

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**IMPROVEMENT OF MECHANICAL
CHARACTERISTICS OF THE THERMOSET
EPOXY POLYMER SYSTEMS BY USING
NANOSTRUCTURES**

by
Zafer AZEM

October, 2022
İZMİR

IMPROVEMENT OF MECHANICAL CHARACTERISTICS OF THE THERMOSET EPOXY POLYMER SYSTEMS BY USING NANOSTRUCTURES

**A Thesis Submitted to the
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**by
Zafer AZEM**

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**IMPROVEMENT OF MECHANICAL CHARACTERISTICS OF THE THERMOSET EPOXY POLYMER SYSTEMS BY USING NANOSTRUCTURES**” completed by **ZAFER AZEM** under supervision of **PROF. DR. UĞUR MALAYOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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IMPROVEMENT OF MECHANICAL CHARACTERISTICS OF THE THERMOSET EPOXY POLYMER SYSTEMS BY USING NANOSTRUCTURES

ABSTRACT

Epoxy thermoset polymer composites are extensively utilized in a variety of industries, including the automotive, aviation, space, marine and electrical-electronic industries due to their outstanding mechanical, chemical, thermal, and electrical properties. However, since the neat epoxy intrinsically has a brittle structure, it should be incorporated with various particles to improve the fracture resistance and toughness.

In this study, silica particles varying with different particle sizes and filler contents were used to prepare diglycidyl ether of bisphenol-A (DGEBA) epoxy composite cured with methyl tetra hydro phthalic anhydride (MTHPA) to examine the impact of filler content and particle size on the composite's fracture behaviour. In accordance with ASTM-D5045 standard, linear elastic fracture mechanics were used to describe the fracture behaviour of composite materials. It was concluded that the fracture toughness increases with increasing particle size at the micro dimension but decreases inversely when shifted towards the nano dimension. The fracture surfaces were examined by SEM imaging technique, and toughening mechanisms were defined depending on the silica particle size and content.

Before the fracture mechanics test studies, a time temperature transformation (TTT) diagram was constructed for the existing epoxy composite system, which can be used as a tool for the optimization of the process parameters.

Keywords: Epoxy composites, silica particles, fracture toughness, linear elastic fracture mechanics, time temperature transformation (TTT)

EPOKSI TERMOSET POLİMER SİSTEMLERİN MEKANİK KARAKTERİSTİKLERİNİN NANOYAPILAR KULLANILARAK GELİŞTİRİLMESİ

ÖZ

Epoksi termoset polimer kompozitler üstün mekanik, kimyasal, termal ve elektriksel özelliklerinden dolayı otomotiv, havacılık, uzay, denizcilik ve elektrik-elektronik endüstrileri gibi birçok farklı alanda yaygın olarak kullanılmaktadır. Ancak, saf epoksi, özünde kırılğan bir yapıya sahip olduğundan, tokluğunu ve kırılma direncini arttırmak için çeşitli partiküllerle karıştırılması gerekir.

Bu çalışmada, partikül boyu ve miktarının kompozitin kırılma tokluğuna etkisini incelemek amacıyla, metil tetra hidroftalik anhidrit (MTHPA) ile kürlenmiş diglisidil eter bisfenol-A (DGEBA) epoksi kompozitini hazırlamak için değişen partikül boyutları ve miktarlarında silika partikülleri kullanıldı. Kompozitlerin kırılma davranışı, ASTM-D5045 standardına göre lineer elastik kırılma mekaniği ile karakterize edildi. Mikro boyutta, partikül boyutu arttıkça kırılma tokluğunun arttığı, ancak nano boyuta doğru kayıldığında ters olarak azaldığı sonucuna varıldı. Kırılma yüzeyleri SEM görüntüleme tekniği ile incelenmiş olup, silika partikül boyutu ve içeriğine bağlı olarak toklaşma mekanizmaları tanımlandı.

Kırılma mekaniği test çalışmalarından önce, mevcut epoksi kompozit sistemine ait proses parametrelerinin optimizasyonu için bir araç olarak kullanılabilecek bir zaman sıcaklık dönüşüm (TTT) diyagramı oluşturuldu.

Anahtar kelimeler: Epoksi kompozitler, silika partiküller, kırılma tokluğu, lineer elastik kırılma mekaniği, zaman sıcaklık dönüşümü (TTT)

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CHAPTER ONE

INTRODUCTION

Epoxy resins, which are perhaps the most widely used thermoset polymers, have become the centre of industrial and research activities since they started to be commercially available in the late 1940s, essentially due to their good processability, low-cost, high-performance characteristics, and many different enormous application fields such as automotive, aviation, aerospace, marine, and electrical-electronic industries. Most of the cured epoxy resins are amorphous thermosets and possess good mechanical strength, outstanding chemical resistance. They have excellent thermal, and electrical properties. High dimensional stability, no volatiles emission and low shrinkage after curing are great advantages of this material. All of these unusual combinations of characteristics are often not present in any other plastic materials (Mark, 2014).

Epoxy resins have acquired widespread recognition as the material of choice for three main fields including bonding, structural, and protective coating applications thanks to their exceptional formulation, versatility, and cost-effectiveness. In adhesive industry, epoxy resin-based adhesives are capable of providing a strong bond between two materials, whether they are the same or different, including ceramics, metals, wood, glass, fibers, and a variety of polymers. The use of epoxy resins in structure materials can be separated into two primary categories. The first category involves combining epoxy resins with other materials, such as fibers to create composite construction components. The other structural field of use is electrical and electronic engineering. Fiber-reinforced epoxy resin composites are particularly lightweight engineering structures and used generally to produce wind turbine blades and aircraft parts. In electrical and electronic engineering field, anhydride cured epoxy systems are dominated due to their long pot-life, low viscosity, low exotherm, and high dielectric properties. Particle reinforced epoxy resin composites are used in a variety of medium and high voltage electrical components and equipment, including switchgears, embedded poles, voltage and current transformers, bushings, printed circuit boards,

and sensors to provide the required electrical insulation (Nowak et al., 2006). The best-known epoxy protective coating field is automotive industry which employs amine cured epoxy resins system by the method of cathodic electrodeposition coating process to protect the car body against the corrosion.

Despite all these superior features described above, highly crosslinked epoxy matrices generally exhibit unfavourable brittle behaviour due to structurally constrained plastic deformation. Therefore, it is a major goal of many researchers to develop epoxy with increased toughness while minimizing considerable loss of other crucial properties like mechanical and thermal properties which are demanded in many applications.

Incorporating some soft or rigid particles with nano- or micron- dimension in the epoxy matrix is commonly applied traditional toughening method. Even though soft modifiers, such as rubber particles, liquid rubbers, core-shell particles, and hyper-branched polymers may provide an excellent toughness to the epoxy matrix, they often reduce other properties such as strength, modulus of elasticity, and glass transition temperature. On the other hand, rigid filler particles with nano- or micron- sizes, such as titanium dioxide (TiO_2), aluminium oxide (Al_2O_3), calcium carbonate (CaCO_3) or silica (SiO_2), as contrary to rubber particles, are effective epoxy resin toughening modifiers without significantly compromising other mechanical properties (Wetzel, Rosso, Hauptert, & Friedrich, 2006). The effect of rigid filler particles on toughening of the matrix is directly dependent on many properties modifying matrix/particle interface such as particle type, particle size, particle filling content, particle surface structure, geometry, and surface chemistry. Therefore, the toughening improving process of epoxy matrix is explained by different mechanisms such as crack deflection, crack tip pinning, crack bridging, microcracking, debonding and shear banding mechanisms, depending on particle size and filler content.

Silica is extensively used as an inorganic filler for particle reinforced composites due to its availability, chemical inertness, and strength. On the other hand, increasing stiffness, decreasing dielectric properties, decreasing overall cost of the material, decreasing coefficient of thermal expansion of the structure, and consequently reduced shrinkage of the product are other contributions of the silica filler on the final

composite structure. Therefore, silica particles with different particle size and filler content were used as an additive material to modify fracture properties of epoxy thermoset resin in this dissertation.

The main objective of the present work is to investigate the effect of particle size and filler content of silica particles on fracture behaviours and thermal properties of the epoxy polymer composite. The relationship between the final structure and fracture property was determined, establishing the toughening mechanisms.

The current research thesis covers, initially construction of TTT diagram of the silica filled epoxy/anhydride composite system, which was created depending on curing temperature and time to optimize the process parameters; then, the preparation of composite systems with different silica particle size and amount and their characterization, evaluation of fracture properties and toughening mechanisms; and finally thermal behaviour analyses of the produced composites. Within this context, the reminder of the current thesis is organized as follows:

Chapter 2 presents a review of the literature to give an overview of the existing body of information regarding the relevant topics. It provides the findings of previous studies on the curing behaviour of the epoxy composite depending on the curing temperature and time, fracture, and thermal properties of particle reinforced polymer composites.

Chapter 3 includes the descriptions about preparation of epoxy composite test specimens, test procedures, and analysis methods.

Chapter 4 focuses on the interpretation of the test results regarding the mechanical, thermal, and micro structural characteristics of the studied epoxy system.

Chapter 5 presents an overall summary of present research. This chapter gives general conclusions on the work completed for this thesis.

CHAPTER TWO

LITERATURE REVIEW

2.1 Thermosetting Polymers

Thermoset polymers are referred to as polymer networks produced by the chemical reaction of monomers, at least one of which has three or more functional sites for each molecule. As a result, during a specific conversion in the synthesis, relative amounts of a gel are generated. A thermosetting polymer can be characterized mostly by formation of macromolecule made up of repeating units that are covalently bound together in the course of polymerization. This macromolecule which infuses throughout the material structure is called a gel. Accordingly, the formation of a network made of covalent bonds gives polymers their thermosetting properties (Pascault, Sautereau, Verdu, & Williams, 2002).

Sol phase initiated by monomers is the first step in the manufacture of a thermosetting polymer, (Figure 2.1a). On the other hand, gelation begins when conversion of specific functional group occurs, causing the formation of a giant macromolecule that infuses the material structure and occur in the system, (Figure 2.1b). This critical transition from sol to gel (known as sol-gel process) is characteristic of thermosetting polymers in general. Prior to gelation, the structure is a sol with a limited viscosity. Viscosity reaches a limited level at gelation. After the gelation an insoluble gel fraction is present in the system, (Figure 2.1c). Finally, in case of stoichiometric formulations, the sol portion vanishes with complete functional group conversion, and the resulting thermoset polymer is made up of a single crosslinked giant gel molecule, (Figure 2.1d). Thermoset polymers are generally amorphous because segments of the network structure are not likely to be ordered because of the limitations made upon by the existence of crosslinks (Turi, 1981). Some of the thermosetting polymers used in the industry are unsaturated polyesters, phenolic and urea-formaldehyde resins, cyanate esters, polyimides, and epoxy resins. Epoxy thermoset resins are within the scope of this dissertation.

