-P layers. These results are in line with literature data [29]. The electrolytic baths containing additives affected the morphology of Fe-P layers as well. The samples deposited with solution containing porous silica particles showed similar morphology as shown in Fig. 4.29. But the samples deposited with electrolytic bath containing PEOX-5K filled silica particles (Fig. 4.29f) showed globular formation at current density of 10 mA/cm². The decrease in surface tension due to the leaching out of additives may have resulted in faster deposition reaction due to faster movement of Fe²⁺ ions in solution. This faster reaction could cause intensive hydrogen evolution reaction that resulted in globular morphology even at lower current densities. The effect of additives on deposition process will be discussed in 4.6.1.3.

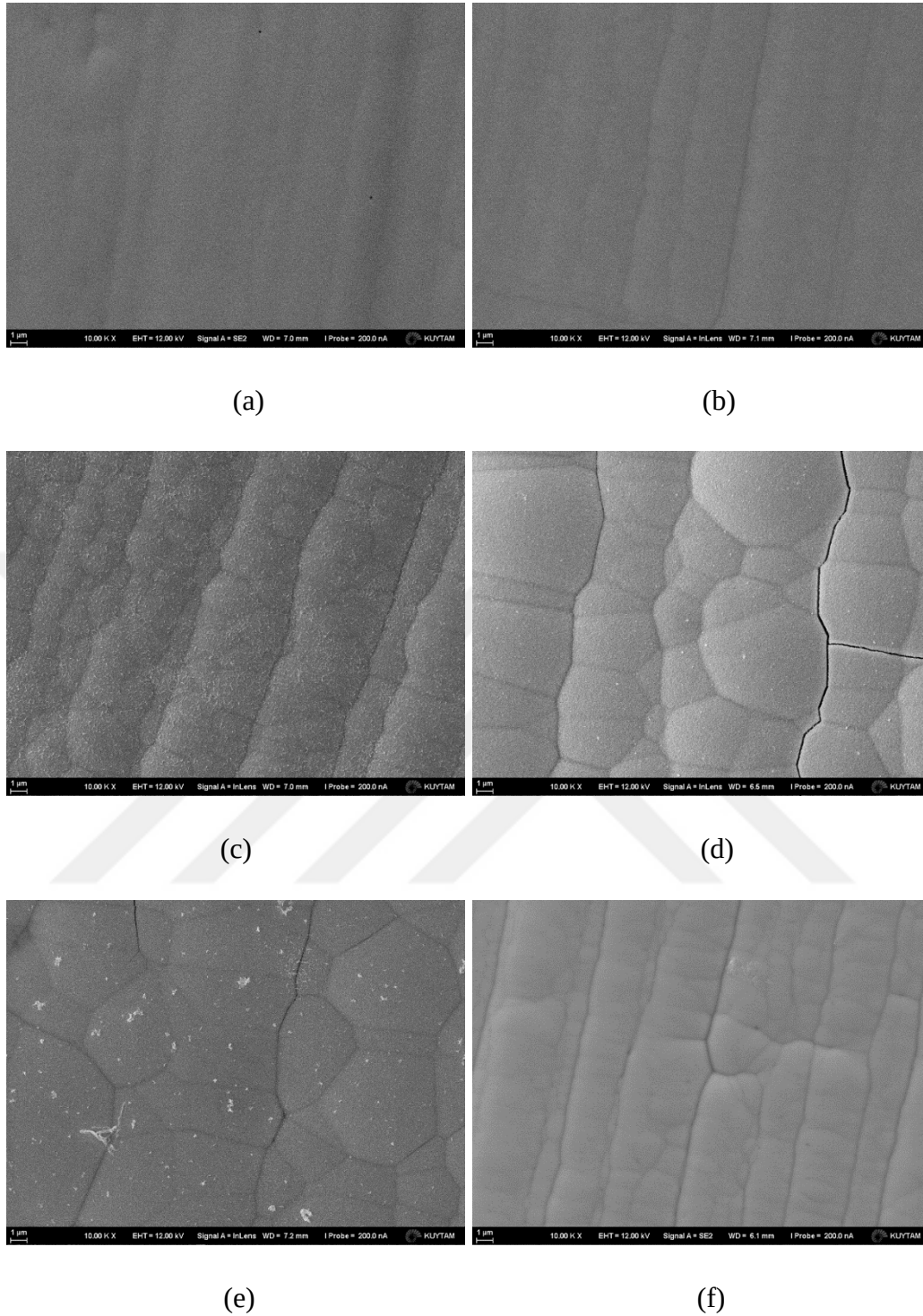


Fig. 4.29 SEM images of electrodeposited Fe-P layers deposited on Cu wires by changing current densities. (a) 10 mA/cm², (b) 30 mA/cm², (c) 50 mA/cm², (d) 70 mA/cm², (e) 100 mA/cm² and (f) deposited at 10 mA/cm² from solution containing PEOX-5K filled silica.

The Fe-P binary alloys of various compositions were electrodeposited on Cu substrates. The composition of these alloys was varied by changing the current density of electrodeposition process. The cathode current efficiency of these

deposited films was investigated. For that purpose, the electrodeposited weight was determined by weighing the substrates before and after the deposition process and the total charge passed through cathode was calculated. These values of total charge and deposition weight along with compositional information were used to calculate cathode current efficiency. The cathodic current efficiency values calculated for Fe-P layers deposited at 10-100 mA/cm² ranged between 55-85%.

4.6.1.3 Electrochemical characterization of electrolyte bath

The synthesis of Fe-P layers on various substrates requires complete investigation of deposition kinetics and stability of electrolyte baths. The cathodic polarization curves give complete information about the electrodeposition mechanism. In order to understand the effect of additives on electrodeposition of Fe-P layers, cathodic polarization curves for Fe-P deposition were obtained from electrolyte bath with and without additives. The role of phosphorous on electrodeposition of Fe-P layers was also evaluated by comparing the cathodic polarization curves of pure Fe with that of Fe-P layers. The cathodic polarization curves measured for various Fe and Fe-P electrolyte baths are shown in Fig. 4.30.

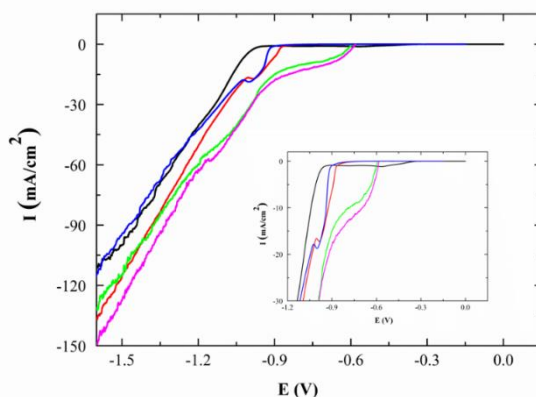


Fig. 4.30 Cathodic polarization curves in Fe and Fe-P bath in the presence of various additives (PEOX-5k, -50k and SiO₂), pure Fe deposition bath (black line), Fe-P deposition bath without additive (red line), Fe-P deposition bath containing 1 g/L PEOX-50K (blue line), Fe-P deposition bath containing 0.1 g/L PEOX-5K (green line) and Fe-P deposition bath containing 0.1 g/L PEOX-5K and 2 g/L silica (pink line). The insert shows the enlarged area between 0-30 mA/cm² current density.

In case of pure iron, the deposition of Fe started at -0.95 V but the addition of phosphorous shifted the onset of deposition towards less negative potentials of -0.86

V. The deposition curve of Fe and Fe-P overlapped with that of hydrogen evolution reaction. In case of electrolyte baths containing PEOX-5K and PEOX-5K combined with silica particles, the deposition process started at -0.58 V and -0.59 V respectively. The addition of PEOX-5K and mesoporous silica particles resulted in the early onset of Fe-P deposition together with hydrogen evolution reaction as compared to electrolytic solution without additives. The increase in concentration of PEOX to 1 g/mL in electrolyte bath delayed the onset of deposition process of Fe-P layers due to slower diffusion and ion migration towards the cathode surface as compared to the samples deposited from the electrolytic bath containing 0.1 g/mL of PEOX-5K. The polarization curves showed that the deposition process is charge transfer controlled. Overall, the addition of phosphorous and additives resulted in earlier onset of Fe deposition process. These results are in line with literature data [254].

4.6.1.4 Effect of additives on chemical composition of Fe-P layers

4.6.1.4.1 Effect of PEOX on chemical composition of Fe-P layers

Fe-P layers were deposited on Cu/brass substrates by using direct current from an electrolyte bath containing PEOX-5K/PEOX-50K as additive. The current densities used for the electrodeposition of Fe-P binary alloy were 10 and 100 mA/cm² and the electrodeposition time for these current densities was 100 and 10 min respectively. These current densities were selected due to their ability to give two different morphologies and chemical composition of Fe-P binary alloy matrices. The concentration of PEOX-5K and PEOX-50K used in electrolyte bath was 0.1 g/L and 1 g/L respectively. The effect of PEOX-5K and PEOX-50K on the chemical composition of electrodeposited Fe-P alloys was investigated by XRF analysis. A qualitative spectrum of XRF analysis was shown in Fig. 4.27. The quantitative data was obtained from XRF spectrums. This quantitative data of the electrodeposited Fe-P binary alloy layers was analyzed to determine the effect of organic PEOX-5K and PEOX-50K on the chemical composition of these layers. The chemical composition of the Fe-P layers obtained from electrolyte baths with/without additives is shown in Table 4.15. It was observed that the chemical composition was almost same for the Fe-P layers deposited from electrolyte bath with and without 0.1 g/L PEOX-5K. These compositional results were consistent with cathodic polarization results (Fig. 4.30). The P content of Fe-P layers was enhanced by increasing the concentration of

PEOX in electrolyte bath. For the Fe-P layers deposited at same current density (10 mA/cm²), P content was 10.47 at 0.1 g/L PEOX-5K concentration and gradually increased to 13.1 at 1 g/L PEOX-50K concentration. The increase in P amount in Fe-P layers obtained at higher concentration of PEOX-50K in solution can be attributed to incorporation ability of P by the indirect reduction process [253, 255]. In addition to this, the slow diffusional movements of ions through solutions containing 1 g/L PEOX as shown by cathodic polarization results (Fig. 4.30) may have changed the composition. The XRF results also showed the presence of Sulphur in deposits. This impurity could be from the sticky tape which was used to cover the side of substrates.

Table 4.15 Composition of Fe-P layers deposited from solution with/without PEOX.

Sample ID	I _{dep} (mA/cm ²)	Property	Fe (wt%)	P (wt%)
21	10	No additive	89.37	10.63
22	100		93.02	6.98
23	10	+0.1 g/l PEOX-5k	89.53	10.47
38	10	+1.0 g/l PEOX-50k	86.77	13.1
39	100		96.31	3.52

4.6.1.4.2 Incorporation of mesoporous silica particles in Fe-P matrices

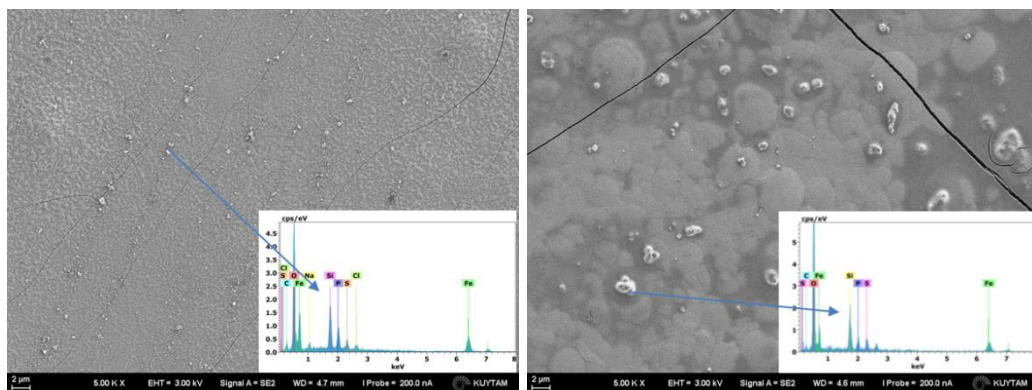
In order to incorporate mesoporous silica particles in Fe-P alloy matrix, Fe-P/SiO₂ composite was electrodeposited by using direct current from an electrolyte bath containing mesoporous silica particles. The current densities used for the electrodeposition of Fe-P binary alloy were 10, 50, 100 mA/cm² and the electrodeposition time for these current densities was 100, 20 and 10 min respectively. The concentration of mesoporous silica particles in electrolyte bath was 2 g/L. The incorporation of mesoporous silica particles in electrodeposited Fe-P alloy matrix was investigated by XRF analysis. The quantitative data of the electrodeposited Fe-P/SiO₂ composites was analyzed to determine the incorporation of mesoporous silica particles in Fe-P alloy matrices. The chemical composition of

electrodeposited Fe-P layers obtained from electrolyte bath containing silica particles is shown in Table 4.16.

Table 4.16 Chemical compositions of Fe-P/SiO₂ composites.