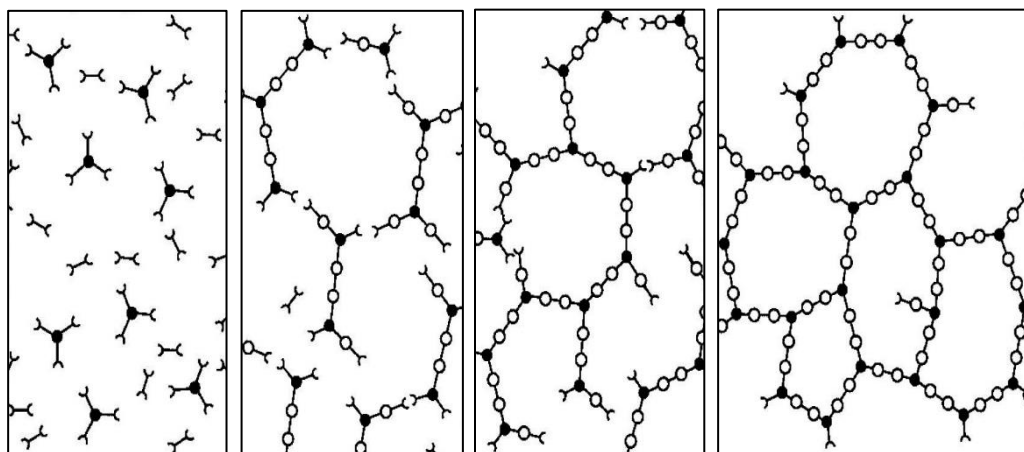


Figure 2.1 Two-dimensional representation of curing of a thermoset: (a) starting with monomers, (b) propagating by simultaneous linear growth and branching lower than the gel point, (c) proceeding to create a gelled but insufficiently cross-linked network, (d) finally resulting with a completely cured thermoset (Turi, 1981)

2.1.1 Epoxy Resins

Epoxy resins are classified in the thermosetting polymer group and have a low molecular weight structure. When heated, thermosetting polymers undergo a chemical reaction, which is also called as curing, that turns them into an insoluble and infusible substance. The three-dimensional covalent network structure that forms during the curing process makes the cured polymer chemically inert (Ratna, 2009). Oligomeric structures with more than one epoxide group for each molecule are referred to be epoxy resins according to DIN 7728. The terms epoxy and epoxide are commonly used to describe the oxirane ring. Oxirane ring constitutes an oxygen atom coupled to two carbon atoms with a planner bridge to create a three membered ring given in Figure 2.2.

The simplest way to produce epoxides is to oxidize alkenes with a peroxyacid (RCO_3H) which can be summarized in Figure 2.3 (Clayton, 1988). Therefore, epoxides can also be called as ethylene oxide or glycidol in the industry and literature. The systematic name for ethylene oxide is 1,2-epoxyethane. Peroxyacids transfer an oxygen atom to the alkene through a one-step mechanism without intermediates on the same side of the double bond where the both C-O bonds are formed. The oxygen atom located on the farthest side of the carbonyl group is the one transferred (Murry, 2016).

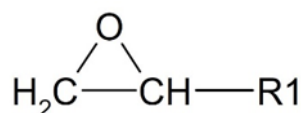


Figure 2.2 Epoxide functional group

High ring strain of about 114 kJ/mol in oxirane is an attribute of epoxides, which is similar to that in cyclopropane. The ring strain emerges from the bond angle of C-O-C, and O-C-C that are 61°, 59°, respectively (Katritzky, 2010). Therefore, epoxides are significantly more reactive than other cyclic ethers as a result of their high ring strain. Due to this reactivity feature, the epoxide group can give a wide variety of chemical reactions and combine with many different materials to produce end products with different properties.

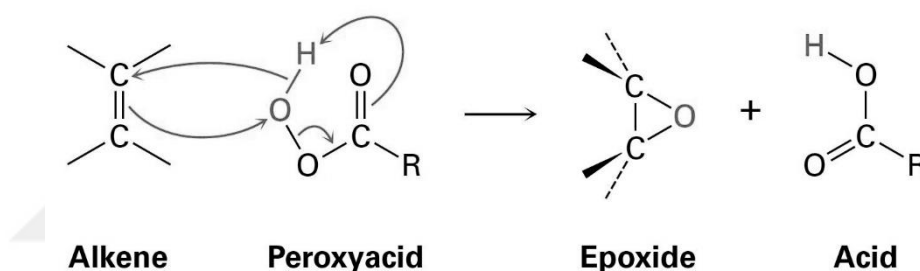


Figure 2.3 Epoxide production reaction by oxidation of alkene with peroxyacid (Murry, 2016)

Many types of epoxy resins, such as novolac resins, cycloaliphatic resins, brominated resins, and phenoxy resins are used in the industry. The most frequently used epoxy resin is produced from epichlorohydrin and bisphenol-A and final epoxy resin is known as diglycidyl ethers of bisphenol-A (DGEBA) which will also be used throughout this dissertation.

Pierre Castan discovered first the reaction of diglycidyl ether of bisphenol-A with phthalic anhydride at the company De Trey AG, Switzerland, while developing dental restoration materials in 1938. He researched on alternatives to vulcanite as a dental base material, such as resins that could be readily molded at low pressures. The DGEBA epoxy resins did not necessitate high moulding pressures since they could be cured by the interaction of epoxide groups with phthalic anhydride without the formation of small molecular species (Ellis, 1993). In Europe Ciba AG of Basel,

Switzerland (now BASF) manufactured products with a patent license from De Trey AG and started to sell them under the trade name Araldite starting from 1945 (Dornbusch, 2016).

In the industry, epichlorohydrin is produced by propylene, chlorine, and glycerol primary raw materials. Synthesis starts with the chlorinating propene to allyl chloride then continue by the reaction with hypochlorous acid to dichlorohydrin of glycerol. Then epichlorohydrin is synthesized by dehydrochlorination through the reaction with sodium hydroxide, which can be summarized in Figure 2.4 (Pembere, Yang, & Luo, 2017).

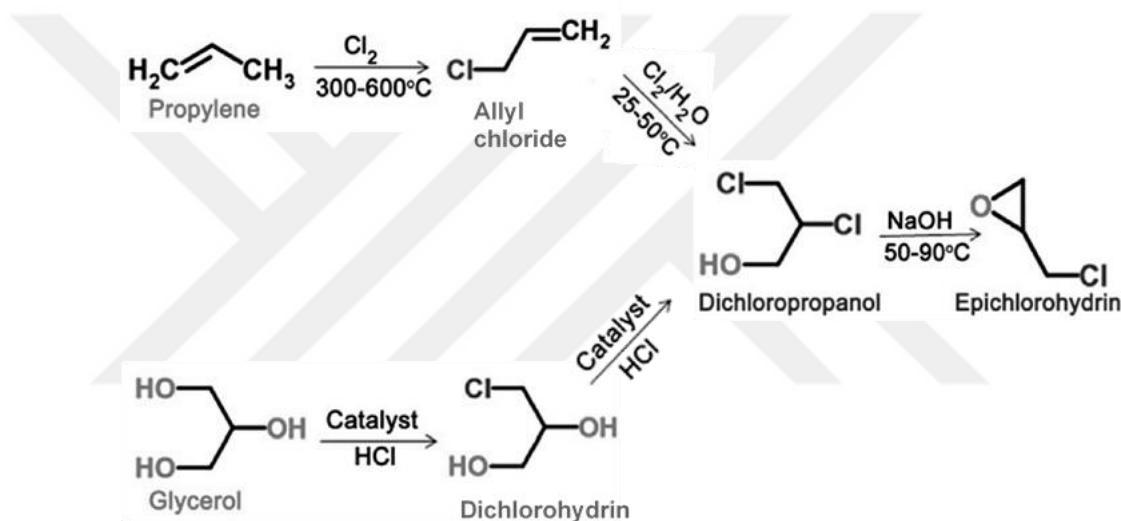


Figure 2.4 Production of epichlorohydrin from glycerol and propylene (Pembere, et al. 2017)

Bisphenol-A is produced by combining two moles of phenol and one mole of acetone in an acid catalysed condensation process (Dornbusch, 2016). Figure 2.5 summarize the rection.

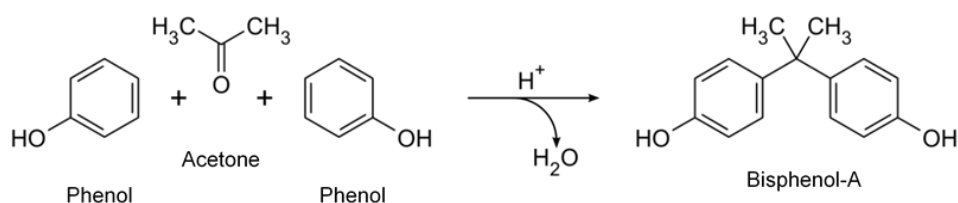


Figure 2.5 Production of bisphenol-A from phenol and acetone (Dornbusch, 2016)

DGEBA epoxy resin thermoset is produced by combining reaction of epichlorohydrin and bisphenol-A with the catalyst of NaOH as given in Figure 2.6. The reaction between bisphenol-A and epichlorohydrin after the dehydrohalogenation process, gives bifunctional epoxies as DGEBA. In order to produce resins with higher molecular weight, DGEBA continues to react with bisphenol-A iteratively, which have the general structure formula given in Figure 2.7. Ongoing reaction is known as Fusion Process and that chain extension process is a stepwise polymerisation (Ellis, 1993).

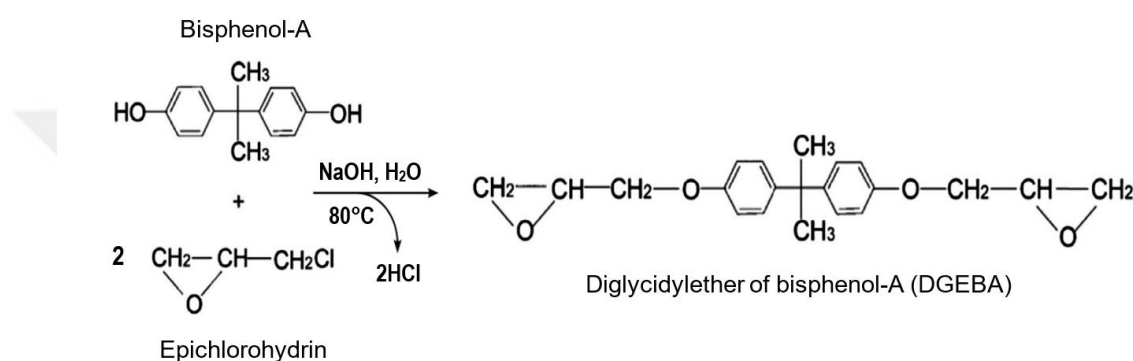


Figure 2.6 Production of diglycidylether of bisphenol-A (DGEBA) from epichlorohydrin and bisphenol-A (Sukanto, 2021)

The number of repeating units (*n*) determines the DGEBA resin's characteristics. Higher molecular weight resins are more likely to be viscous liquids or solids while low molecular weight resins are often liquids. Oxirane groups in DGEBA epoxy monomers have two of carbon bonded reactive rings and are prone to undergo a ring-opening reaction with various curing or hardening agents. Each monomer molecule has a reactive epoxy part at the end. The hydroxyl group provides as an extra reactive component in the nucleophile reaction and can contribute to wetting of the surface and consequently adhesion during application of curing processes, and other chemical reactions. The growth of thermoset chains and cross links is considerably promoted by these curing and nucleophile processes. While the aromatic rings in the structure provide high temperature performance and rigidity, the linear carbon group in the repeating unit creates the necessary toughness for the structure. When the terminal epoxy groups are cross-linked, the longer backbones provide greater space between cross-links, improving the material's flexibility and toughness (Mark, 2014).

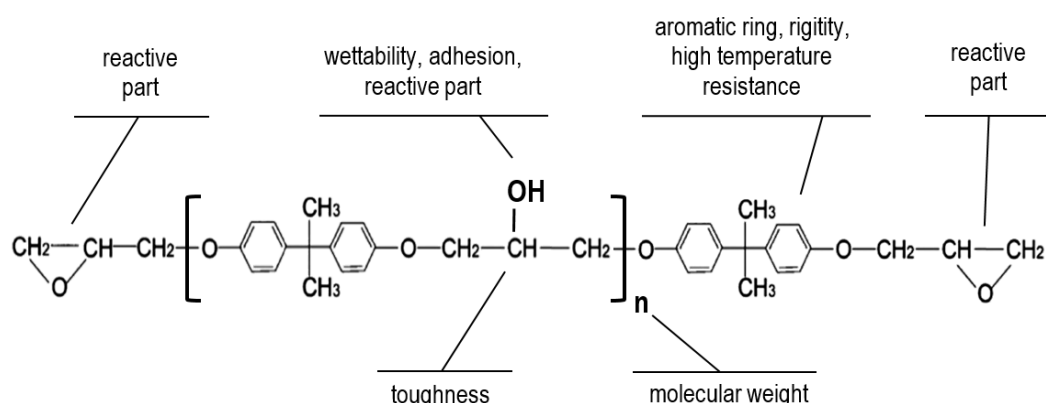


Figure 2.7 General formula of diglycidylether of bisphenol-A (DGEBA) with higher molecular weight, where n is the number of structural repeating unit ($n=0$ for DGEBA, and $n>0$ for the derivatives) (Ellis, 1993)

2.1.2 Carboxylic Acid Anhydrides as Curing Agent

Epoxy resins need crosslinking agents to convert insoluble and hard three-dimensional cross-linked thermoset network through a curing process. These cross linkers, which are generally known as hardeners or curing agents in the industry, facilitate the epoxy resin to cross-linking or curing. Curing process is described as initial chain formation, followed by linear growth, then gelation and finally crosslinking of linear polymers to form an infinite network. Copolymerization reaction with a multipurpose curing agent or homopolymerisation started by a catalytic curing agent are two methods of curing that are available (Ellis, 1993). Anhydride or an amine molecule attack as nucleophilic to one of the epoxide carbons during the copolymerization reaction. Homopolymerisation requires acid or base catalysts to carry out elimination processes on the oxygen atom of the epoxide group by the activated process of radiation. The main difference between two curing process is that the network in homopolymerisation is entirely comprised of cross-linked epoxy monomers, whereas the network in the copolymerisation reaction is composed of a copolymer of both epoxy monomers and a curing agent.

There are many types of curing agents such as aliphatic or aromatic amines, polyamides, isocyanates, carboxylic acids, anhydrides, polysulphides, and imidazoles. One of the early curing agents for epoxy resins was dicarboxylic acid anhydride. Although long times at high temperatures are necessary to complete the cure, the

reaction with epoxy resin is characterized by a low exotherm. This curing regime leads to low shrinkage and stress-free structures, which gives the product superior electrical insulating capabilities. Due to their excellent thermal stability, these properties are maintained even at high continuous working temperatures, which has enabled their application in the heavy electrical industry.

Since Phthalic Anhydride (PA) is difficult to handle owing to a strong susceptibility to sublimation in the process, hydrogenated derivative Hexa-Hydro Phthalic Anhydride (HHPA) and Tetra-Hydro Phthalic Anhydride (THPA) are used mainly for moulding for electrical applications. Low melting point THPA is used with other anhydrides to create low viscosity liquid eutectic mixes since it does not sublime.

Methyl Tetra Hydro Phthalic Anhydride (MTHPA), which is a special liquid cyclic form of carboxylic acid anhydrides, will be used as a curing agent throughout this dissertation. MTHPA is produced by Diels-Alder reaction between isoprene and maleic anhydride. The final product is a liquid eutectic mixture of regioisomers and stereoisomers and is generally used as anhydride hardener for pipe manufacturing, encapsulation, potting, and electrical molding applications (Ellis, 1993). The Diels-Alder reaction is a cycloaddition between a diene and a dienophile, which is used in organic synthesis, to get new cyclic molecules. Synthesis reaction of MTHPA by the Diels-Alder reaction is given in Figure 2.8 (Gogin, Zhizhina, & Pai, 2015).

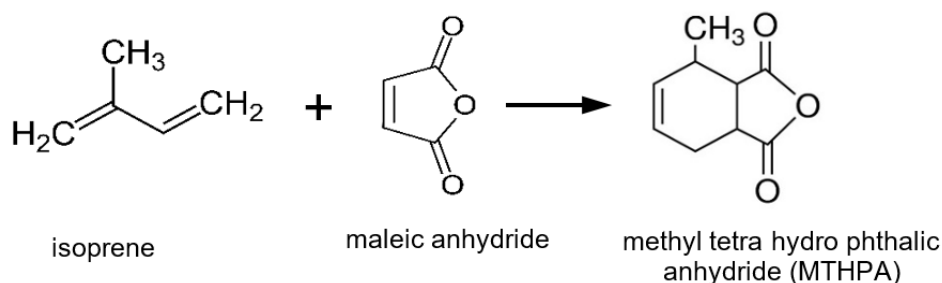


Figure 2.8 Synthesis reaction of MTHPA by the Diels-Alder reaction (Gogin, 2015)

2.1.3 Trichloro(N,N-dimethyloctylamine)boron as an Accelerator

Epoxy groups are capable of reacting with both electrophilic and nucleophilic substances. As a result, chain polymerization of epoxy monomers can be initiated by Lewis acids and bases. Imidazoles, tertiary amines, ammonium salts, and boron trifluoride complexes and boron trichloride amine complex for cationic chain polymerization are examples of commonly used initiators, which are typically called as catalytic curing agents or accelerators in the industry. Catalytic curing agents can operate either as a curing agent to achieve crosslinking by homopolymerisation, or as an accelerator to promote main polymerisation reaction.

Even though faster cure rates may be achieved by adding too much catalyst to the formulations excessive use of catalysts should be avoided due to the risk of shrinkage, embrittlement, and shortened material life.

Lewis acids such as BCl_3 -amine complexes are a strong catalyst for the epoxy-anhydride reaction. Furthermore, this type of catalysis significantly promotes the esterification reaction (Ellis, 1993). Trichloro(N,N-dimethyloctylamine)boron ($\text{C}_{10}\text{H}_{23}\text{BCl}_3\text{N}$) which is also a quaternary ammonium salt (QAS), will be used as an initiator as premixed condition to MTHPA during this dissertation. This salt is known as amine-boron trichloride complex in the industry and schematic formula is given in Figure 2.9. QAS is a polyatomic ion of the compound that is positively charged, where alkyl groups and an anion which are connected to it. The quaternary ammonium cations are permanently charged. Among the alkyl groups, one is a long alkyl chain group which contains more than eight hydrocarbons, and they serve as the hydrophobic group. Quaternary ammonium salts are phase transfer catalysts. Such catalysts enhance the migration of a reactant from one phase into another where a reaction occurs and increase the rate of the reactions between chemicals dispersed in liquid solvent.

Boron trihalides and amines can react as latent catalysts for epoxy homopolymerisation, producing stable donor acceptor compounds (Ellis, 1993). Because amine-boron trichloride complex requires temperatures above 120°C to be activated it is also an effective catalyst for the advancement of liquid epoxy-anhydride

resin system during the hot mold filling operation, which allows to complete filling operation before reaching to the gel point. The amine-boron trichloride complex is a strong Lewis acid which affects the cure. Since the connected amine group is thought to occur as tertiary amine after the activation due to the connected three carbon atom, it is an aliphatic monoamine. Consequently, it doesn't considerably promote crosslinking reactions. In contrast to the anhydride crosslinking agent in the curing system, the amine-boron trichloride complex is therefore regarded as a separate and independent component (Palmese, 2019).

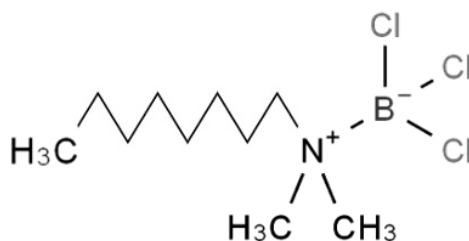


Figure 2.9 Trichloro(N,N-dimethyloctylamine)boron as a catalyzer. Abbreviated formula of amine-boron trihalide complex is $R_1R_2R_3N^+-B^-X_3$ where R_1 , R_2 , R_3 are aryl or alkyl, while X is F or Cl

Atchekzai et al. (1991) synthesized BCl_3 Lewis acid associated with N,N-dimethyloctylamine type tertiary amine (BCl_3 DMOA) and investigated stability and curing capability of the catalyser. They cured DGEBA epoxy resin with this BCl_3 -tertiary amine complex catalyser and investigated that the reactivity was determined strong when the sample transformed to a gel after the sample had been cured for an hour at $120^\circ C$ in an oven. The reactivity was considered as moderate when the gel phase was reached following a new treatment of one hour at $150^\circ C$ (Atchekzai et al. 1991).

2.1.4 Curing Reaction of DGEBA with MTHPA

It is well known that the high reactivity of the epoxy resin is due to extremely stretched bond angles and, in turn, the polarity of the C-O and C-C bonds. While the electron-rich oxygen can react with electrophiles, the electron-deficient carbon can only perform nucleophilic reactions as given in Figure 2.10. Since the nucleophiles donate electrons, they are Lewis bases. In contrast because electrophiles accept

electrons, they are called Lewis acids (Murry, 2016). In the epoxy industry, these reactions are frequently described using the words "anionic" (nucleophilic transition state) and "cationic" (electrophilic transition state) reactions (Mark, 2014).

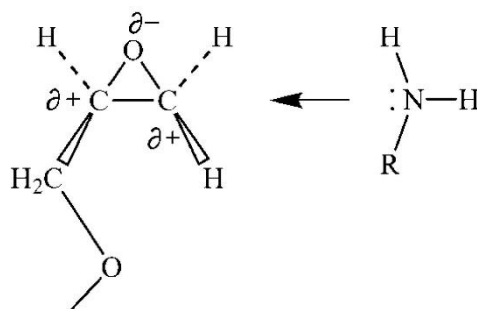


Figure 2.10 Polarization of epoxy bonds

It has long been common to use anhydride curing agents with DGEBA epoxy resins to increase high-temperature stability and provide improved physical and electrical properties. Many of anhydride formulations need to be cured at elevated temperatures, and the final properties depend on post-curing at temperatures of higher than 150°C to achieve full curing (Smith, 1979). Accordingly, anhydride cured systems have high glass transition temperatures (Penn, 1998). The epoxy-anhydride resin has extremely poor curing capabilities in the absence of an accelerator, with a gel time at 150°C exceeding 10 hours. At higher temperatures and at larger accelerator concentrations, the homopolymerisation of epoxy catalysed by quaternary ammonium salt might become more considerable, but at a rather slow rate (Smith, 1979).

Because of the prolonged curing process and high temperatures required to achieve ideal properties for the epoxy-anhydride system, using catalysts is generally required to eliminate this drawback. Tertiary amines are the most commonly used catalysts among them (Foix et al., 2009).