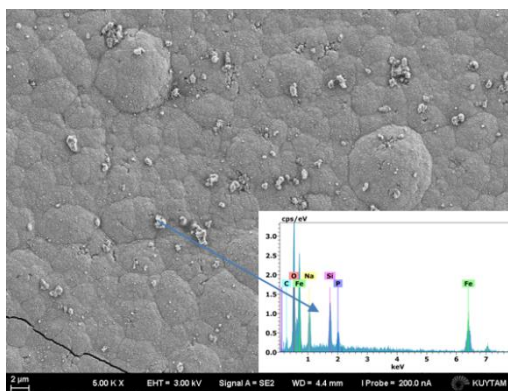
Sample ID	I _{dep} (mA/cm ²)	Fe (wt%)	P (wt%)	Si (wt%)	S (wt%)
47	10	84.35	12.62	0.18	2.84
51	50	90.05	8.15	-	1.79
48	100	95.89	3.78	0.23	-

The presence of silicon in XRF analysis confirmed the incorporation of silica particles in Fe-P alloy matrix. These results showed that the silica content increases in the alloy matrix by increasing the current density of deposition process. There was no silicon content observed for the Fe-P alloy coating obtained at 50 mA/cm². This sample could contain the silicon content below the detection limit of XRF. The incorporation of mesoporous silica particles in all these samples was further confirmed by SEM/EDX analysis. SEM images of electrodeposited Fe-P alloys deposited at 10, 50 and 100 mA/cm² are shown in Fig. 4.31. The surface morphology of all these samples showed the presence of silica particles. The presence of silica particles on the surface of these samples was confirmed by presence of silicon peaks in EDX spectrum of these samples. Silica particles are incorporated as agglomerates. The pH of the electrolytic bath was around 2. The isoelectric point of silica is also pH 2. The compression of double layer around the silica particles due to higher ionic strength at their isoelectric point have resulted in agglomeration [256].



(a)

(b)



(c)

Fig. 4.31 SEM images of electrodeposited Fe-P alloy matrix containing silica particles, (a) deposited at 10 mA/cm², (b) deposited at 50 mA/cm² and (c) deposited at 100 mA/cm². The inserts show the EDX spectrum of these samples.

4.6.1.4.3 Effect of PEOX on the incorporation of silica particles in Fe-P layers

The purpose of this work is to incorporate mesoporous silica particles with/without inhibitor loading into Fe-P matrix for enhancing their surface properties and corrosion resistance. To enhance the co-deposition of silica particles in Fe-P matrix, the effect of PEOX as an additive on co-deposition of silica in Fe-P matrix was investigated. Fe-P/SiO₂ composite coatings were electrodeposited by using direct current from an electrolyte bath containing both PEOX as an additive and mesoporous silica particles with/without inhibitor loading. The concentration of PEOX-5K and PEOX-50K in electrolyte bath was 0.1 g/L and 1 g/L respectively. The concentration of mesoporous silica particles in electrolyte bath was 0.1-2 g/L. The current densities used for the electrodeposition of Fe-P binary alloy were 10 and 100 mA/cm² and the electrodeposition time for these current densities was 100 and 10 min respectively. The incorporation of unloaded porous silica particles in Fe-P alloys matrix was investigated by XRF analysis. The chemical composition of Fe-P/SiO₂ composite coatings obtained from an electrolyte bath containing 1 g/L PEOX-50K as an additive and 2 g/L silica particle is shown in Table 4.17. The composition analysis revealed the presence of silicon which confirmed the presence of silica particles in Fe-P alloy matrices. The amount of silica particles incorporated in these samples is higher than the amount retained when no additive was present in electrolyte bath (Table 4.16). This difference in silica incorporation can be explained by the absolute values of zeta potential of silica particles. The zeta potential of silica

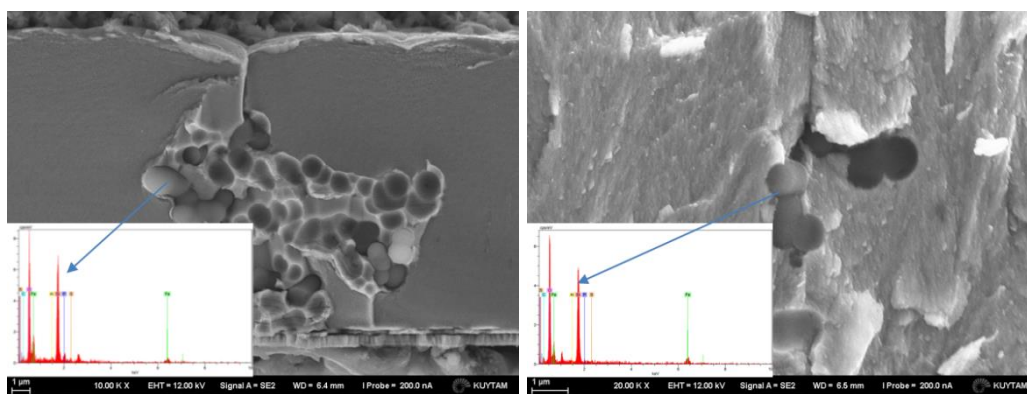
particles in DI water and DI water containing 1 g/L PEOX-50K is -41.42 mV and -32.68 mV respectively. This slightly positive zeta potential in presence of PEOX-50K in solution may helped in reducing the repulsion between silica particles and negatively charged cathode surface.

Table 4.17 Chemical compositions of Fe-P/SiO₂ composites electrodeposited from electrolyte bath containing PEOX-50K.

Sample ID	I_{dep} (mA/cm²)	Fe (wt%)	P (wt%)	Si (wt%)	S (wt%)
36	10	88.6	9.6	0.39	1.44
41	100	95.37	4.19	0.23	-

The incorporation of silica particles in these electrodeposited Fe-P matrices was further characterized by analyzing the cross sections of Fe-P/SiO₂ composite coatings with SEM. Fig. 4.32 shows the SEM images of cross sections of Fe-P/SiO₂ composite coatings. These images clearly showed the incorporation of mesoporous silica particles in them. The mesoporous silica particles are embedded in the Fe-P matrix. Their presence was confirmed by EDX analysis as well. The insert of the images shows the EDX spectrum for these samples. The presence of silicon peak in the spectrum confirmed the co-deposition of the silica particles in the Fe-P alloy matrix. The agglomeration of silica particles due to the compression of their electric double at low pH was still evident in Fe-P/SiO₂ composites. These images showed the crack initiation due to the stress induced by the deposition of silica particles in Fe-P layers. After the successful incorporation of unloaded silica particles in Fe-P alloy matrix, the aim was to incorporate inhibitor loaded mesoporous silica particles in Fe-P alloy matrix. For that purpose, mesoporous silica particles preloaded with 300 mg/mL PEOX-5K/PEOX-50K solution were dispersed in electrolytic bath with/without PEOX additive. The loading of mesoporous silica particles with inhibitor has been explained in section 4.4.2.2. Fe-P/SiO₂ composites were electrodeposited by using direct current from an electrolyte bath containing inhibitor loaded mesoporous silica particles. The incorporation of inhibitor loaded mesoporous silica particles was investigated with/without the addition of PEOX in electrolytic bath. The concentration of PEOX-5K as an additive in electrolytic bath was 0.1 g/L. The concentration of inhibitor loaded mesoporous silica particles in electrolyte bath

was 0.1 and 2 g/L. The current density used for the electrodeposition of Fe-P binary alloy was 10 mA/cm^2 and the electrodeposition time for this current density was 100 min. The incorporation of inhibitor loaded silica particles in Fe-P alloys matrix was investigated by XRF analysis. The chemical composition of Fe-P/SiO₂ composite coatings obtained from an electrolyte bath containing 0.1-2 g/L silica particle is shown in Table 4.18. The composition analysis revealed the presence of silicon in sample 31 which confirmed the presence of silica particles in Fe-P alloy matrices. There was no silicon peak observed in sample 40. There is a possibility that the amount of silica loaded in sample 40 was below the detection limit of the XRF. The zeta potential of PEOX-5K and PEOX-50K filled mesoporous silica particles in DI water was -38 mV and -41 mV respectively. The comparison of zeta potentials of PEOX-5K loaded mesoporous silica particles showed a slight positive value than PEOX-50K filled particles. This slight difference could result in more silica particles loading in Fe-P matrix. The sample 32 showed the highest silicon content which meant the highest silica particles incorporation in Fe-P matrix. This highest loading of silica particles in Fe-P matrix was confirmed by the zeta potential value. The zeta potential value of PEOX-5K loaded silica particles in DI water containing 1 g/L PEOX-5K solution was -23.7 mV. This zeta potential value is more positive than the zeta potential values for unloaded silica particles/inhibitor loaded silica particles in DI water/DI water containing PEOX in it.



(a)

(b)

Fig. 4.32 SEM images of electrodeposited Fe-P alloy matrix containing silica particles, (a) deposited at 10 mA/cm^2 , (b) deposited at 100 mA/cm^2 . The inserts show the EDX spectrum of these samples.

Table 4.18 Chemical compositions of Fe-P/SiO₂ composites electrodeposited from electrolyte bath containing inhibitor loaded silica.

Sample ID.	Property	I _{dep} (mA/cm ²)	Fe (wt%)	P (wt%)	Si (wt%)	S (wt%)
31	+0.1 g/l SiO ₂ (PEOX-5k filled)	10	88.8	11.0	0.25	0.49
40	+2.0 g/l SiO ₂ (PEOX-50k filled)	10	86.78	13.2	-	-
32	+0.1 g/l PEOX-5k +0.1 g/l SiO ₂ (PEOX-5k filled)	100	88.3	11.3	0.42	0.6

The incorporation of silica particles in these electrodeposited Fe-P matrices was further characterized by analyzing the cross sections of Fe-P/SiO₂ composite coatings with SEM. Fig. 4.34 shows the SEM images of cross sections of Fe-P/SiO₂ composite coatings. These images clearly showed the incorporation of mesoporous silica particles in them. The mesoporous silica particles are embedded in the Fe-P matrix. Their presence was confirmed by EDX analysis as well. The insert of the images showed the EDX spectrum for these samples. The presence of silicon peak in the spectrum confirmed the co-deposition of the inhibitor loaded silica particles in the Fe-P alloy matrix. The SEM image of sample 40 showed the incorporation of inhibitor loaded silica particles in it which was confirmed by the presence of silicon peak in EDX spectrum. The amount loaded in that particle could be less than the detection of XRF due to that no silicon peak was observed in XRF spectra. The SEM image of sample 32 confirmed more loading of inhibitor filled silica particles in Fe-P matrix. The agglomeration due to the compression of double layer was still evident in Fe-P/SiO₂ composites. The inhomogeneous distribution of unloaded and inhibitor loaded silica particles in Fe-P matrices could be attributed to the transport of these particles in electrolyte bath during the electrodeposition process [256].

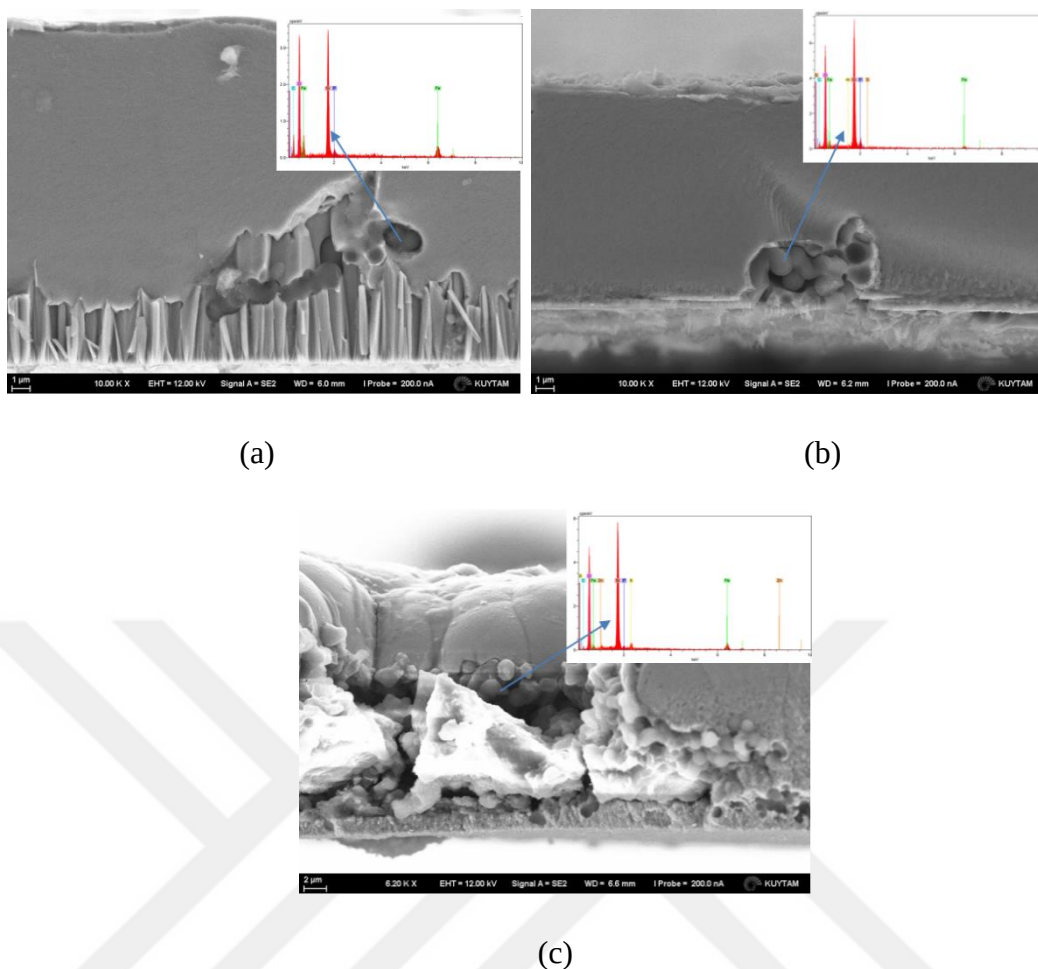


Fig. 4.33 SEM images of inhibitor loaded silica/Fe-P composites, (a) sample 31, (b) sample 40 and (c) sample 32.