Epoxides react with cyclic anhydrides in a chain-wise polymerization process, which was initiated with Lewis bases, and includes steps of chain initiation, propagation, and termination, or chain transfer (Pascault, 2002). In general, these reactions are very complex due to some phenomena such as autocatalysis at early stages and initiation of gelation at later phases of cure reaction. Epoxy resin cross-

linking can take place through hydroxyl or epoxide groups and is primarily accomplished by one of two curing mechanisms: either direct coupling of the resin molecules through catalytic homopolymerisation or indirect coupling through a reactive initiator compound (Tess, 1985). However, the competing epoxy homopolymerisation is effectively suppressed in the presence of anhydride hardener and any catalyst such as tertiary amine complexes, which has been reported in literature by many authors (Fischer, 1960; Tanaka, & Kakiuchi, 1964; Antoon, & Koenig, 1981; Steinmann, 1989).

Due to the possibility of several competing reactions, there are great deal of explanations regarding epoxy-anhydride curing reactions accelerated by a catalyst in the literature, some of them are even controversial (Fischer, 1960; Tanaka, & Kakiuchi, 1964; Antoon, & Koenig, 1981; Steinmann, 1989).

2.1.4.1 Ring Opening Reaction as Initiation Step

In epoxy-anhydride system to initiate the reaction, asymmetric cleavage of the anhydride groups is required, which is called as a ring opening reaction. A small quantity of accelerator, a compound that acts as a catalyst to accelerate the epoxide-anhydride reaction, is used to achieve the initial cleavage. Even though a tertiary amine was not used as the catalyst in this dissertation, the same catalytic process would be assumed. The quaternary ammonium salt used in this study lacks two unshared electrons, in contrast to a tertiary amine. Anyway, the attack on the carboxylic group in the anhydride structure is carried out by the electron negativity of one of the salt's ions, just like by the unshared electron. This causes ring opening of the anhydride which is given in Figure 2.11 (Woo, & Seferis, 1990). Another presumption for the utilisation method of the catalyst is the thermal decomposition of quaternary ammonium salt to the tertiary amine compound by Hoffman elimination reaction during the high temperature curing reaction (Patai, 1968; Kroschwitz, 1998; Vryonis, 2020). Even though most of the authors agree that epoxy-anhydride reaction catalysed by tertiary amine undergoes an anionic reaction, there is still not a certain confirmation as to whether the initiator remains chemically bound throughout the entire reaction.

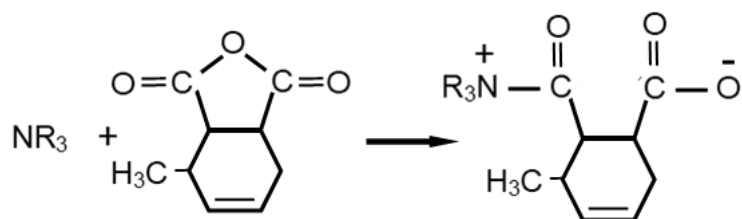


Figure 2.11 Anhydride ring opening reaction by tertiary amine catalyst (Woo, 1990)

The main function of tertiary amine catalyst is to take part in the synthesis of carboxylate and alkoxide ions in the epoxide-anhydride-tertiary amine system, which starts an anionic alternating copolymerization (Antoon, 1981). Carboxyl, hydroxyl, or other proton-donating compounds can accelerate the reaction rate by causing the development of a hydrogen-bonded complex of the tertiary amine and proton donor such as acid, water, or alcohol, before the reaction with the cyclic anhydride (Tanaka, 1964).

However, the secondary hydroxyl groups linked to the backbone of DGEBA resins may also react in the anhydride initiation process (Saeedi, Andritsch, & Vaughan, 2019). First step of curing reaction between anhydride and secondary hydroxyl group of the resin is to create monoester and carboxylic acid groups as given in Figure 2.12. Then the carboxylic acid group reacts with another epoxide group to form diesters with new hydroxyl group which might itself react with another anhydride groups (Teil, 2004).

Ring opening by basic catalysts result in mainly in esterification, while hydroxyl reaction finally leads to both esterification and etherification. However, significant etherification can lead to unfavourable levels of unreacted anhydride and half-acid ester in the cured system, which prevent the whole curing reaction (Tess, 1985; Foix, 2009). Hydrophobic tail of the quaternary ammonium salt takes an important role to prevent these excessive hydroxyl reactions with anhydride.

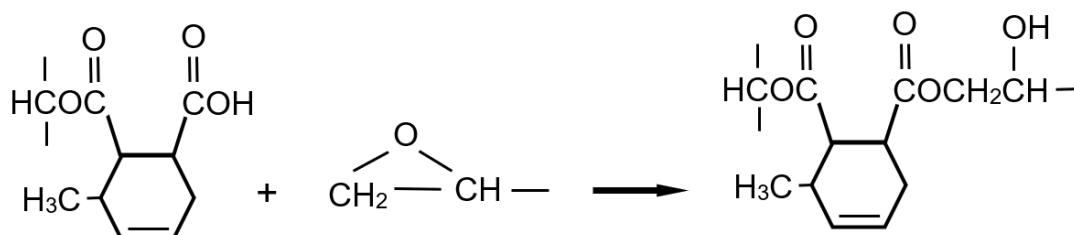
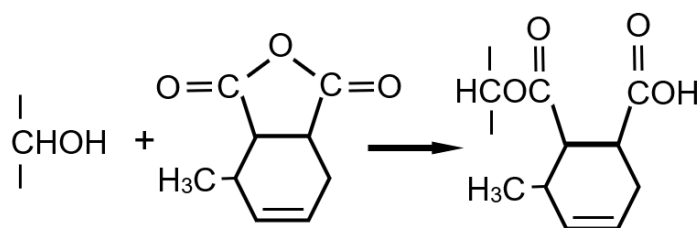


Figure 2.12 Anhydride ring opening reaction by secondary hydroxyl groups linked to the backbone

2.1.4.2 Propagation Reaction Step

The general curing mechanism reported in the literature regarding the reaction of epoxy resin cured with anhydride by the assist of tertiary amine catalysts is shown in Figure 2.13 (Foix, 2009; Peters, 1998; Woo, 1990).

The propagation stage involves the formation of carboxyl anion on the other end of the opened anhydride ring. Reaction of this carboxylate anion with the epoxy group, which is called as an esterification reaction, creates an ester-alkoxide anion. This anion can then interact with another anhydride to create an ester linkage and another carboxyl anion, which in turn causes the process to propagate (Woo, 1990). In summary, the reaction mechanism continues as alternating copolymerization of epoxy groups and anhydrides. Consequently, only di-ester groups would constitute the cross-links in the cured products. Ester linkages created between epoxide and anhydride are remarkably stable in the most of hostile environments and at high temperatures. Epoxy and anhydride stoichiometric equivalents are cured at high temperatures, which has been reported to produce the best properties in implementations, which is coherent with this curing system and does not contain etherification reactions (Mark, 2007).

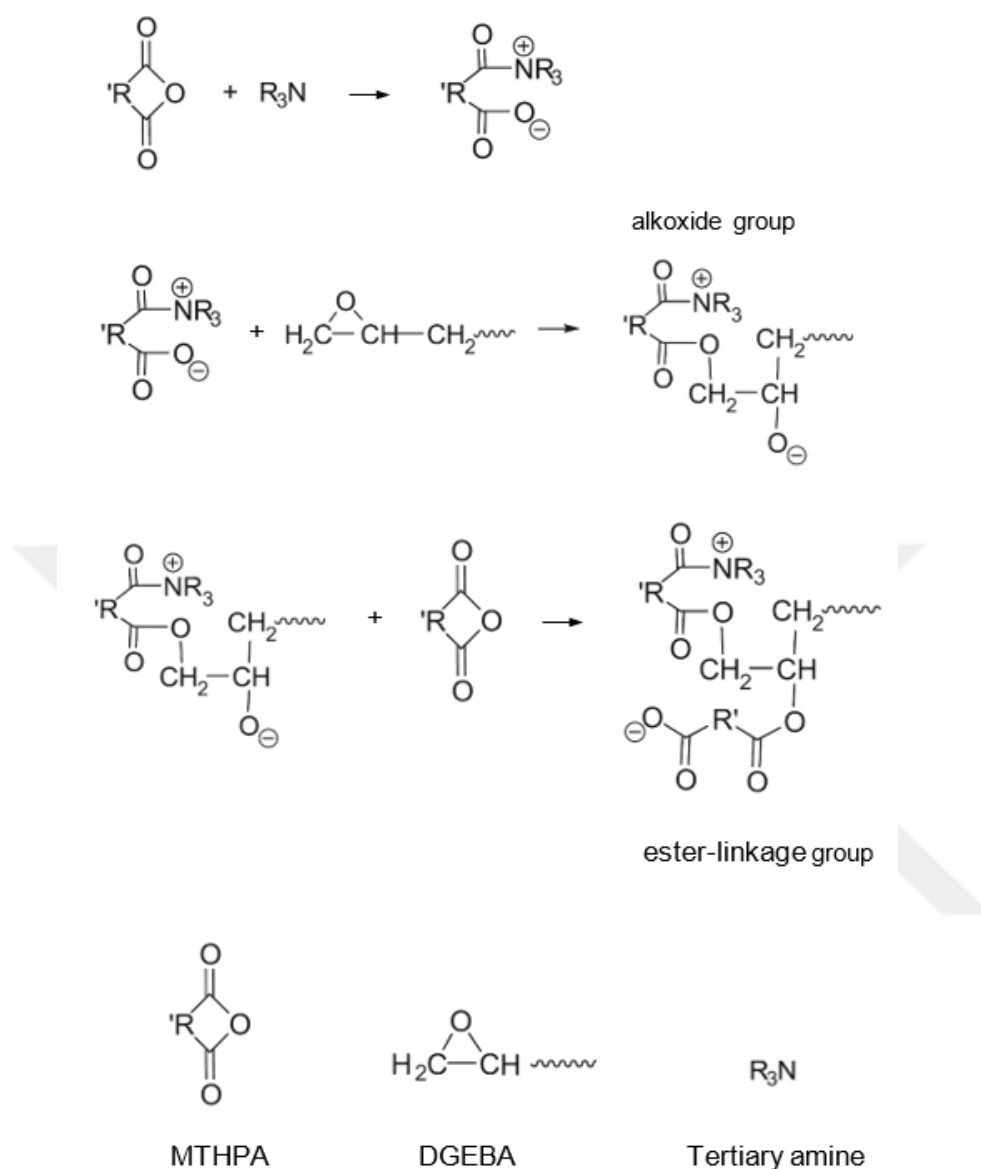


Figure 2.13 Mechanism of a tertiary amine-catalysed epoxide curing reaction with anhydrides (Foix, 2009)

The structure of the interchain bonding and high degree of crosslinking provide cured epoxides numerous useful properties. These properties include high tensile and compressive strength, and chemical and electrical resistance, and excellent adhesion capability to a variety of substrates. On the other hand, processing is also simplified due to low shrinkage and the absence of volatile waste products. The uncured properties of epoxides, such as viscosity, which are significant in processing, and the final properties of cured epoxides, such as mechanical strength or electrical resistance,

can be adjusted by choosing the right epoxy monomer, curing agent, and some specific additives.

2.1.5 Silica Particles and Interaction with Epoxy Polymer

It is a general practice to add organic and inorganic particles in nano and micron dimensions to the polymer during the process to improve the physical, electrical, thermal, and mechanical properties of the structure. Silica, or silicon dioxide (SiO_2) as an inorganic additive, is widely used in the industry as a polymer additive due to its high mechanical strength, very low thermal expansion coefficient, high electrical resistivity, and cost-effective availability.

The predominant polymorph of silica within sedimentary rocks found in the earth's crust is α -quartz, which is one of the most abundant minerals after feldspar. Since α -quartz has a hardness of 7 Mohs because of high covalent bonded structure and relatively high melting point of 1723°C , it is extremely resistant to mechanical strains. Other common metastable polymorphs of silica are tridymite, cristobalite, coesite, and stishovite crystals (Heany, 1994). All of these structures, with the exception of stishovite, are built upon SiO_4 tetrahedral frameworks as given in Figure 2.14.

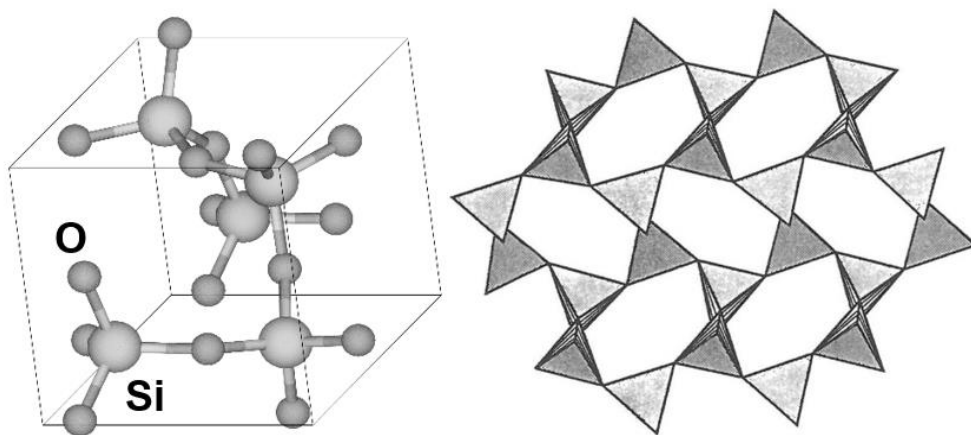


Figure 2.14 Crystal structure of α -cristobalite (Heany, 1994)

The numerous systems that the $(\text{SiO}_4)^{-4}$ structures are connected with three-dimensional arrangements give rise to the distinct framework silica structures where one O atom is connected with two Si atoms and one Si atom is connected with four O atoms. The tendency for the generation of the $(\text{SiO}_4)^{-4}$ tetrahedron in both crystalline and glassy silicas can be attributed to the ionic and covalent natures of the Si–O bonding. Additionally, the coordination of each O anion by two Si cations results in corner sharing of the oxide tetrahedra, which prevents the close packing of anion layers and creates relatively open structures (Shackelford, 2008). These open structures of silica crystal give them the ability to form an ionic bond with other compounds via their surfaces.

It is not uncommon for hydrogen complexes to saturate on the surface sites of quartz crystal faces and fractures, and as a result, they may occupy places on dislocations and other crystalline imperfections to fulfil loose bonds. Hydrogen point defects can occur in many different regions to compensate for the charges related with the impurity cations. Numerous features that depend on surface and interfacial energy are influenced by hydrogen species that have adsorbed on the surfaces of quartz (Heany, 1994).

Three-dimensional network structure of SiO_4 units terminate at the surface in two different ways, which are with oxygen on the surface through silanol groups ($\equiv\text{Si}-\text{OH}$) or siloxane groups ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$). There are three types of silanol groups, which are geminal (two silanol groups bonded to the same silicon atom), vicinal (hydrogen-attached silanol), or isolated silanol sites that have not possible hydrogen bonds, as given in Figure 2.15 (Sharma, 2015).

Hydrogen complexes can easily be formed at the surfaces of quartz by reaction with H_2O . Highly strained siloxanes at surfaces may be replaced by silanol. Silanol groups then provide sites for the adsorption of water. In an aqueous medium free valence of the surface silicon atoms become saturated with hydroxyl groups. SiOH groups may form hydrogen bonds with adjacent silanols or water molecules. In early stages of hydration, water molecules adsorb to surfaces and form hydrogen bonds between the oxygen and surface silanol. Then, water produces hydrogen-bonded clusters and continuous layers in the latter phases of hydration (Heany, 1994). These silanol groups

on the SiO_2 surface make the silica hydrophilic while siloxane groups give it a hydrophobic characteristic. In many instances, the surface characteristics of silica, which acts as an oxide adsorbent, are influenced by the presence of silanol groups.

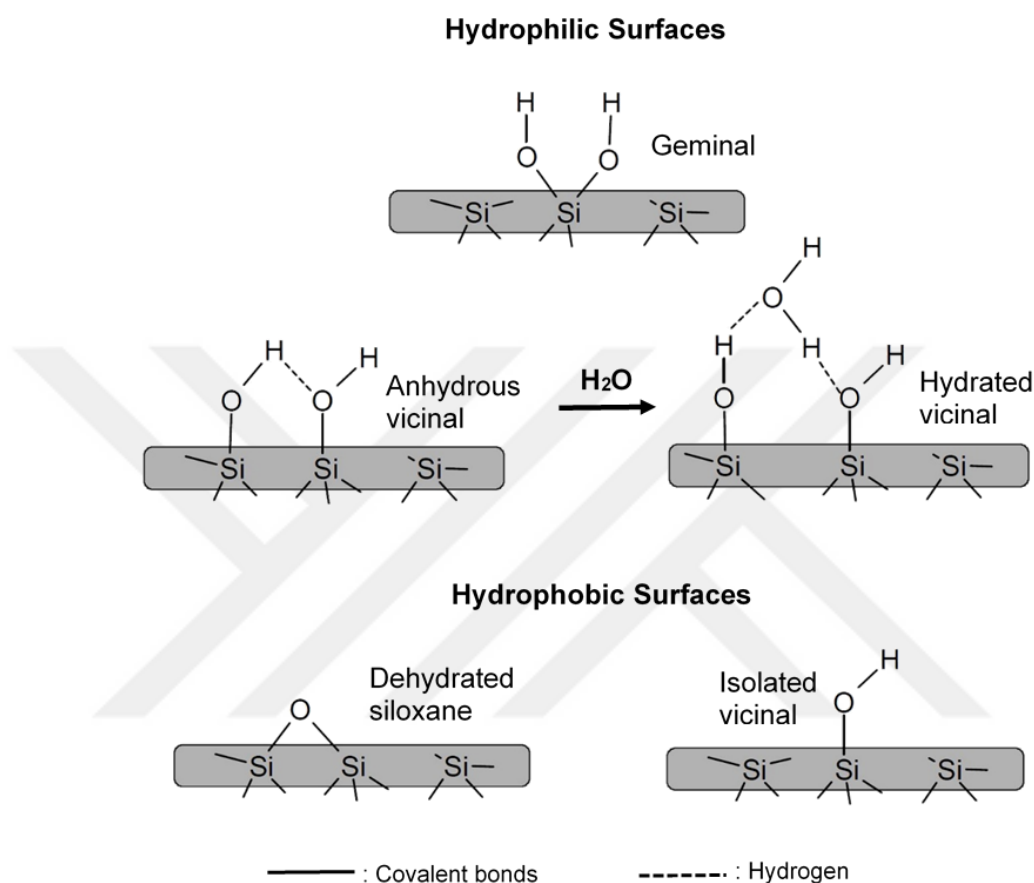


Figure 2.15 On the surface of silica, the several types of hydroxyl groups regarding their hydrophilic and hydrophobic properties (Napieriska et al., 2010)

The hydrophilicity property of a silica increases with the amount of silanols which are able to create hydrogen bonds with the molecules of water. Vicinal silanols strongly interact with water molecules, giving silica its superior water adsorption abilities, which are also used in industrial gas drying processes (Napieriska et al., 2010). The adsorption can be reduced when the hydroxyl groups on the surface of silica are eliminated. When silica is heated at 170°C and atmospheric pressure, or at ambient temperature under vacuum, water molecules bonded via hydrogen can be eliminated. vacuum (Napieriska et al., 2010). As the temperature rises, hydroxyl groups start

to condense, creating siloxane bonds thus water is released (Iler, 1979; Zhuravlev, 1993).

The total free surface energy of siloxane is about twice that of silanol, which means siloxane has much better wettability function that gives it much stronger adhesion property (Brunauer, 1956). Wetting is one of the most important parameters for the adhesion phenomena, which increases proportionally with increasing surface energy. It is generally accepted that strong adhesive bonds between solids and liquids are related to strong wetting capacities, highlighting the significance of wetting as a kinetic process (Kinloch, 1987).

The epoxy resin as an adhesive comprises hydroxyl ($-OH$) and ether ($-O-$) groups that may build hydrogen bonds with the surfaces of hydrophilic adherends. It is assumed that hydrogen bonds may build between the hydroxyl and ether groups of epoxy resin and the $SiOH$ groups on the silica surface as given in Figure 2.16. It has been verified that epoxy resin and silica surface interactions that formed by the hydrogen bonds are crucial for increasing the strength of the adhesive bond (Higuchi, 2021). On the other hand, Yoshizawa et al. claim that electrostatic and van der Waals effects, which are related with the hydrogen bonds, are significantly effective in the adhesive interaction due to the hydrophilic surface, in their study using the pair interaction energy decomposition (PIEDA) theoretical simulation analysis with epoxy and OH -functionalized α -cristobalite surface (Yoshizawa et al., 2017). Higuchi et al. found in their theoretical work that, the adhesion between silica surface and epoxy resin under moist condition decreases. The structural deformation of the water molecules' hydrogen bonding network at the adhesion interface caused by atmospheric water vapor can have a detrimental effect on the adhesion properties. Additionally, the structural flexibility of the hydrogen-bonded network can also be damaged during the detachment process by water vapor (Higuchi et al., 2019).

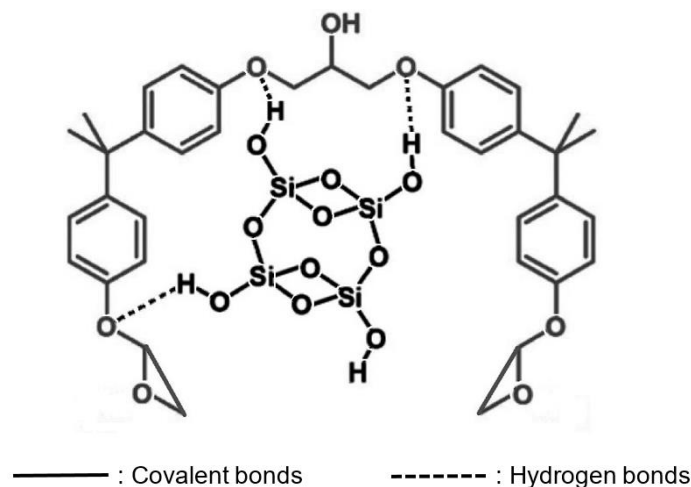


Figure 2.16 A representative interface linking structure of epoxy polymer and silica particle surface (Afzal, 2011)

Although a wide variety of polymer composite systems exist, the common feature among all the systems is that there is a phase boundary between the matrix and the filler, and an interphase layer formed between them. In the interface region there might be two types of polymer chains present. The first one is located as an absorbed contact on particle surface, but the second does not have a link with the particle surface and instead forms entanglements with other polymers. Depending on how close to the bonded surface it is, the interphase has a different structure than either the filler or matrix phases. For a given particle-polymer system, the interphase thickness is not constant and is affected by the degree of chain entanglements, chain flexibility, and adsorption energy, all of which are governed by the surface energies of the nanoparticles and the polymer. The characteristics of the polymer near the interface can significantly differ from the bulk polymer due to the structural differences. The interphase structural features are significant to the overall final mechanical properties of the composite because they govern the load transfer characteristic between the matrix and filler (Ciprari, 2006).