4.6.1.5 Effect of PEG-10K addition on the composition of Fe-P layers

4.6.1.5.1 Electrochemical characterization of electrolyte bath containing PEG bath

In order to understand the effect of PEG-10K on electrodeposition of Fe-P layers, cathodic polarization curves for Fe-P deposition were obtained from electrolytic bath with and without PEG-10K. The effect of PEG-10K on the electrodeposition process of Fe-P layers was investigated. The concentration of PEG-10K was varied between 1-30 wt% in electrolytic bath. The cathodic polarization curves measured on copper substrates for Fe-P electrolyte baths with/without PEG-10K are shown in Fig. 4.34. The cathodic polarization curves showed that the deposition of Fe started in potential range of -0.86 V to -0.88 from all the electrolytic baths under consideration. Unlike PEOX the addition of PEG-10K in solution didn't affect the onset of Fe deposition process. The addition of PEG-10K suppressed the hydrogen evolution reaction. This suppression can be attributed to adsorption of PEG on the cathode surface that

prevented the proton access to the cathode surface [257]. The addition of PEG helped in easier removal of hydrogen bubbles from the electrolyte bath. The PEG concentration of 1-30 wt% in electrolyte bath resulted in slow ion migration towards the cathode surface as compared to the samples deposited from the electrolytic bath without any additive.

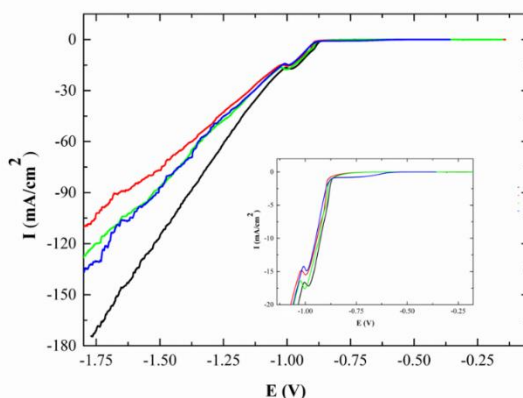


Fig. 4.34 Cathodic polarization curves in Fe-P bath with/without PEG-10K, Fe-P deposition bath without additive (black line), Fe-P deposition bath containing 1 wt% PEG-10K (red line), Fe-P deposition bath containing 5 wt% PEG-10K (green line) and Fe-P deposition bath containing 30 wt% PEG-10K (blue line). The insert shows the enlarged area between 0-30 mA/cm² current density.

4.6.1.5.2 Effect of PEG-10K on the chemical composition of Fe-P layers

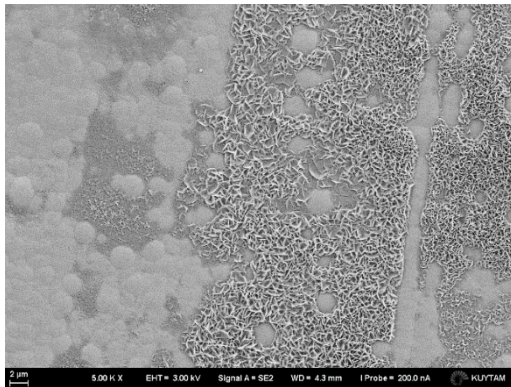
Fe-P layers were deposited on Cu sheets by using direct current from an electrolyte bath with/without PEG-10K. The current densities used for the electrodeposition of Fe-P binary alloy were 10, 50 and 100 mA/cm² and the electrodeposition time for these current densities was 100, 20 and 10 min respectively. The concentration of PEG-10K used in electrolyte bath was varied in the range of 1-30 wt%. The effect of PEG-10K on the chemical composition of electrodeposited Fe-P alloys was investigated by XRF analysis. The quantitative data was obtained from XRF spectrums. This quantitative data of the electrodeposited Fe-P binary alloy layers was analyzed to determine the effect of organic PEG-10K on the chemical composition of Fe-P layers. The chemical composition of the Fe-P layers obtained from electrolyte baths with/without additives is shown in Table 4.19. The compositional analysis showed that the addition of PEG from 1-5 wt% in electrolyte solution resulted in increase of P content of the coatings deposited at 10 mA/cm². This increase in P

content in electrodeposited Fe-P layers is consistent with cathodic polarization results (Fig. 4.34).

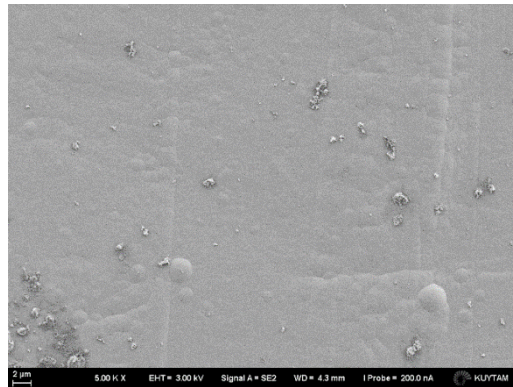
Table 4.19 Composition of Fe-P layers deposited from solution with/without PEG.

Sample ID.	I_{dep} (mA/cm ²)	Property	Fe (wt%)	P (wt%)	S (wt%)
21	10	additive free	89.37	10.63	-
22	100		93.02	6.98	-
52	10	+1 wt% PEG	83.31	15.06	1.55
49	10	+5 wt% PEG	88.32	11.68	-
50	100		95.31	3.32	1.38
42	10	+30 wt% PEG	87.25	10.96	1.78
46	50	+30 wt% PEG	88.93	11.07	-

The increase in P content could be attributed to the slow migration of ions towards cathode surface. The maximum increase of ~5 wt% in P content was observed for coatings obtained from solution containing 1 wt% PEG. The P content of composites deposited at 10 mA/cm² from solution containing 30 wt% solution was almost same as for the sample coated without PEG. The could be attributed to the phase separation of solution at such high concentration of PEG. The cathodic polarization curves obtained from the solution containing 1 wt% PEG (Fig.4.34) showed the slowest migration of ions towards cathodic surface. But in case of coatings obtained from solutions containing 5 and 30 wt% PEG, the increase in P content and the ion migration in these solutions is almost same. The effect of PEG-10K on the surface morphology of the electrodeposited Fe-P layers was investigated by SEM analysis.



(a)



(b)

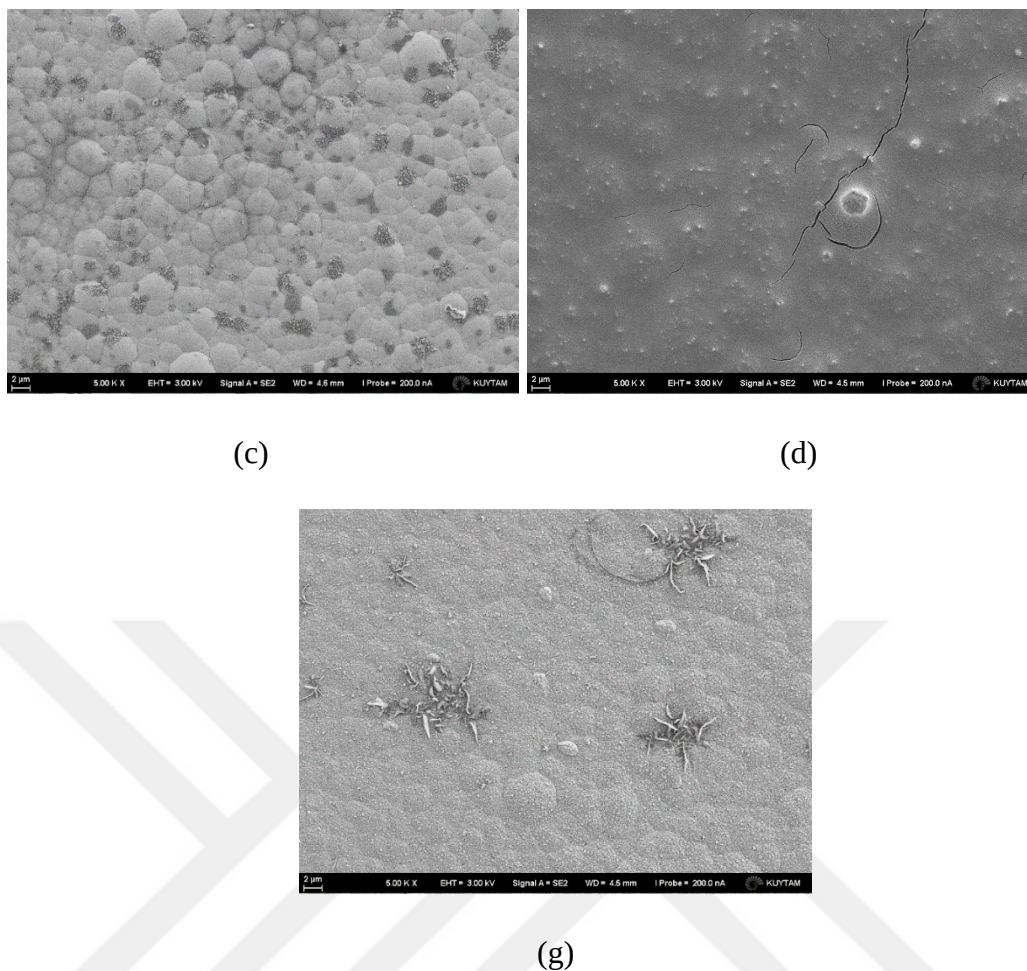


Fig. 4.35 SEM images of Fe-P alloy layers obtained from solutions with/without the addition of PEG-10K, (a) sample 52, (b), sample 49, (c) sample 42, (d) sample 50 and (g) sample 46. The description of sample id is given in Table 4.19.

Fig. 4.35 shows the SEM images of Fe-P alloy layers obtained from solutions with/without the addition of PEG-10K. These SEM images showed that the addition of PEG-10K in electrolyte bath resulted in smoother morphology than uneven globular morphology of Fe-P deposited in absence of PEG-10K (Fig. 4.29). This smoothness could be due to the increase in P content of Fe-P layers. The white foggy deposits on the surface of samples could be iron hydroxide. This iron hydroxide could be deposited due to the local pH change near the electrode surface. The sample 52 and 49 (Fig. 4.35 a-b) showed smoother morphology as compared to the sample 42 which was synthesized at same current density. This globular morphology can be attributed to higher PEG concentration of 30 wt% in electrolyte bath that may have resulted in more hydrogen evolution reaction. The sample 50 showed cracks due to hydrogen embrittlement at higher deposition current density of 100 mA/cm^2 . These

results were consistent with our results obtained for samples deposited at different current densities (Fig. 4.29).

4.6.1.6 Incorporation of halloysite nanotubes in Fe-P matrices

In order to incorporate halloysite nanotubes in Fe-P alloy matrix, Fe-P layers were electrodeposited on Cu sheets by using direct current from an electrolyte bath containing halloysite nanotubes. Both unloaded and inhibitor loaded halloysite nanotubes were used for incorporation in Fe-P alloy matrix. Chitosan and PEG-10K were used as corrosion inhibitor. The loading of halloysite with these inhibitors have been discussed in section 4.4.2.2. The concentration of both unloaded and inhibitor loaded halloysite nanotubes in electrolyte bath was 2 g/L. PEOX-50K (1 g/L) was used as an additive in electrolyte bath due to its ability to increase the P content of alloy matrices (Table 4.15). The current densities used for the electrodeposition of Fe-P binary alloy were 10 and 100 mA/cm² and the electrodeposition time for these current densities was 100 and 10 min respectively. These current densities were selected due to their ability to give two different morphologies and chemical composition of Fe-P binary alloy matrices. The incorporation of halloysite nanotubes in electrodeposited Fe-P alloy matrix was investigated by XRF analysis. The quantitative data of the electrodeposited Fe-P/halloysite nanotubes composites was analyzed to determine the incorporation of halloysite nanotubes in Fe-P matrices. The chemical composition of electrodeposited Fe-P layers obtained from electrolyte bath containing halloysite is shown in Table 4.20. The presence of silicon and aluminum peaks in XRF analysis confirmed the incorporation of halloysite nanotubes in Fe-P alloy matrix. The difference in the Si/Al content in these samples can be explained by the absolute zeta potential values of these samples. The zeta potential of these samples was not observed in electrolyte bath since Fe can be deposited on the electrode surface and it can affect the results. So, the zeta potential of unloaded and inhibitor loaded nanotubes was investigated in DI water. The zeta potential values for inhibitor loaded halloysite and unloaded halloysite nanotubes in DI water are shown in Table 4.21. The zeta potential values for halloysite nanotubes loaded with higher chitosan content is slightly positive than unloaded and loaded with lower chitosan concentration. This slightly positive value resulted in more loading of these nanotubes in Fe-P matrices. The zeta potential value of PEG loaded halloysite nanotubes were almost similar to the unloaded halloysite nanotubes. There

was no peak of Si/Al was observed for samples containing unloaded/PEG loaded halloysite nanotubes. The reason for the absence of these peaks could be the thickness of the deposited layers which did not allow the deeper penetration of X-rays and ultimately the proper determination of composition was affected. In addition to this, the amount loaded could be less than the detection limit of instrument.

Table 4.20 Chemical composition of electrodeposited Fe-P/halloysite composites.

Sample ID	I _{dep} (Acm ⁻²)	Property	Fe (wt%)	P (wt%)	Al (wt%)	Si (wt%)	S (wt%)
67	10	+2.0 g/l HallNT	89.37	10.63	-	-	-
68	100	(not filled)	95.73	3.46	- 0.07	-	1.32 -
69	10	+2.0 g/l HallNT	88.82	10.05	0.79	0.34	-
70	100	(chitosan filled 1 mg/l)	93.26	3.73	-	-	3.01
72	10	+2.0 g/l HallNT	87.31	12.64	-	0.056	-
73	100	(PEG-10k filled 10 wt%)	94.98	3.56	-	-	1.45
74	10	+2.0 g/l HallNT	82.77	10.48	4.02	2.73	-
75	100	(chitosan filled 5 mg/l)	95.05	3.08	0.26	0.15	1.45

Table 4.21 Zeta potential for loaded/unloaded halloysite nanotubes.

Sample	Zeta Potential (mV)
Halloysite	-31.68
Halloysite loaded with chitosan (1 mg/mL)	-24.30
Halloysite loaded with chitosan (5 mg/mL)	-16.60
Halloysite loaded with PEG-10K (100 mg/mL)	-31.98

The incorporation of halloysite nanotubes in all these samples was further confirmed by SEM/EDX analysis. SEM images of some selected electrodeposited Fe-P/halloysite are shown in Fig. 4.36. The presence of halloysite either on the surface

or in the cross sections of these samples confirmed their incorporation in Fe-P matrices. The surface morphology and cross section of all these samples showed the presence of halloysite. Fig. 4.36a showed the presence of unloaded halloysite nanotubes. Similarly, Fig. 4.36c confirmed the PEG filled halloysite nanotubes in Fe-P alloys matrices. These images showed that halloysite nanotubes were incorporated as agglomerates similar to silica particles (Fig 4.32 and Fig 4.33).

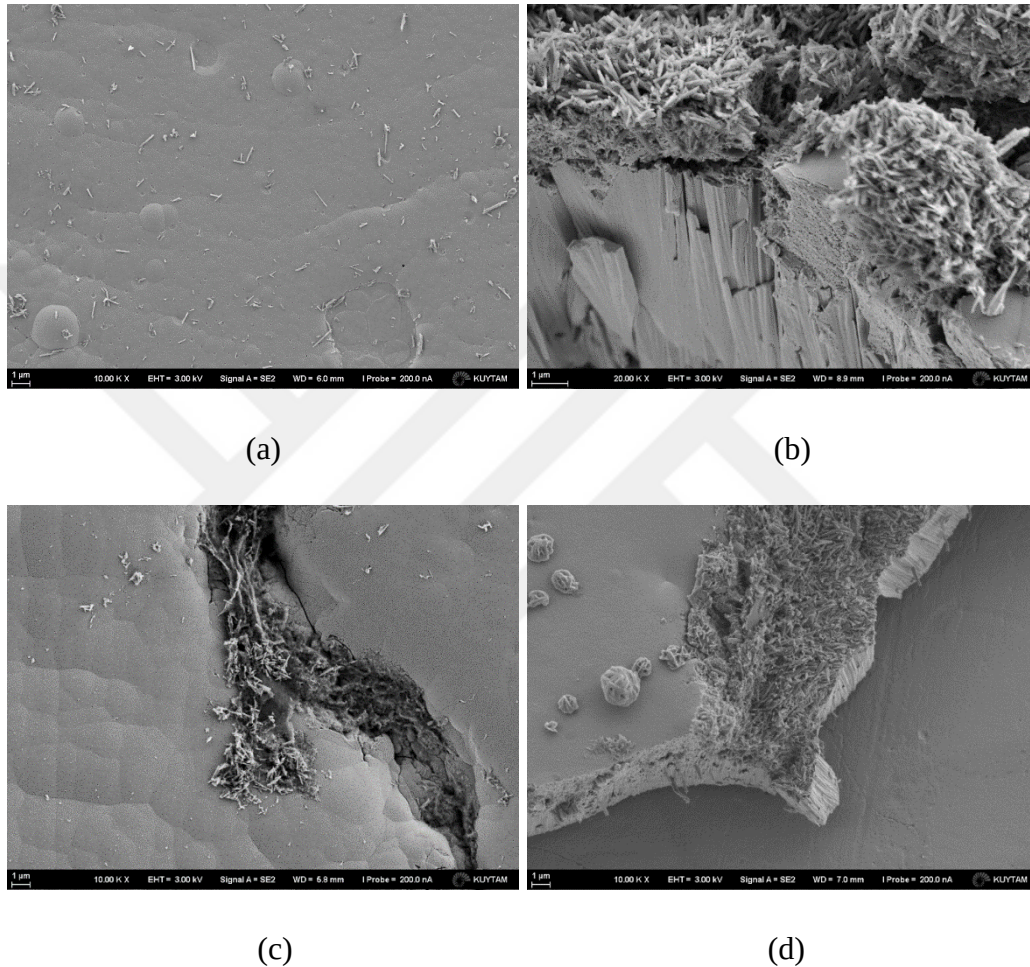


Fig. 4.36 SEM images of Fe-P/halloysite composites, (a) sample 67, (b) sample 69, (c) sample 72 and (d) sample 74. The sample description is given in Table 4.20.

4.6.2 Crystallinity and phase formation of Fe-P

Fe-P binary alloy and Fe-P/silica-based filler composite coatings with varying amount of P content were electrodeposited by changing the current density and electrolyte bath concentrations. Depending on the P content in Fe-P deposited films, the microstructure can change from crystalline to amorphous structure. The formation of new phases in electrodeposited Fe-P binary alloys that resulted in these structural changes were determined by Fe-P phase diagram. Fig. 4.37 shows the

phase diagram of Fe-P binary system [258]. The phase diagram of Fe-P binary system showed that the solubility of P in α -Fe is about 2.8 wt% at eutectic temperature. But P and α -Fe can form various intermetallic compounds over a long range of P composition [253]. The Fe-P amorphous alloys are formed at 7.65-15.5 wt% of P [245, 258].

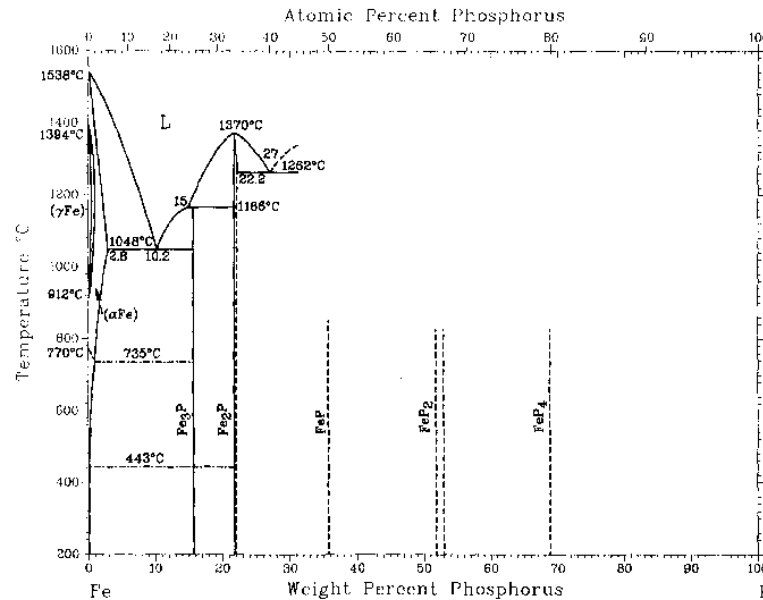


Fig. 4.37 Phase diagram of Fe-P [258].

4.6.2.1 Effect of current density on structure of Fe-P layers

The effect of current density on the structure of electrodeposited Fe-P layers was investigated by XRD measurements. Fig. 4.38 shows the XRD patterns of Fe-P films deposited at 10 and 100 mA/cm². The diffraction peaks at 42.4°, 49.3°, 72.2° and 87.5° corresponded to the brass substrate [259]. The chemical composition and properties of sample 21 and 22 are shown in Table 4.19. The sample 21 showed no peak in XRD pattern but a peak appeared at 2 θ of 44.8° in sample 22. This peak in sample 22 corresponds to Fe-P nano crystals. The presence of peak in sample 22 confirmed the presence of crystalline phase along with amorphous phase. The sample 21 and 22 contained P amount of 10.63 and 6.98% respectively. These results revealed that the peak corresponding to crystalline Fe-P disappeared by increasing the P content in Fe-P layers. The sample 21 exists as a homogenous amorphous Fe-P phase whereas sample 22 exists as a crystalline phase. The sample prepared at low current density (sample 21) showed amorphous structure due to higher P content in Fe-P layers.

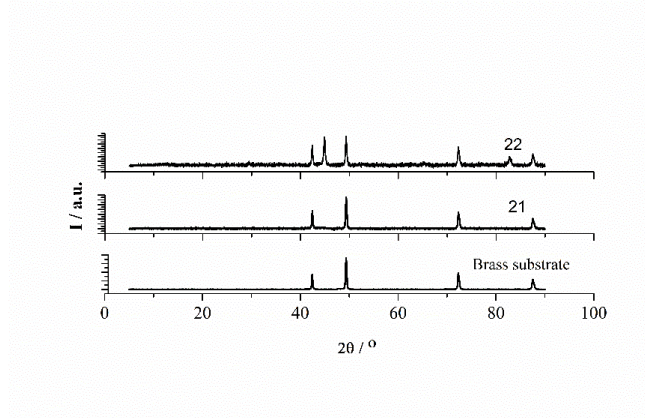


Fig. 4.38 XRD pattern of Fe-P films electrodeposited by changing current density.

4.6.2.2 Effect of additives on crystal structure of Fe-P layers

4.6.2.2.1 Effect of incorporation of silica on the structure of Fe-P matrix

The crystal structure of electrodeposited Fe-P/SiO₂ composite coatings was determined by XRD technique. Fig. 4.39 shows the XRD patterns of samples coated on Cu sheets from electrolyte bath containing 2 g/L of unloaded silica particles. The chemical composition and sample descriptions are given in Table 4.16. The diffraction peaks at 42.9°, 50.1° and 73.2° correspond to the Cu substrate. The sample 51 and 47 showed a broad peak which confirmed the amorphous nature of these samples. The sample 48 showed a small peak of Fe-P nano crystals at diffraction angle of 45°. The presence of Fe-P peak suggested that sample 48 contained Fe-P nano crystallites in amorphous Fe-P phase. These results suggested that the samples consist of amorphous phase when the P content is more than 7.65 wt% [245, 258]. The P content of sample 48 was 3.78 wt% which was less than the amount required for the formation of amorphous structure. The amount of P in sample 47 was 12 wt% which was more than the P amount required for amorphous structure formation. The incorporation of mesoporous silica particles has no effect on the structure of Fe-P matrix. These results also suggested that sample 48 prepared at higher current densities (100 mA/cm²) composed of both crystalline and amorphous phases.

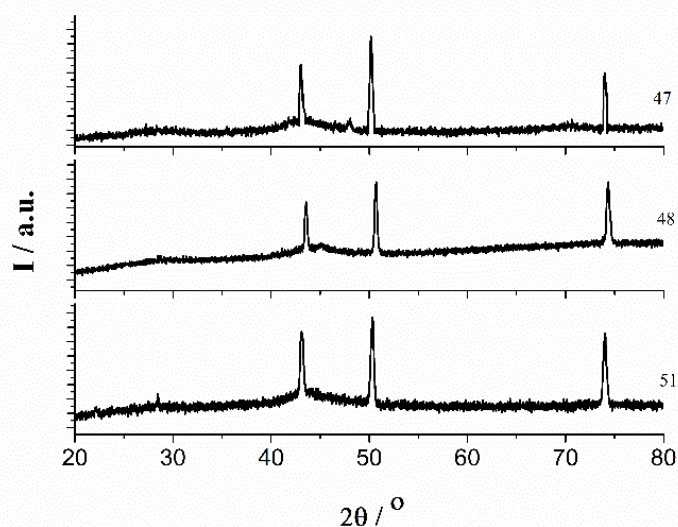


Fig. 4.39 XRD patterns of electrodeposited Fe-P/SiO₂ composite coatings. The details of the samples are given in Table 4.16.