The final properties of particle reinforced composites (PRC) are thought to be primarily determined by the interface regions that form between the polymer matrix and the particles (Tanaka, 2013). Although important models such as Wilkes' Model, Tsagaropoulos' Model, Lewis' Model, and Tanaka's Model, which describe the

features and effects of the interface region, have been established, these models are based on experimental data and theories are limited to explain exact phenomena since the interface region has not been visually examined until now. Detailed information about the interface properties can be found in a comprehensive review study published by Pleşa et al. (2016).

In a specific case of nano particles, high surface energy owing to their large specific surface area makes them extremely unstable, which enable them to undergo chemical reactions with the environment to lead self-aggregating. Therefore, they are strongly prone to agglomerate. Then, the surface of nano particles must be modified to provide an effective repulsive force between them in order to increase their dispersion stability. Due to the high concentration of hydroxyl groups on the surface of SiO_2 nanoparticles, they can easily be functionalized with different molecules (Mallakpour, 2014). For the surface modification of the SiO_2 nanoparticles, a variety of methods are applied, including mechanochemical such as ultrasound sonication, physical by physisorption and chemical by covalent bonding procedures as well as grafting of polymers (Mallakpour, 2018). For example, it is very common application to use a silane coupling agent modified silica nanoparticles to form organic chains with the epoxy by creating Si-O-Si bonds (Li, 2018).

Using electrostatic interactions to disperse nanoparticles is one practical and potential approach. It is well known that the dissociation of the surface silanol groups to create SiO^- causes the surface potential of silica nanoparticles to be negative in an aqueous solution. The dispersion capability of silica and the interfacial adhesion between the matrix and fillers might both be enhanced by electrostatic interactions if positive charge is added to the fluid polymer matrix. Copolymerizing with cationic monomers is another method of introducing positive charge (Wang et al., 2013).

One of the most obvious physical effects of silica particles on the polymer matrices is to improve their mechanical properties. A balance between strength, stiffness, and toughness can be reached in the presence of SiO_2 . The mechanism underlying this phenomenon can be defined as the inorganic silica particles have higher mechanical strength compared to the polymer matrices. Provided that the external force is strong enough, it passes from the polymer matrices to the inorganic phase via the interphase

region. As a result, by using this approach, PRCs perform better mechanical performance than the pure polymers (Mallakpour, 2018).

2.2 Polymer Network Formation and TTT Diagrams

In a complex commercial process like APG (automatic pressure gelation) it is crucial for both economic and product quality purposes to achieve correlations between moldability and the optimum properties of the molding products. On the other hand, establishing a connection between processing variables and material parameters is important for an effective process. The moldability of the resin and the final qualities of the molded products are both significantly influenced by the molding parameters. Besides, the fundamental chemical and physical material characteristics of the resin have a major impact on the final characteristics of molded products and the material's moldability. For instance, cure time in a mold should have a significant impact on the mechanical properties and shrinkage since the final behaviour of molded products depends greatly on the degree of cure reached during the molding cycle. In fact, increasing the cure temperature typically has the same effect as increasing the curing process time. Thus, it would be desired to provide effective methods with a broader scope for the control and optimization of process and product quality. Within this framework, it is a must to know time and temperature dependence of the reaction rate (Kamal, 1974).

2.2.1 Gelation and Vitrification

The principal process used in the thermoset production industries is the use of chemical processes to convert low molecular weight liquid polymers into amorphous solid polymers that consist high molecular weight structure (Dusek, 1986). During the development of a polymer network, there are two basic transitions that might occur, gelation and vitrification. Gelation can be defined as the formation of an infinite network of cross-linked polymer molecules, the critical transformation where the average molar mass is infinite. Vitrification (or glass transition) refers to the transformation from a liquid or rubbery phase to a glassy phase due to increased molecular weight, in which polymer exhibits the typical glass properties (Enns, 1983). The physical features of the thermosetting polymer are significantly changed by

vitrification and gelation. Since the elastic properties of the network are not characteristic of linear or branched low molecular weight resin, gelation is responsible for the transformation from a liquid to a rubbery and covalently cross-linked gel state. When vitrification occurs, the system is transformed from a liquid or gel into a glass when the glass transition temperature increases to the curing temperature (Pascault, 2002).

Gelation and vitrification can be represented together to create different kinds of transformation diagrams. Time-temperature transformation (TTT) diagram is the most popular one which was proposed by Gillham et al. (Enns, 1983). The TTT cure diagram is a visual representation indicating the required time to achieve gelation and vitrification, respectively, during an isothermal cure as a function of curing temperature. It provides a convenient instrument for understanding and visualizing the changes that take place during cure and assists manufacturers to choose a heat schedule to produce cured resin with the required properties.

An isothermal (TTT) curing diagram can be constructed with a series of isothermal cures by plotting the curing temperature (T_c) versus gelation and vitrification times. A logarithmic scale is more suitable for representing time since the reaction rate changes exponentially with temperature (Pascault, 2002). The TTT diagram may be used to understand the relationships between curing reactions, structure of the phases, and properties of the final product.

The majority of the behaviour of thermoset polymers may be explained by the TTT cure diagram, with the effect of gelation, vitrification, and devitrification on the characteristics of the material. Gelation, for instance, inhibits the propagation of a dispersed phase as being in rubber modified systems and slows down macroscopic flow. Vitrification hinders the chemical transformation due to slow nature of diffusion process. Devitrification is the time limit for the material to be able to support a significant load due to thermal degradation. For thermosetting systems, such a diagram may allow the selection of time-temperature curing pathways so that gelation, vitrification, and phase separation take place in a controlled way, resulting in predictable properties of the thermosetting matrices. Since the transformations happen

as a function of time, the TTT diagram is a non-equilibrium diagram (Aronhima, & Gillham, 1986).

Since gelation and vitrification govern all of the characteristics of a thermoset polymer, such as reaction rate, density, rheology, dimensional stability, internal stresses, these transformations can be taken advantage of during cure to enhance process and final properties of material (Simon, & Gillham, 1994). Before explaining the generalized schematics of the TTT cure diagram, it is useful to briefly explain the concept of glass transient temperature (T_g), which is used to determine the phase transitions and creates the basis for creating the diagram.

2.2.2 Glass Transient Temperature (T_g)

The chemical conversion is the fundamental factor affecting the state of the material. The glass transition temperature (T_g) is a characteristic that significantly rises because of chemical conversion changes that occur during thermosetting material cure. T_g can be measured precisely and easily throughout the whole range of cure. These facts imply that T_g can be an accurate and useful parameter for observing the cure of reactive thermoset systems (Wisanrakkit, 1990). T_g is a crucial feature from a practical standpoint since it identifies the temperature at which a material may soften to a catastrophic level in the short term. Important properties such as fracture toughness or yield stress at a given temperature T are directly related to the temperature difference with T_g .

The glass transition that occurs during curing is due to the reduced mobility of the system through the formed covalent bonds, and thus the cooperative movement of a large number of polymers, which are the characteristic of the liquid and rubbery phase of the polymers, are no longer possible. Typically, the glass transition is referred to as a second-order thermodynamic transition. A discontinuity in the first derivative of a thermodynamic function, such as volume (dV/dT) or enthalpy (dH/dT) corresponds to T_g . Traditionally, a first-order thermodynamic transition like melting requires the discontinuity of a thermodynamic functions like enthalpy (H) or volume (V). Nevertheless, since the glassy state is out of equilibrium, T_g cannot be regarded as a true thermodynamic transition (Pascault, 2002).

The majority of the polymer's physical characteristics, including expansion coefficient, gas permeability, storage modulus, refractive index, heat capacity, etc., exhibit discontinuous changes at the glass transition. Differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermomechanical analysis (TMA) are the most extensively employed techniques to measure T_g (Pascault, 2002).

DSC provides the benefit of providing kinetic and thermal data on the reacting system at the same time. The characterization of thermosets via DSC involves measurement of heat flow into or from the sample and a reference, which is used for the comparison purpose depending on the temperature and time (Kamal, 1974).

2.2.3 Time Temperature Transformation (TTT) Diagram of Thermoset

A generalized schematic TTT isothermal cure diagram, which illustrates the main features of the thermoset curing process, is given in Figure 2.17. The diagram shows the different regions of the material encountered in the thermoset curing process, which involves liquid, sol/gel rubber, gel rubber, sol/gel glass, gel glass, sol glass, and char phases in the reaction order. Three critical temperatures which are T_{g0} , $_{gel}T_g$, and $T_{g\infty}$ can be seen on the diagram. T_{g0} is the glass transition temperature of the uncured reactants. Principally, the system is non-reactive below this temperature. $_{gel}T_g$ is the temperature where gelation coincides with vitrification. The system between T_{g0} and $_{gel}T_g$ will vitrify prior to gelling, in principle slowing down chemical reactions and thus preventing gelation. At vitrification below $_{gel}T_g$, the system possesses a low molecular weight, so subsequent heating of the material increases fluidity and easy processability (Aronhima, 1986).

$T_{g\infty}$ is the maximum glass transition temperature of the curing system. The material is initially in the liquid zone between $_{gel}T_g$ and $T_{g\infty}$, which enables it here soluble and low molecular weight. Gelation starts as the reaction proceeds, and the sol/gel rubber zone is entered. In this region, a miscible binary combination is typically formed by finite molecular weight sol and infinite molecular weight gel. T_g eventually reaches T_c at the point where vitrification is considered to begin. Vitrification significantly slows down molecular and sub-molecular mobility, which in theory causes chemical

processes to proceed more slowly. The material is fluid or rubbery when $T_c > T_g$ and it is glassy when $T_c < T_g$. The vitrified zone formed between $_{gel}T_g$ and $T_{g\infty}$ in the absence of complete curing comprises both gel and sol components (Gillham, 1986).

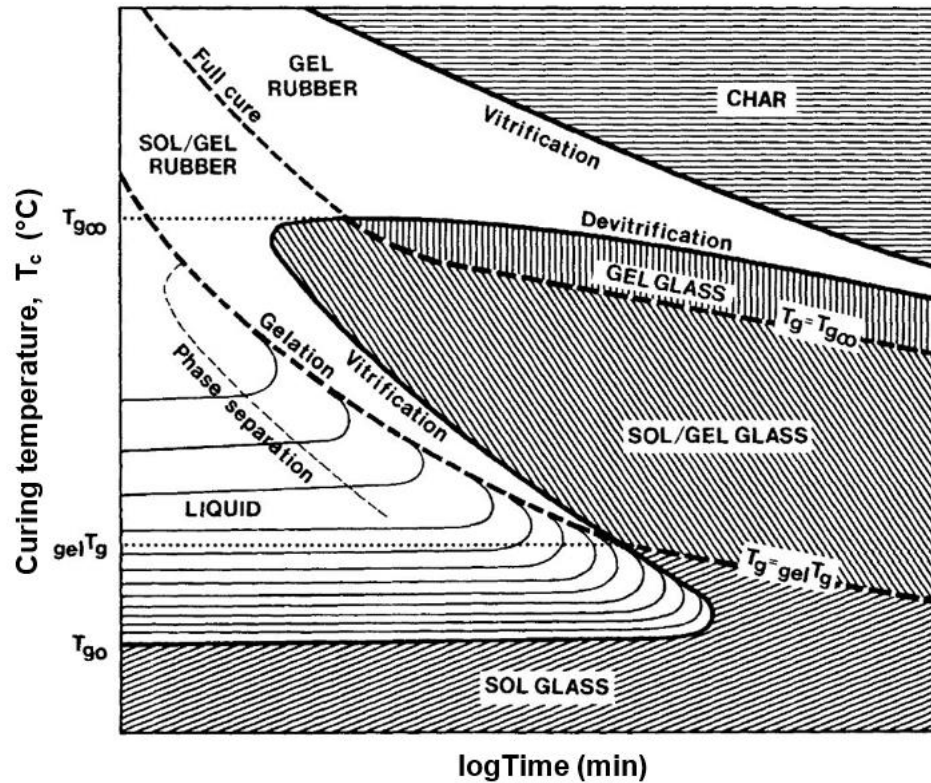


Figure 2.17 Three critical temperatures, T_{g0} , $_{gel}T_g$, and T_g , are shown on a schematic TTT isothermal cure diagram representing a thermoset system (Gillham, 1986)

Full cure line represents the time required for T_g to equal $T_{g\infty}$ for any given T_c temperature. Hence, the full cure line where $T_g = T_{g\infty}$ separates the sol/gel glass zone from the gel glass zone, and the sol/gel rubber zone from the gel elastomer zone, respectively. Full cure must be determined as only fully cured materials can be considered to establish meaningful structure-property connections between the various systems. The most direct way to achieve full cure for systems where $T_{g\infty}$ may be reached without degradation is by curing above $T_{g\infty}$. The material will be in gel condition but not vitrify during an isothermal process above $T_{g\infty}$ if there is no degradation. As can be seen from the upper part of the full cure line, gel rubber or elastomer is formed at temperatures above $T_{g\infty}$ after prolonged isothermal cure.