4.6.2.2.2 Effect of PEOX on structure of Fe-P and Fe-P/SiO₂ coatings

The effect of PEOX-5K/PEOX-50K as an additive on structure of electrodeposited Fe-P layers or Fe-P/SiO₂ composite coatings was investigated. The samples were electrodeposited on brass sheets by using direct current from an electrolyte bath containing either PEOX as an additive or both PEOX and mesoporous silica particles with/without inhibitor loading. Fig. 4.40 shows the XRD patterns of Fe-P layers and Fe-P/SiO₂ composite coatings. The chemical composition and properties of samples shown in Fig. 4.40 are given in Tables 4.15, 4.17 and 4.18. The diffraction peaks at 42.4°, 49.3° and 72.2° corresponded to the brass substrate. The XRD patterns showed that the samples electrodeposited at current density of 100 mA/cm² showed Fe-P peak at diffraction angle of ~45°. This peak indicated the presence of nano crystallites of Fe-P in amorphous Fe-P matrix. The P content of all these samples was less than 7.65 wt% which is the minimum amount required for formation of amorphous structure. The broadness and size of Fe-P peaks is also affected by the grain size of crystals. These sample contained nano crystallites that resulted in crystalline structure of these samples. The sample obtained at current density of 10 mA/cm² showed a broad peak that indicated the presence amorphous structure. The P content of all these samples was above the critical value of 8 wt%. The structure of Fe-P layers and Fe-P/SiO₂ composite coatings was not affected by the presence of

additives. The increase in current density of electrodeposition process from 10-100 mA/cm² affected the structure of Fe-P layers and Fe-P/SiO₂ composites by reducing the P content in them.

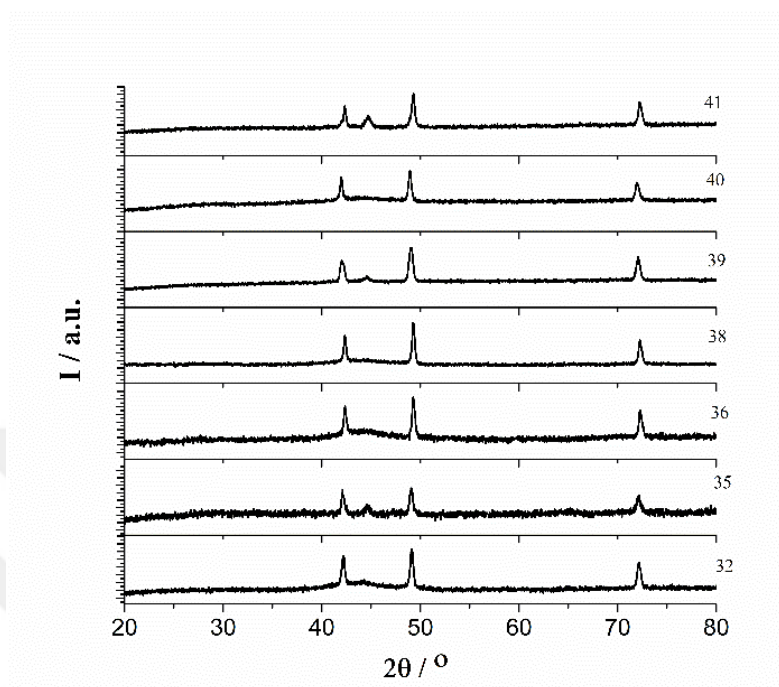


Fig. 4.40 XRD patterns of electrodeposited Fe-P layers and Fe-P/SiO₂ composite coatings. The details of sample numbers are given in Tables 4.15, 4.17 and 4.18.

4.6.2.2.3 Effect of PEG-10K on the structure of Fe-P layers

The effect of PEG-10K on the structure of Fe-P layers was investigated. For that purpose, Fe-P layers were electrodeposited on Cu sheets from an electrolyte bath containing PEG-10K as an additive. The concentration of PEG-10K was varied in the electrolyte bath. The XRD patterns of Fe-P layers deposited from solution containing PEG-10K are shown in Fig. 4.41. The properties of the samples are shown in Table 4.19. The sample 50 showed a strong Fe (100) peak at diffraction angle of ~44.8°. This sample was synthesized at 100 mA/cm² current density. The P content for sample 50 was 3.32 wt% which is less than the minimum amount required for the formation of amorphous Fe-P alloys. The sample 52 showed a broad amorphous peak and its P content is 15.68 wt%. This sample exists as amorphous structure. Sample 49 showed the small peak of Fe-P nano crystals at 45° even though the P content of this sample was 11 wt%. The small peak appeared in sample 49 could be attributed to the nano-crystallites of Fe-P. The structure of this sample showed the presence of nano-crystallites in amorphous Fe-P phase. The results reiterated that current density

of electrodeposition process affected the structure of Fe-P layers by changing the P content in them.

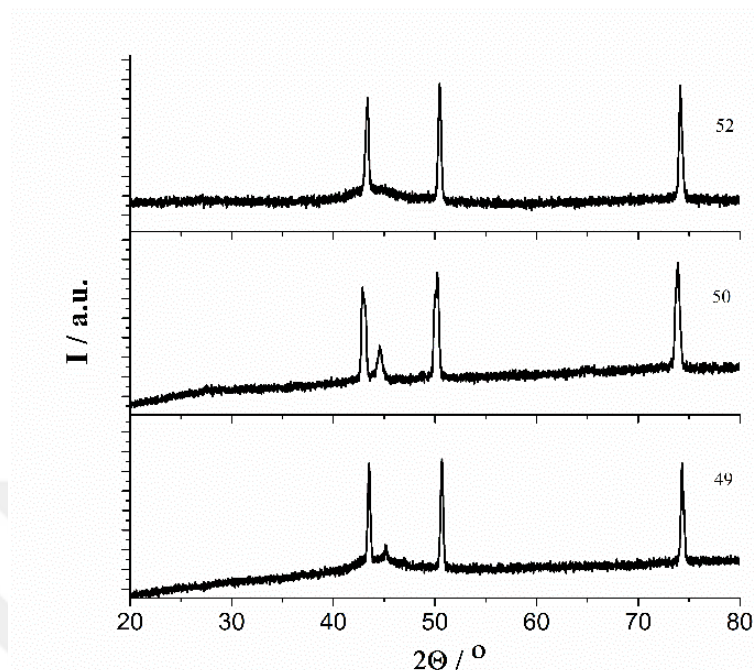


Fig. 4.41 XRD patterns of electrodeposited Fe-P layers. The details of sample numbers are given in Table 4.19.

4.6.2.2.4 Effect of incorporation of halloysite nanotubes on the structure of Fe-P matrix

The effect of halloysite nanotubes on the structure of Fe-P matrices were investigated by XRD. Both un-loaded and inhibitor loaded nanotubes were used for this purpose. The samples were electrodeposited from an electrolyte solution containing halloysite nanotubes. PEOX-5OK was used as an additive in electrolyte bath. The XRD patterns of Fe-P/halloysite nanotubes composite coated samples are shown in Fig. 4.42. The detailed descriptions of the samples are given in Table 4.20. The diffraction peaks at 42.9° , 50.1° and 73.2° correspond to the Cu substrate. The samples which were electrodeposited at current density of 10 mA/cm^2 showed a broad peak that indicated the presence amorphous structure. The P content of all the samples deposited at 10 mA/cm^2 was above the critical value of 7.65wt% (Table. 4.20). But the samples obtained at current density of 100 mA/cm^2 showed a peak at the position of Fe-P peak. This peak was attributed to the nano-crystallites of Fe-P present in amorphous Fe-P matrix. The P content of all the samples deposited at 100 mA/cm^2 was below 7.65 wt%. The structure of these samples is a mixture of amorphous

phase and a nano crystalline Fe-P. The presence of inhibitor loaded/unloaded halloysite nanotubes couldn't change the structure of Fe-P matrices. These results further confirmed that the increase in current density of electrodeposition process affected the structure of Fe-P layers by reducing the P content in them. The increase in current density resulted in enhanced hydrogen evolution reaction which decreased the P content in Fe-P matrices.

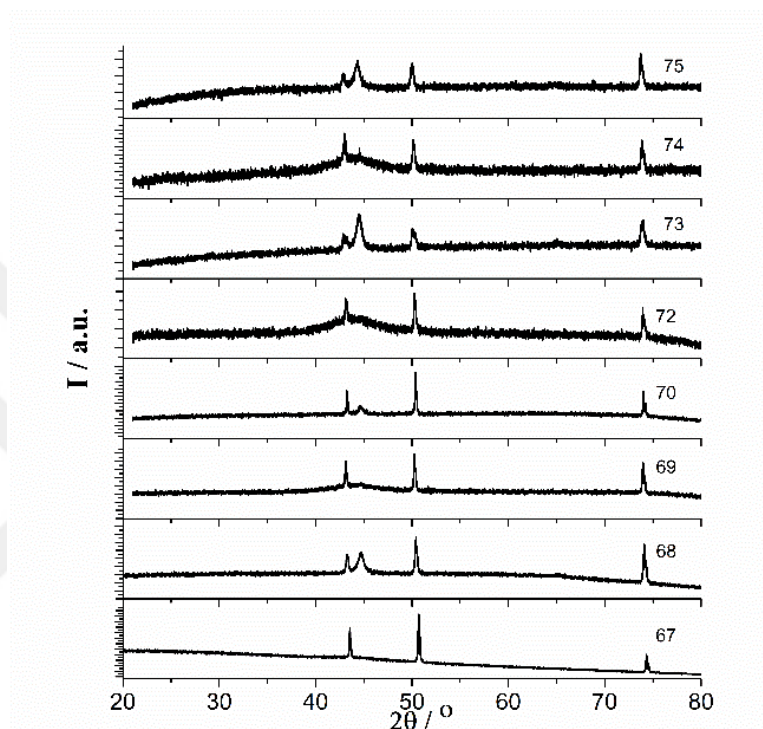


Fig. 4.42 XRD patterns of electrodeposited Fe-P/halloysite composites. The details of sample numbers are given in Table 4.20.

4.6.3 Electrochemical properties of Fe-P layers and Fe-P/silica-based fillers composites

Thin Fe-P layers and Fe-P/silica-based fillers composite films were electrodeposited on metallic substrates from sulphate solutions with/without additive. The electrochemical properties of Fe-P layers and Fe-P/silica-based fillers composites were investigated to determine the corrosion behavior of these samples. The effect of additives and corrosion inhibitors on the corrosion behavior of Fe-P layers and Fe-P/silica-based composites was investigated.

4.6.3.1 Effect of deposition current density and additives on corrosion behavior of Fe-P layers

The effect of deposition current density and additives on electrochemical properties of Fe-P layers was investigated. For that purpose, the electrodeposited Fe-P layers were examined in 0.1 M NaCl solution with and without additives. The additives used in NaCl solution were PEOX and PEG-10K. Prior to electrochemical polarization experiments, the open circuit potential of the samples was investigated. The potentiodynamic polarization curves were used to investigate the corrosion current density and corrosion potential. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were obtained by extrapolating the Tafel lines to corrosion potential. The corrosion rate in millimeter per year was obtained by using the ASTM-G59 standard method. The equation used for this calculation is shown below [231].

$$CR \text{ (mmpy)} = \frac{3.268 \times 10^{-3} \times (I_{\text{corr}} \times M \text{ of Fe})}{\text{no. of electrons} \times \text{density of Fe}}$$

The corrosion potentials, corrosion rate and corrosion current density values derived from Tafel curves are shown in Table 4.22. The corrosion current density as a function of deposition current density is shown in Fig. 4.43.

Table 4.22 Characteristic electrochemical parameters obtained for Fe-P layers.

I_{dep} (mA/cm ²)	Properties	I_{corr} (A cm ⁻²)	E_{corr} (mV)	Corrosion rate (mmpy)
10	No additive	4.8×10^{-5}	-448.06	0.56
50	No additive	1.2×10^{-4}	-597.04	1.41
100	No additive	1.4×10^{-6}	-649.46	1.58
10	0.1 g/L PEOX in NaCl solution	5.2×10^{-5}	-447.31	0.59
10	1 g/L PEOX in deposition solution	5.4×10^{-5}	-420.35	0.62
10	1 g/L PEOX in deposition solution + 1 g/L PEG in NaCl	3.5×10^{-5}	-407.36	0.41

The corrosion potential values changed from -448 mV to -649 mV by increasing the deposition current density. The corrosion current density increased by increasing the deposition current of Fe-P layers. The corrosion rate results showed that the corrosion rate is faster for the samples electrodeposited at 100 mA/cm² and slowest for the samples electrodeposited at 10 mA/cm². This could be attributed to the formation of amorphous structures of Fe-P layers at 10 mA/cm² and crystalline structure at 100 mA/cm² (Fig. 4.38). The amorphous resulted in decreasing the corrosion rate of Fe-P layers. The decrease in corrosion rate can also be attributed to the higher P content of Fe-P layers deposited at 10 mA/cm² compared to the Fe-P layers deposited at 100 mA/cm². The effect of PEOX on electrochemical properties of Fe-P layers deposited at 10 mA/cm² was investigated by adding 0.1 g/L PEOX in NaCl solution or 1 g/L in electrolyte solution. The results showed that the addition of PEOX did not have a significant effect on the corrosion current density of Fe-P layers. The inhibiting effect of PEG on the electrochemical properties of electrodeposited Fe-P layers was investigated by adding 1 g/L PEG-10K in NaCl solution. The results showed that the corrosion current density was decreased from 4.8×10^{-5} to 3.7×10^{-5} by the addition of PEG-10K in NaCl solution. This decrease in current density showed the corrosion inhibition ability of PEG-10K.

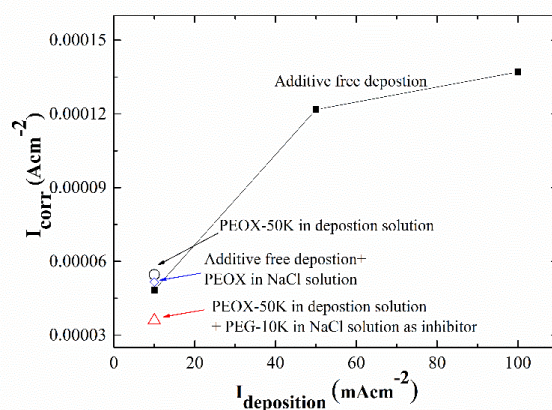


Fig. 4.43 The corrosion current density as a function of deposition current density for Fe-P layers.

The results were further investigated through linear polarization measurements by measuring the linear polarization resistance of electrodeposited samples. The polarization resistance as function of deposition current is shown in Fig. 4.44. The polarization resistance decreased by increasing the deposition current density. This

observation is in line with corrosion current density data obtained from Tafel curves (Fig. 4.43). The addition of PEOX in deposition bath or in NaCl solution enhanced the polarization resistance of the Fe-P layers. This enhancement in polarization resistance showed the corrosion inhibition ability of PEOX. The polarization resistance of Fe-P layers deposited by using 1 g/L PEOX in electrolyte bath and then by using 1 g/L PEG in NaCl solution increased from $258 \Omega \text{ cm}^2$ to $505 \Omega \text{ cm}^2$. This increase in polarization resistance showed the inhibition ability of PEG and PEOX. The electrochemical properties showed that corrosion resistance ability of Fe-P layers decreased by increasing the deposition current density. The enhancement in polarization resistance and decrease in corrosion current density values showed the corrosion inhibition ability of PEG and PEOX.

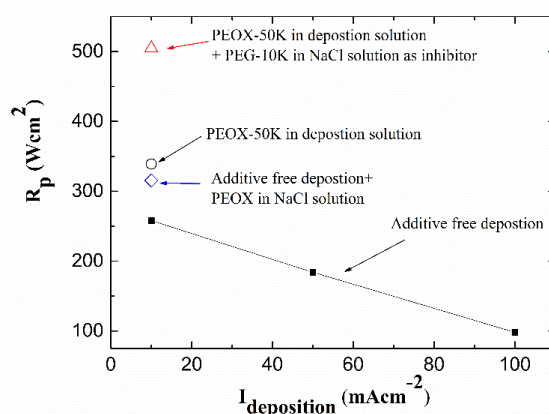


Fig. 4.44 Polarization resistance as a function of deposition current density for Fe-P layers.

4.6.3.2 Effect of PEG on the corrosion behavior of Fe-P layers

The effect of PEG-10K on the electrochemical properties of Fe-P layers was investigated. Fe-P layers were electrodeposited from an electrolyte bath containing PEG-10K as an additive at a current density of 10 mA/cm^2 . The concentration of PEG-10K was varied in the range of 1-30 wt% in the electrolyte bath. The electrodeposited Fe-P were examined in 0.1 M NaCl solution. Prior to electrochemical polarization experiments, the open circuit potential of the samples was investigated. Fig. 4.45 shows the open circuit potential of all samples as function of time. The open circuit potentials for all these samples were in the range of -0.37 to -0.60 V. The equilibrium potential values were reached within 150-200 s of immersion time in 0.1 M NaCl solution. The open circuit potentials of

electrodeposited samples obtained from an electrolyte bath containing higher concentrations of PEG-10K were shifted in less noble directions.

The potentiodynamic polarization curves were used to investigate the corrosion current density and corrosion potential. The polarization curves for electrodeposited Fe-P layers coated were obtained by dipping them in 0.1 M NaCl solution. The Tafel plots are shown in Fig. 4.46 The parameters calculated from Tafel curves are shown in Table 4.23 These parameters included corrosion potential (E_{corr}) and corrosion current density (I_{corr}) and corrosion rate (mmpy).

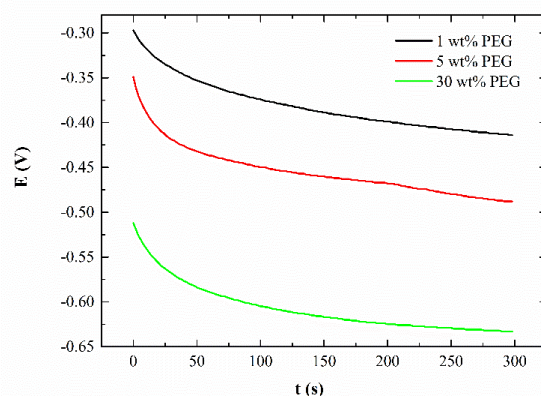


Fig. 4.45 Open circuit potential of Fe-P layers electrodeposited from solution containing PEG-10K as an additive.

The corrosion potential changed from -452 mV to -665 mV by increasing the concentration of PEG-10K in dipping solution. This shift in corrosion potential values towards more negative potentials could be attributed to the decrease in amount of P content in Fe-P layers (Table 4.19). The anodic curves of all these samples showed that the dissolution kinetics is similar for all the samples. The main dissolution mechanism is the oxidation of Fe to Fe^{2+} . The cathodic curves were affected by the reduction of oxygen especially in case of electrodeposited sample obtained from the solution containing 1 wt% PEG-10K in deposition solution. The corrosion current density results showed that the lowest corrosion current density was obtained for the sample obtained from solution containing 5 wt% PEG-10K in deposition solution. The corrosion current density of samples obtained from solution containing 1 wt% PEG is comparable with samples obtained from 5 wt% PEG containing solution. The corrosion rate results showed that the corrosion rate is faster for the samples electrodeposited from the solution bath containing 30 wt% of

PEG-10K and slowest for the samples electrodeposited from the solution bath containing 5 wt% of PEG-10K.

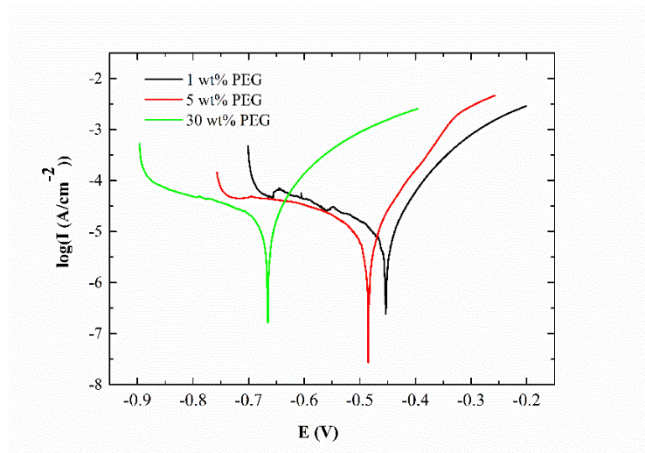


Fig. 4.46 Tafel curves for electrodeposited Fe-P layers (obtained from a solution containing PEG-10K as an additive) acquired by dipping them in 0.1 M NaCl at room temperature.

Table 4.23 Characteristic electrochemical parameters obtained for Fe-P layers.

Sample ID	Properties	LP slope	R _p (Ω cm ²)	I _{corr} (A cm ⁻²)	E _{corr} (mV)	Corrosion rate (mm/year)
52	1 wt% PEG-10K in deposition bath	1.61*10 ⁻³	621.11801	1.237*10 ⁻⁵	-452.15	0.14
49	5 wt% PEG-10K in deposition bath	6.78*10 ⁻⁴	1474.92625	1.026*10 ⁻⁵	-483.63	0.12
42	30 wt% PEG-10K in deposition bath	2.04*10 ⁻³	490.19608	1.825*10 ⁻⁵	-665.08	0.21

These results were further investigated through linear polarization measurements by determining the polarization resistance of these samples. The linear polarization

measurements of these samples were performed by moving ± 15 mV from the open circuit potential with a scan rate of 0.2 mV/s in a solution of 0.1 M NaCl. The linear polarization plots are shown in Fig. 4.47. The slope of these current versus potential curves was used to determine the polarization resistance (R_p). The slope and polarization resistance of these samples are shown in Table 4.23. The results suggested that the higher polarization resistance is showed by the Fe-P sample obtained from the bath solution containing 5 wt% of PEG-10K as an additive. These results are consistent with the data obtained from Tafel curves. These results are consistent with surface morphology (Fig. 4.35), crystallinity (Fig. 4.41) and chemical composition analysis (Table 4.19) results. The samples deposited showed P content of 11 % in them and they had amorphous structure. The samples also had smooth morphology compared to the globular morphology for samples deposited from solution containing 1 wt% and 30 wt% PEG. The amorphous structure and more P content resulted in enhanced corrosion resistance of samples obtained at 5 wt% PEG containing deposition solution.

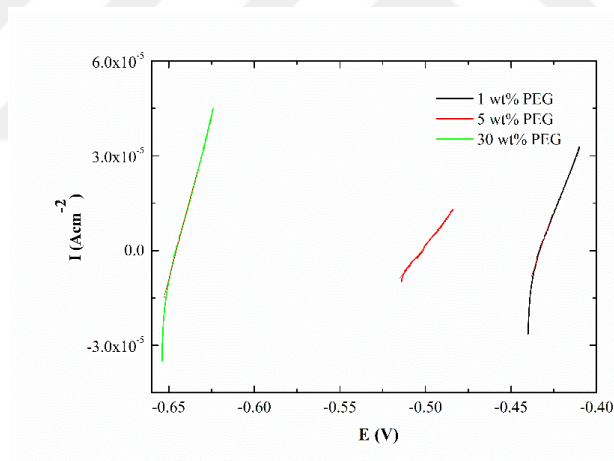


Fig. 4.47 Linear polarization curves for Fe-P layers (obtained from a solution containing PEG-10K as an additive) acquired by dipping them in 0.1 M NaCl at room temperature.

4.6.3.3 Effect of current density on the corrosion behavior of Fe-P/silica composites

The Fe-P/silica composites were electrodeposited from an electrolyte solution containing 2 g/L mesoporous silica particles. These electrodepositions were carried out by changing the current density between 10-100 mA/cm². The effect of current density on the corrosion behavior of these samples was investigated in 0.1 M NaCl solutions. Prior to polarization measurements, the open circuit potential of the

samples was investigated. The open circuit potential measurements are shown in Fig. 4.48. The open circuit potentials for all these samples were in the range of -0.38 to -0.63 V. The equilibrium potential values were reached within 150-200 s of immersion time in 0.1 M NaCl solution. The open circuit potentials of electrodeposited Fe-P/silica composite samples were shifted in more noble directions by increasing the current density of the deposition process.

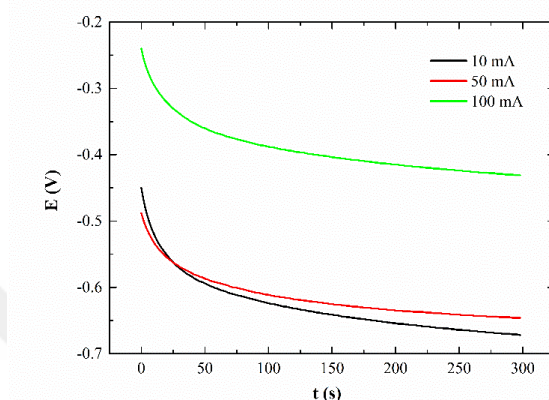


Fig. 4.48 Open circuit potential of Fe-P/silica composites.

The potentiodynamic polarization curves were used to investigate the corrosion current density and corrosion potential. The polarization curves for electrodeposited Fe-P/silica composites were obtained by dipping them in 0.1 M NaCl solution. The Tafel plots are shown in Fig. 4.49. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) and corrosion rate (mm/year) calculated from Tafel plots are shown in Table 4.24. The corrosion potential changed from -529 mV to -742 mV by decreasing the deposition current density. This shift in corrosion potential values towards more negative potentials could be attributed to the decrease in amount of Si content in Fe-P layers (Table 4.16). The anodic curves of all these samples showed that the dissolution kinetics is similar for all the samples. The main dissolution mechanism is the oxidation of Fe to Fe^{2+} . The cathodic curves were affected by the reduction of oxygen especially in case of electrodeposited sample obtained at the current density of 100 mA/cm². The lowest corrosion rate was determined for the Fe-P composites electrodeposited at 100 mA/cm². Even the structure of electrodeposited Fe-P/silica composite films obtained at 100 mA/cm² is a mixture of crystalline and amorphous phases (section 4.6.2.2.1), the presence of silica in Fe-P matrix resulted in higher corrosion resistance of these composites. These results suggested that the

increase in silica content in Fe-P matrix resulted in enhanced corrosion resistance of Fe-P/silica composites. Silica particles enhanced the corrosion resistance of Fe-P/silica composites by acting as an inert physical barrier to the initiation and development of corrosion defects either by modifying the structure of Fe-P layers or by filling the cracks and gaps in Fe-P layers. In addition to this silica particles may have formed microcells by acting as cathode due to more positive potential than Fe-P matrix which acted as anode and prevented the localized corrosion of Fe-P/silica composites [260-262]. The corrosion rate of Fe-P layers was decreased by incorporation of silica particles as compared to the Fe-P layers without any silica particles in them (Table 4.22). The corrosion rate was decreased from 1.58 mm/year for Fe-P layers without silica to 0.04 mm/year for Fe-P/silica composites deposited at 100 mA/cm².