Since almost all of a thermoset's characteristics, including rheology, reaction rate, density, dimensional stability, and internal stresses, are controlled by gelation and vitrification, these transitions can be taken advantage of during cure to optimize processing and final material properties (Enns, 1983).

At high temperatures with prolonged cure time, chemical processes that don't cure result in degradation. Thermal degradation can cause devitrification as T_g decreases at isothermal temperature because of reduction in crosslinking or formation of plasticizer material. When T_g rises at isothermal temperature due to an increase in crosslinking or volatility of low molecular weight plasticizer compounds, degradation can also lead to vitrification, as in the case of char production. Thermal degradation and curing reactions compete in systems with high T_g (Gillham, 1986).

2.2.4 Determination the Degree of Cross-Linking by DiBenedetto Equation

The mechanical properties and physical behaviour of the long-chain polymers depend on the chain mobility and chemical structure. Besides, the relationship between neighbouring molecules, which may be in the form of chain entanglements, crystallinity, hydrogen bonding or rigidity also effect physical and mechanical properties. Crosslinking, which represents durable chemical interactions between molecules that were once separate, is a very significant kind of this intermolecular binding. They can form directly between polymer chains, such in C-C bonds, or indirectly, like in S bonds in the vulcanization of rubber (Güven, 1988). The process of forming a polymer network because of the chemical interactions between the chains of linear polymer or forming a three-dimensional fishnet like configuration from monomeric resin reactants, is called crosslinking. With chemical interconnections that prevent moving or slipping of long chains, the developed network polymer has an infinite molecular weight. Schematic representation of a linear and a crosslinked polymer is given in Figure 2.18.

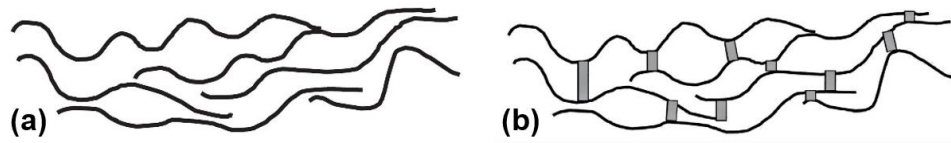


Figure 2.18 Schematic representation of a thermosetting polymer, (a) before crosslinking, and (b) after crosslinking (Biron, 2014)

Figure 2.19 also shows the crosslinking reaction of DGEBA epoxy resin with 2 functionality and a hardener with 4 functionality such as hexamethylenediamine. In crosslinking of this system, tetravalent hardener reacts via its reactive hydrogen atoms, which generates great number of hydroxyl groups. These groups play an important role in terms of adhesive properties (Gnanou, 2008).

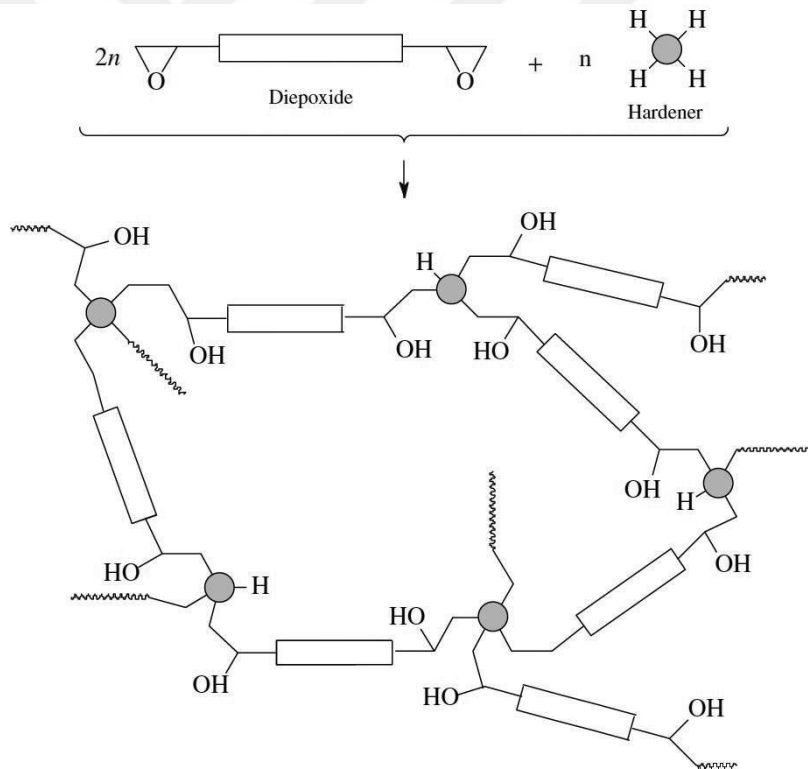


Figure 2.19 Schematic representation of a crosslinking polymerization of a diepoxide polymer with a hardener with 4 functionality (Gnanou, 2008)

Crosslinking can be explained by the viscosity change in time at a determined temperature. Regarding the Figure 2.20 the viscosity of the polymer mixture is η_0 beginning at t_0 . At the beginning of the curing process under the influence of heat,

larger and branch-like molecules are formed, and number of molecules are reduced. Since all the crosslinked reactions are exothermic, viscosity decreases because of the heat produced by the exothermic activity. The mixed viscosity develops along with its molecular weight and soon outpaces any decline driven on by heat. The molecular growth proceeds until a macroscopic solid palpable mass which is similar to a gel can be detected. This time is usually known as gel time or t_{gel} .

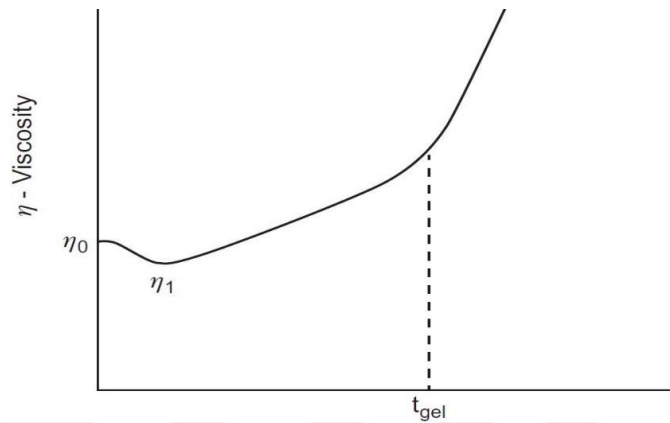


Figure 2.20 Changing of the viscosity depending on time for a fluid thermoset system at a fixed temperature (Dodiuk, 2014)

Consequently, all the chains in the structure are linked together at the gel point to form an infinite molecular weighted network. After the gel point, polymerization continues to complete network generation. Viscosity, from this point reaches to infinity, in which the viscous polymer structure transforms to a nonfluid macromolecule solid. In the industry, the word "curing" is most generally used to describe this gelling process. Curing of a thermoset means to cause it crosslinking (Dodiuk, 2014).

The increase in viscosity depending on time, the formation and progression of the crosslinked network structure at the gel point, and finally the formation of the structure with mechanical properties are given in the Figure 2.21 depending on the conversion degree or time (Turi, 1997).

Crosslink density known as conversion degree (or degree of crosslinking) is a critical parameter, especially in determining the mechanical properties of the cured resin. The mole fraction of monomers in the polymer that are crosslinked is known as

the conversion degree (α). In general, a thermoset with an increased crosslink density has more brittle structure, while a lower density provides greater flexibility, better impact strength and increased elongation (Dodiuk, 2014). On the other hand, the relation between T_g and the conversion α of the thermoset polymer is crucial to understand the curing process (Pascault, 1990).

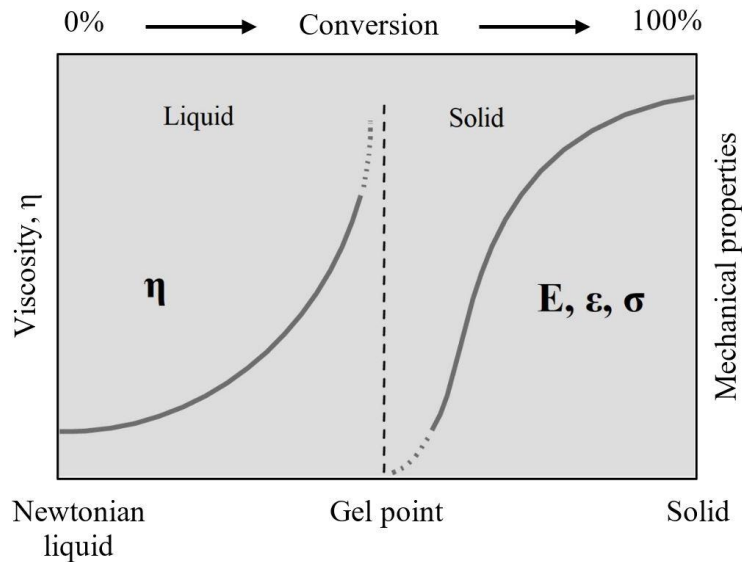


Figure 2.21 Macroscopic evolution of rheological and steady-state mechanical properties of the epoxy thermoset as a function of conversion during network formation (Turi, 1997)

There are several methods to measure the crosslink density of a thermoset resin including chemical analysis, swelling, parallel plate rheometry, infrared spectroscopy (IR), and differential scanning calorimetry (DSC), which measure the degree of consumption of the active resin sites (Dodiuk, 2014). Crosslink density has a significant impact on the glass transition temperature of the thermoset (T_g). Crosslinking always increases the T_g of the polymer (Nielsen, 1969).