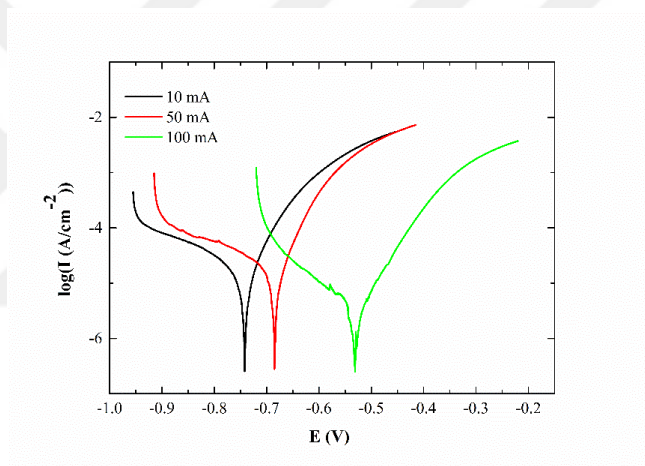


Fig. 4.49 Tafel curves for electrodeposited Fe-P/silica (obtained by changing current density of deposition process) acquired by dipping them in 0.1 M NaCl at room temperature.

The electrochemical behavior was further investigated through linear polarization measurements by determining the polarization resistance of these samples. The linear polarization plots are shown in Fig. 4.50. The slope of these current versus potential curves was used to determine the polarization resistance (R_p). The slope and polarization resistance of these samples are shown in Table 4.24. The results suggested that the higher polarization resistance is showed by the Fe-P/silica composites obtained at current density of 100 mA/cm². These results are consistent with the data obtained from Tafel curves. These results suggested that increase in silica content resulted in higher polarization resistance (Table 4.16). The samples containing less amount of silica in them showed lower polarization resistance. The

presence of silica particles enhanced the corrosion resistance of the Fe-P/silica composites compared to Fe-P layers.

Table 4.24 Characteristic electrochemical parameters obtained for Fe-P/silica composites.

Sample ID	Properties (Deposition current)	LP slope	R _p ($\Omega \text{ cm}^2$)	I _{corr} (A cm^{-2})	E _{corr} (mV)	Corrosion rate (mm/year)
47	10 A cm^{-2}	2.69×10^{-3}	371.74	1.746×10^{-5}	-742.42	0.20
51	50 A cm^{-2}	2.85×10^{-3}	350.87	1.991×10^{-5}	-683.78	0.23
48	100 A cm^{-2}	2.32×10^{-3}	431.03	3.519×10^{-6}	-529.70	0.04

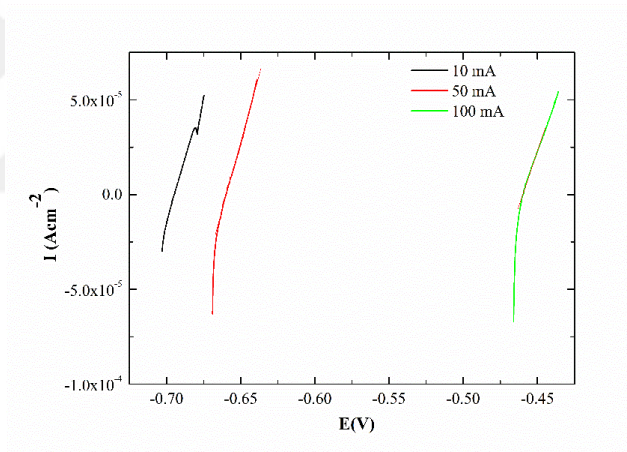


Fig. 4.50 Linear polarization curves for Fe-P layers (obtained by changing current density of deposition process) acquired by dipping them in 0.1 M NaCl at room temperature.

4.6.3.4 Effect of halloysite incorporation on corrosion resistance of Fe-P/halloysite composites

In order to investigate the effect of halloysite nanotubes on the corrosion resistance, Fe-P/halloysite composites were electrodeposited from an electrolyte bath containing halloysite nanotubes at current density of 10 mA cm^{-2} . Both un-loaded and inhibitor loaded halloysite nanotubes were used for incorporation in Fe-P alloy matrix. Chitosan and PEG-10K were used as corrosion inhibitor. The electrochemical properties were investigated by dipping these composite coated samples in 0.1 M

NaCl. Prior to polarization measurements, the open circuit potential of the samples was investigated. The open circuit potential measurements are shown in Fig. 4.51. The open circuit potentials for all these samples were in the range of -0.23 to -0.51 V. The equilibrium potential values were reached within 50-75 s of immersion time in 0.1 M NaCl solution. The open circuit potentials of electrodeposited Fe-P/halloysite composite samples were shifted in less noble directions by filling the halloysite nanotubes with corrosion inhibitors.

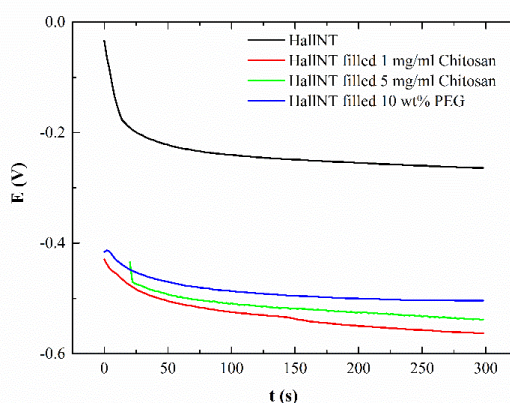


Fig. 4.51 Open circuit potentials of Fe-P/halloysite composite samples. These composites contain either unloaded or inhibitor loaded halloysite nanotubes (HallNT).

The potentiodynamic polarization curves were used to investigate the corrosion current density and corrosion potential. The polarization curves for electrodeposited Fe-P/halloysite composites were obtained by dipping them in 0.1 M NaCl solution, and shown in Fig. 4.52. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) and corrosion rate (mm/year) calculated from Tafel plots are shown in Table 4.25. The corrosion potential changed from -295 mV to -579 mV by incorporating the inhibitor loaded halloysite nanotubes in Fe-P matrices. This shift in corrosion potential values towards more negative potentials could be attributed to the decrease in amount of halloysite content in Fe-P matrices. The addition of inhibitor loaded halloysite may have resulted in agglomerates and less uniform distribution of halloysite nanotubes as compared to unloaded halloysite nanotubes (Fig. 4.36). The anodic and cathodic curves remained almost same for Fe-P/Halloysite composites containing inhibitor loaded halloysite nanotubes. The lowest corrosion rate is shown by the Fe-P/ halloysite composites containing unloaded halloysite nanotubes. This could be attributed to the homogeneous distribution of halloysite nanotubes in Fe-P

layers (Fig. 4.36). Halloysite nanotubes may have protected the corrosion of Fe-P matrices by two different mechanisms. First, halloysite nanotubes acted as physical barrier to the development of corrosion process by filling the gaps or cracks in Fe-P layers or by modifying the structure of Fe-P layers. Secondly, the dispersed halloysite nanotubes may have formed microcells by acting as cathode due to more positive potential than Fe-P matrices. These microcells prevented the local corrosion of Fe-P matrices [260-262]. In case of inhibitor loaded halloysite nanotubes, the Fe-P layers containing PEG filled halloysite nanotubes showed lower corrosion rate than chitosan loaded halloysite containing Fe-P matrices. The difference in performance of PEG and chitosan as inhibitors can be attributed to the lower loading concentrations of chitosan into halloysite nanotubes, because of the solubility limitations of chitosan.

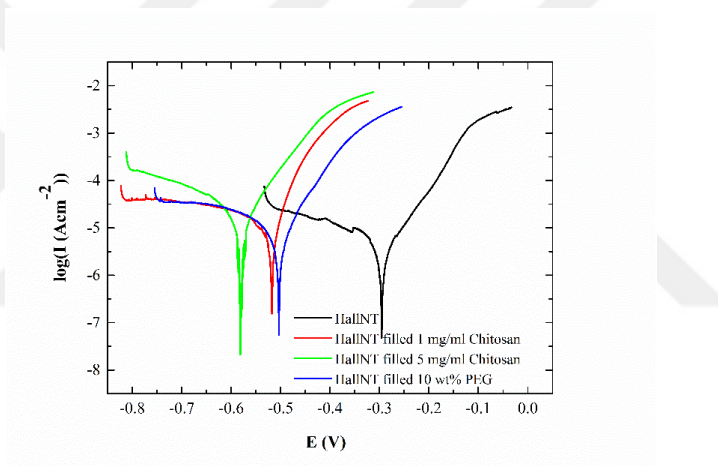


Fig. 4.52 Tafel curves for electrodeposited Fe-P/halloysite composites acquired by dipping them in 0.1 M NaCl at room temperature. These composites contain either unloaded or inhibitor loaded halloysite nanotubes (HallNT).

The electrochemical behavior of Fe-P/halloysite composites was further investigated through linear polarization measurements by determining the polarization resistance of these samples. The linear polarization measurements of these samples were performed by moving ± 15 mV from the open circuit potential with a scan rate of 0.2 mV/s in a solution of 0.1 M NaCl. The linear polarization plots are shown in Fig. 4.53. The slope of these current versus potential curves was used to determine the polarization resistance (R_p). The slope and polarization resistance of these samples are shown in Table 4.25. The results suggested that the higher polarization resistance is showed by the Fe-P/halloysite composites containing unloaded halloysite

nanotubes. The higher amount or better dispersion of unloaded halloysite in Fe-P matrices may have resulted in better corrosion resistance than inhibitor loaded halloysite nanotubes. In case of inhibitor loaded halloysite nanotubes, the Fe-P/halloysite composites containing PEG loaded halloysite nanotubes showed higher polarization resistance than chitosan loaded halloysite containing composites. These results are consistent with the data obtained from Tafel curves (Table. 4.25). The corrosion rate and corrosion resistance results suggested that Fe-P/halloysite composites showed enhanced corrosion resistance than Fe-P layers (Table 4.23). The corrosion rate was decreased from 0.56 mm/year for Fe-P layers without silica to 0.04 mm/year for Fe-P/halloysite composites deposited at 10 mA/cm².

Table 4.25 Characteristic electrochemical parameters obtained for Fe-P/halloysite composites.

Sample ID	Properties	LP slope	R _p (Ω cm ²)	I _{corr} (A cm ⁻²)	E _{corr} (mV)	Corrosion rate (mm/year)
67	HallNT	7.4*10 ⁻⁵	13513.51	3.41*10 ⁻⁶	-295.46	0.04
69	HallNT-filled 1 mg/mL Chitosan	7.35*10 ⁻⁴	1360.54	1.435*10 ⁻⁵	-517.61	0.16
74	HallNT-filled 5 mg/mL Chitosan	2.281*10 ⁻³	438.36	1.648*10 ⁻⁵	-579.20	0.19
72	HallNT-filled 10 wt% PEG 10k	5.75*10 ⁻⁴	1739.13	5.59*10 ⁻⁶	-503.25	0.06

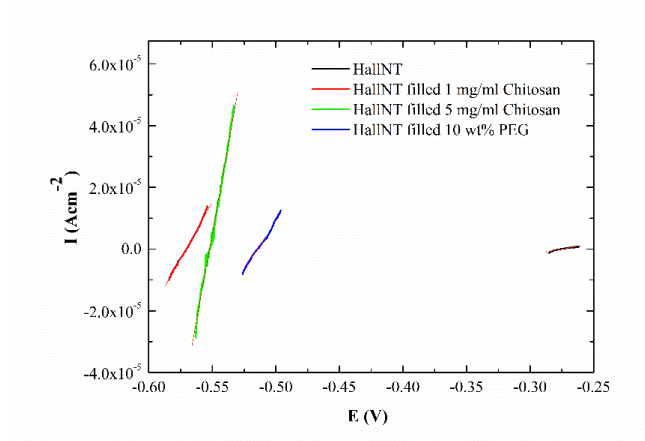


Fig. 4.53 Linear polarization curves for Fe-P/halloysite composites acquired by dipping them in 0.1 M NaCl at room temperature.

4.7 Conclusions

In first part of chapter, inhibitor loaded silica-based fillers/SBS composites were synthesized for corrosion protection of copper. The silica-based fillers were successfully loaded with PEG and chitosan. The inhibitor uptake capacity of silica-based fillers was investigated by TGA. The composite dispersion was prepared by dispersing 15% by mass inhibitor loaded silica-based fillers in SBS stock solution (20mg/mL). The copper samples were successfully dip coated with composite dispersions. SEM analysis showed the successful incorporation of inhibitor loaded silica-based fillers in SBS matrix. These fillers were observed as individual particles as well as agglomerated particles on the top surface of the copper substrates in all coated samples. The SEM images also showed that a significant amount of inhibitor loaded particles is buried in SBS matrix. The electrochemical properties of bare copper and composite coated copper samples were investigated in 0.5 M NaCl solution. The surface morphology of bare Cu and composite coated Cu was investigated by optical microscope. The composite coated samples showed less pitting corrosion than bare Cu. The electrochemical results clearly showed that SBS coatings prevented the active dissolution of copper in corrosive environments. The introduction of inhibitor loaded silica-based fillers in SBS matrix further decreased the dissolution of copper. The Tafel curves were used to investigate corrosion current, corrosion potential and corrosion inhibition efficiency of bare copper and composite coated copper samples. The Tafel results clearly showed that the corrosion current density of all composite coated samples was significantly less than bare

copper samples. The Tafel plots showed that both chitosan and PEG acted as anodic corrosion inhibitors. The maximum corrosion inhibition efficiency of 92% was achieved for composite coated samples containing PEG filled DE particles. According to Tafel curves, both PEG and chitosan minimized the active dissolution of copper samples, but PEG filled silica samples performed better due to their homogeneous distribution in composite coatings. The cyclic voltammograms were used to further investigate the electrochemical properties of copper and composite coated copper samples. These cyclic voltammograms were used to determine passive current density, passive potential, repassivation potential and charge during due to active passive dissolution of copper. The cyclic voltammograms showed that the passive current density of composite coated samples is significantly lower than that of bare copper samples. The lowest passive current density of 1.6 mA/cm^2 was obtained for samples containing chitosan filled halloysite nanotubes. The electrochemical results clearly showed that the composite coated copper samples containing PEG filled DE/ chitosan loaded halloysite nanotubes showed better anti-corrosive ability than their counterparts. The anti-corrosion ability of PEG filled DE and halloysite filled chitosan containing composites was further investigated by changing their concentration to 3, 6 and 21% by mass in dipping dispersions. The electrochemical results showed that passive current density and corrosion current density decreased by increasing the concentration of both PEG filled DE and chitosan filled halloysite in composite coatings. The extent of pitting corrosion was decreased by increasing the concentration of particles in composite coated samples. The corrosion inhibition ability of PEG and chitosan was compared with AETDA, which is a commercially used copper corrosion inhibitor. The electrochemical results showed that PEG and chitosan have comparable inhibition efficiency with AETDA. These results suggested the probability to use green inhibitors for corrosion protection of copper. These composite coated copper samples can maintain their anti-corrosive ability for longer durations due to the presence of inhibitor filled particles inside the SBS matrix. Scratches and wear allow the release of inhibitors from inhibitor loaded particles buried in SBS upon exposure to corrosive environment.

In second part, Fe-P layers and Fe-P/silica-based filler composites were successfully electrodeposited by direct current electrochemical method from aqueous FeSO_4 and NaH_2PO_4 bath containing various additives. The effect of current density on the

composition and structure of Fe-P layers was investigated. The P content of the Fe-P layers decreased from 25 wt% to 8 wt% by increasing the current density from 10-100 mA/cm². The increase in current density and decrease in P content changed the surface morphology from smooth to globules and phase structure from amorphous to mixture of crystalline and amorphous. PEOX-5K, PEOX-50K and PEG-10K were used as additives to reduce the surface tension of the electrolyte bath solution. The effect of PEOX-5K, PEOX-50K and PEG-10K on the structure and composition of Fe-P layers was investigated. The addition of PEOX in electrolyte bath at lower concentration of 0.1 g/L did not affect the composition of Fe-P layers. The higher concentration of PEOX-50K (1 g/L) enhanced the P content of the coatings. Similarly, the increase in concentration of PEG-10K resulted in higher P content in Fe-P layers. This increased P content was due to the slow migration of Fe²⁺ ions towards the cathodic surfaces. The enhanced P content resulted in smoother morphology of Fe-P films. The Fe-P layers containing P content higher than 7.45 wt% showed amorphous structure. Mesoporous silica particles were successfully incorporated in Fe-P layers. The amount of silica particles in Fe-P layers was enhanced by the addition of PEOX in electrolyte bath. This enhancement in silica incorporation was attributed to slightly positive zeta potential values of silica particles in presence of PEOX in solution. The incorporation of mesoporous silica particles in Fe-P layers was demonstrated by SEM, EDX and XRF analysis. PEOX-5K was used as corrosion inhibitor for mesoporous silica particles. The mesoporous silica particles loaded with PEOX-5K were also incorporated in Fe-P layers. The Fe-P/silica composites electrodeposited at 10 mA/cm² showed amorphous structure and the samples electrodeposited at 100 mA/cm² showed mixture of amorphous and crystalline structure. Halloysite nanotubes were successfully incorporated in Fe-P layers from an electrolyte containing 1 g/L PEOX-50k as an additive. Chitosan and PEG-10K were used as corrosion inhibitors for loading halloysite nanotubes. PEG-10K and chitosan loaded halloysite nanotubes were successfully incorporated in Fe-P layers. The incorporation of halloysite nanotubes in Fe-P layers was demonstrated by SEM, EDX and XRF analysis. The Fe-P composites containing P content more than 7.65 wt% showed amorphous structure. The electrochemical properties of Fe-P layers and Fe-P/silica-based fillers composites were investigated in 0.1 M NaCl solutions. The Tafel curves were used to investigate corrosion current density, corrosion rate and corrosion potential. The polarization resistance was measured

from the slope of linear polarization measurements. The incorporation of silica and halloysite improved the corrosion resistance of Fe-P layers. The corrosion rate of 0.04 mm/year was recorded for Fe-P/silica and Fe-P/halloysite composites as compared to 0.56 mm/year for Fe-P layers. These results were consistent with the polarization resistance results. The addition of inhibitor loaded halloysite resulted in improved corrosion resistance of Fe-P composites. The composites containing PEG loaded halloysite nanotubes showed better corrosion resistance ability than chitosan loaded halloysite containing composites. These composite coatings have the great advantage of keeping the inhibitor in the micro- and nano- containers and releasing it locally in damaged or scratched regions. The preparation of Fe-P composites loaded with inhibitor filled silica-based fillers is expected to attract attention in future due to their better corrosion protection abilities as compared to Fe-P layers.

Chapter 5: Conclusions

The demand for novel materials having new and different properties and improved performances has been growing with technological advances. Functional composite materials consisting of nano- and micro- filler particles are suitable candidates to meet these emerging needs. The challenge is to bring together various inorganic and organic, thermodynamically incompatible components in a stable end product together with the desired function. Functional composites are being used in numerous applications ranging from aerospace to electronics, but the potential for new applications still expand. In this thesis work, several novel composites having anti-icing or anti-corrosion functions have been designed and realized. In all composites, silica based porous nano- and/or micro- filler particles were used due to their higher specific surface area, chemical stability, biocompatibility, easy surface functionalization and easy-to-tailor morphologies. Porous silica particles filled with anti-icing agent or corrosion inhibitor were incorporated either in SBS matrix or in Fe-P electrodeposited films to obtain composite coatings with unique anti-icing or anti-corrosion properties based on the release of the agents filled into porous silica particles in the matrix.

Mesoporous silica assemblies having different pore structures and morphologies were synthesized by sol-gel method using different types of non-ionic surfactants (polyethylene oxide-based block copolymers) and tetra ethyl orthosilicate (TEOS) precursor in highly acidic region and at room temperature. The synthesis of micro/mesoporous silica having high specific surface area of 200-600 m²/g at room temperature from Pluronic F127/TEOS/HCl acid system was demonstrated without any heat treatment or aging of the samples at elevated temperature. The change of the mesoporous silica assembly morphology from spherical particles to monoliths were successfully controlled by surfactant/TEOS ratio and acid catalyzer concentrations. The mesoporous silica spherical particles were formed due to fast aggregation of 20-30 nm diameter particles at higher hydrolysis and condensation rates. The mesoporous monoliths were obtained at low acid concentration and slow evaporation of solvents. The spherical silica particles were composed of primary particles. Primary particles had cylindrical mesopores aligned in the same direction. However, the alignment direction of each primary particle was randomly distributed within the

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spherical particle. The size of the mesoporous silica particles was controlled by acid catalyzer concentrations. The monolith samples synthesized at pH4 showed short range ordered structure. The loading and release kinetics of Rhodamine 6G in mesoporous silica particles confirmed the potential of these mesoporous silica particles as possible absorbers of water pollutants and nanocarriers for various chemical compounds for applications including drug delivery, anti-icing and anti-corrosive systems.

For anti-icing applications, anti-icing agent filled silica-based fillers/SBS composites were prepared. Diatomaceous earth (DE) and mesoporous silica were used as anti-icing agent carrier in SBS matrix. The anti-icing agents were post filled into DE/silica pores by a novel method in which SBS matrix was swollen to allow the diffusion of anti-icing agent in DE/silica pores. The filling of the pores was driven by the favorable interaction between the hydrophilic agents and hydrophilic silica-based particles. SEM and EDX analysis confirmed the presence of anti-icing agents in the pores of DE particles of composites. The amount of anti-icing agents retained in the composites was optimized by increasing the concentration of anti-icing agent in binary solvent mixture. The anti-icing ability of the composite surfaces was characterized by the freezing delay of water droplets. The freezing time of water droplets increased with the amount of anti-icing agents retained in composites. At -14 °C, the freezing time of water droplets on the silica/SBS and DE/SBS composites filled in 50 volume % PEG solution was 140 s and 120 s respectively compared to 35 s on unfilled composites. The better anti-icing ability of silica/SBS composites as compared to DE/SBS composites was attributed to their smaller size, higher specific surface area and more loading and release of anti-icing agent from surface exposed silica particles. The release of anti-icing agent from the inner pores of DE/silica was enabled by increasing the water/composite interfacial area. The release of anti-icing agents from the inner pores of silica-based fillers showed that the developed composites can retain their anti-icing ability for longer periods in the presence of scratches and wear.

For the corrosion protection of Cu, a comparative study was done on silica based nanocontainers filled with environment friendly corrosion inhibitors and embedded in SBS polymer matrix. The silica-based nanocontainers used included mesoporous silica nano/micro particles, DE and halloysite nanotubes. PEG and Chitosan were use

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as corrosion inhibitors. The inhibitor filled nanocontainers were dispersed in SBS solution and applied to Cu surface by a simple dip coating method. The anti-corrosion properties of the coatings were electrochemically measured in 0.5 M NaCl solution. SBS coating itself acted as passive barrier by protecting the metal from dissolution while the addition of inhibitor loaded nano- and micro- particles in SBS matrix enhanced the protective ability of these coatings. The Tafel plots and cyclic voltammograms clearly showed that the corrosion current density and passive current density of composite coated copper samples were significantly lower than bare copper samples. The effect of the concentration of inhibitor loaded fillers in composite coatings on the electrochemical properties of composite coated samples was investigated. The electrochemical results showed that passive current density and corrosion current density decreased by increasing the concentration of inhibitor loaded silica-based containers in composite coatings. Similarly, the extent of pitting corrosion was decreased by increasing the concentration of inhibitor filled particles in composite coated samples. The corrosion inhibition ability of PEG and chitosan was compared with AETDA, which is a commercially used copper corrosion inhibitor. The electrochemical results showed that PEG and chitosan have comparable inhibition efficiency with AETDA. These results suggested the probability to use green inhibitors for corrosion protection of copper. The Cu metal was protected by possible physisorption and chemisorption of inhibitors on the metal surface. The composite coated copper samples maintained their anti-corrosive ability for 96 h in 0.5 M NaCl solution due to the presence of inhibitor filled particles inside the SBS matrix.

Fe-P layers and Fe-P/silica-based filler composites were successfully electrodeposited by direct current electrochemical method from aqueous FeSO_4 and NaH_2PO_4 bath containing various additives. The most important factors that affected the behavior of Fe-P layers were morphology, structure (amorphous vs crystalline), composition and additives used in deposition bath. Mesoporous silica particles and halloysite nanotubes were separately incorporated in Fe-P layers. The amount of silica particles and halloysite nanotubes in Fe-P layers was enhanced by the addition of PEOX in electrolyte bath. This enhancement in silica and halloysite incorporation was attributed to slightly positive zeta potential values of silica particles in presence of PEOX in solution. The corrosion resistance of Fe-P layers improved by the

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addition of silica particles and halloysite nanotubes in Fe-P matrix. The addition of halloysite and silica separately in Fe-P layers decreased the corrosion rate of Fe-P layers from 0.56 mm/year to 0.04 mm/year. This improvement was attributed to the ability of silica/halloysite to form microcells by acting as cathode due to more positive potential than Fe-P matrices. These microcells prevented the local corrosion of Fe-P matrices. The corrosion inhibitor filled halloysite nanotubes were also incorporated in Fe-P layers and they showed almost similar corrosion rate of Fe-P layers as shown by Fe-P layers doped with unloaded halloysite nanotubes. The results showed that the presence of nanoparticles successfully minimized the corrosion of metallic matrix. This model system can be used in future to improve the corrosion protection of other metals as well.

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