Nielsen (1969) reported the unpublished results performed by DiBenedetto, which included the effect of crosslinking on the physical properties of the polymers and led to a theoretical equation regarding the shift in glass transition temperature and the degree of reaction. As the crosslinking reactions progress, the segmental mobility of the polymer chains, which is influenced partially by the crosslinked structure, decreases. This decrease in segmental mobility is reflected by the increase in T_g as the

network expands. The proposed model as given with Equation 2.1 relates the crosslink network formation in the polymer structure to chain segmental mobility (Fuller, 1990).

$$\frac{T_g - T_{g0}}{T_{g0}} = \frac{\frac{\epsilon_\alpha}{\epsilon_m} - \left(\frac{F_\alpha}{F_m}\right)\alpha}{1 - \left(1 - \frac{F_\alpha}{F_m}\right)\alpha} \quad (2.1)$$

In Equation 2.1, α is the crosslink density expressed as the mol fraction of monomer units present at crosslinks at any stage of the reaction, T_{g0} is the glass transient temperature of uncured system where $\alpha=0$, F_α/F_m is the ratio of segmental mobilities for crosslinked and un-crosslinked polymers while $\epsilon_\alpha/\epsilon_m$ is the corresponding ratio of lattice energies which may be defined as:

$$\frac{\epsilon_\alpha}{\epsilon_m} = \frac{d_m (M_0)_\alpha}{d_\alpha (M_0)_m} \left(\frac{\delta_\alpha}{\delta_m}\right)^2 \quad (2.2)$$

In Equation 2.2, d is density, M_0 is the molecular weight of a participant repeating unit in the crosslinked or un-crosslinked state, and δ is the solubility parameter. Enns (1983) demonstrated that when both $\epsilon_\alpha/\epsilon_m$ and F_α/F_m were taken into consideration as variable parameters, a very good fit of numerous experimental T_g - α correlations could be achieved. Additionally, by using Equation 2.1 the ratio of both parameters can be demonstrated by the Equation 2.3,

$$\frac{(\epsilon_\alpha/\epsilon_m)}{(F_\alpha/F_m)} = \frac{T_{g\infty}}{T_{g0}} \quad (2.3)$$

where $T_{g\infty}$ is the maximum glass transition temperature at $\alpha=1$. Pascault (1990), by incorporating Equation 2.3 into Equation 2.1 and making $F_a/F_m=\lambda$ introduced Equation 2.4, the most practical and convenient form of expression proposed by DiBenedetto,

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha} \quad (2.4)$$

where λ is regarded as a variable parameter with a range of 0 to 1.

The general outline of the derived curves is shown in Figure 2.22. The relative increase in glass transition is greater at higher reaction ranges. This agrees with the sharp rise in crosslinking density observed above the gel point, which provides a qualitative explanation for why Equation 4 exhibits fair agreement with the results of the experiments (Pascault, 1990).

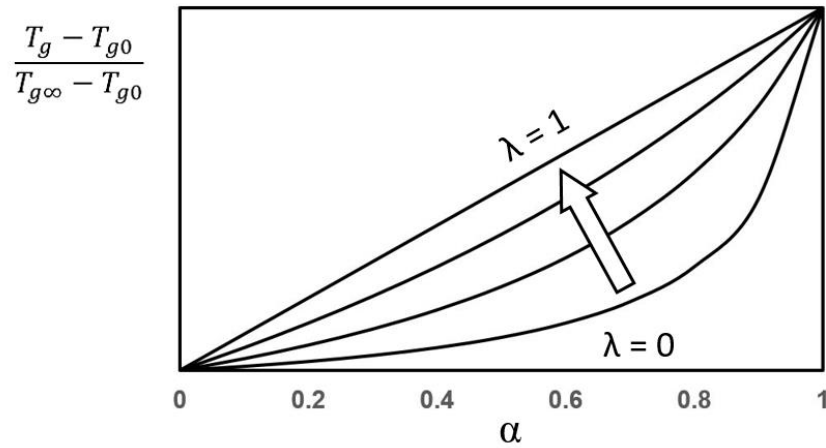


Figure 2.22 Relative increase in T_g as a function of α where λ changes between 0 and 1 (Pascault, 1990)

2.3 Fracture Behaviour of Unreinforced Epoxy Resin

2.3.1 Amorphous Polymers and Entanglement Structure

Any material that is entirely non-crystalline is referred to as amorphous. Amorphous solids such as epoxy resins combine the disordered structure of a liquid with the rigidity of a crystal. Amorphous polymers in the solid state can be thought of simply as frozen polymer liquids and regarded as the state of aggregation of the elements in the solids. The major element of amorphous polymers is the formation of solid-state coils by non-crystalline macromolecules in a significantly diluted solvent. The diameter of the coil, which varies typically between 10 and 30 nm, is proportional to molecular weight. A loosely arranged, single coil of this type has a density that is less than 1% of the density of the bulk polymer. Consequently, several segments of other adjacent macromolecules may occur in the volume of a coil. As a result of this intense interpenetration, great number of molecular entanglements are created as can be seen in Figure 2.23. These entanglements serve as physical points of connection and play a significant role in the stress transmission between macromolecules as well as the strength and toughness of a polymeric body by holding the macromolecules together (Michler, & Calleja, 2012). Another contribution of entanglements is to create van der Waals forces between adjacent segments of macromolecules.

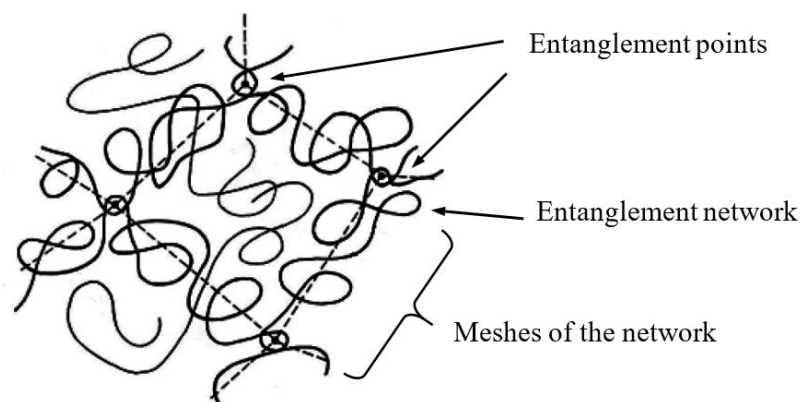


Figure 2.23 Entanglement structure of amorphous polymer (Michler, 2012)

Coiled macromolecules have a lower packing density than morphologies in which the molecular units are arranged parallel to one another. "Free volume" refers to the space between molecular segments that is not occupied by molecules and has a substantial effect on the mechanical characteristics of the polymer. A network of meshes can be formed by connecting the entanglement zones between the macromolecules. There are signs that the interior of the meshes in the entanglement network may contain unentangled macromolecular fragments, chain ends, or shorter macromolecules, making the interior of the meshes slightly weaker than the entanglement network. These small density fluctuations can be considered as a weak molecular structure, which may prompt craze formation micromechanical processes (Michler, 2012).

The primary function of cross-linking is to restrict a molecule's overall flow in relation to its neighbours. Since two cross-links per molecule are sufficient to create a continuous network, this condition is satisfied as soon as they are present. Cross-linking between macromolecules decreases molecular mobility, increasing yield stress and reducing strain at break values with a tendency for embrittlement. The strength of covalent intramolecular bonds dominates the bond breakage energy per area in cross-linked polymers and high molecular weight glasses. The more cross-links, tie points, or entanglements present, the more covalent bonds must be broken per unit area, which leads to an increased strength of the polymer (Andrews, & Reed, 1978).

The average molecular weight between crosslinks and final toughness of the polymer can be arranged by changing epoxy/anhydride mixing ratio. At stoichiometry ($A/E=0.8$ for current dissertation), all resin chain tips are in principle attached by anhydride crosslinks, and the chain length of the final network is the shortest. However, in out of the stoichiometric compositions, completely detached chains and chain branching are inevitable, which effectively improve the overall average chain length of the network. Thus, when compositions deviate from stoichiometry, the molecular weight of the epoxy network increases. The findings show that the rise is often more evident for epoxy excess formulations (Dusek, 1986). It is generally acknowledged that stoichiometric mixtures of resin and hardener produce the highest crosslink density and maximum possible T_g (Lemay et al., 1984).

The main characteristic of amorphous polymers is their high-strength mechanical properties and brittle and to some extent ductile deformation behaviours. This behaviour is caused by the localized deformation zones that occur under stress, such as crazes or shear bands, which are the main deformation mechanisms for the amorphous thermoset polymers. These two deformation mechanisms, as given schematically in Figure 2.24, can produce quite different results. Typically shear deformation is attributed to ductile failure, while crazing often results in brittle fracture. Generally, one deformation mechanism is typically favoured over the other. For instance, crazing might be seen at high strain rates, but shear deformation develops at low strain rates. Ductile shear flow is frequently seen at elevated temperatures, but at low temperatures, brittle fracture caused by a craze is more common for bulk materials. As a result, these two damage mechanisms may develop according to the loading conditions, and they can also replace each other locally during deformation (Kausch, 1990).

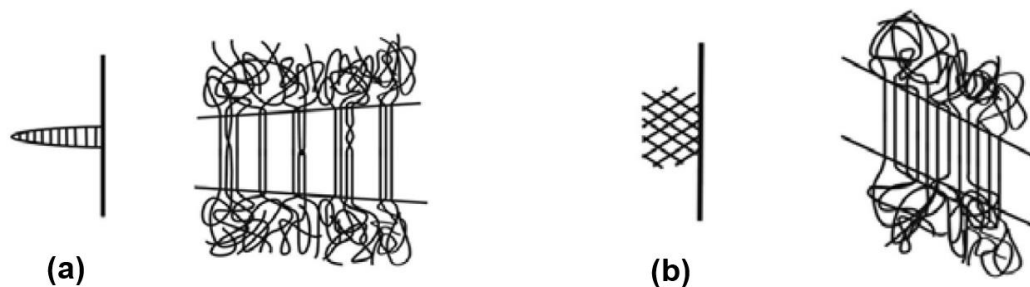


Figure 2.24 Comparing the deformation mechanisms of amorphous polymer under tensile loading, (a) crazing due to nanovoid formation by stretching of macromolecules, and (b) shear yielding due to gliding and stretching of macromolecules (Michler, 2012)

2.3.2 Crazing

A craze can be defined as a flat deformation zone with significantly elongated, mostly fibrillar matter and intermittent voids that forms in amorphous and semicrystalline polymers perpendicular to the primary stress axis. Crazes are localized microcracks bridged by fibrils of plastically deformed polymer material. The polymer fibrils of about 5~15 nm diameter are strained in loading direction and elongated voids

with diameters up to about 50 nm separate the crazes. The craze-bulk interface is about 10 nm thick and reasonably sharp (Michler, 2012).

The shape of crazes is significantly influenced by molecular entanglements. Surface flaws or particulates of dust on the polymer matrix, as well as interior flaws like entrapped air bubbles and molecular imperfections typically serve as the initiating sites for the crazes. Crazing is the result of localized or inhomogeneous plastic deformation of the structure caused by strain softening. Sharp cracks or flaws in products with thick sections promote initiation of the craze, which leads to a brittle fracture, rather than a bulk shear yielding process, which leads to ductile failure. Crazes can start, develop, and eventually break down to form cracks at stresses lower than those required to generate bulk shear yielding. This results in brittle fracture, which only requires a minimal amount of fracture energy (G_c) or stress-intensity factor (K_{Ic}). Brittle crazing process is also favoured by plane-strain deformation condition, increased strain rates, low temperature conditions, as well as hostile environments (Argon, 1975).

According to Kramer (1983) three different consecutive mechanisms can lead to craze nucleation which are initially the formation of shear-induced local plastic deformation around a flaw that causes the accumulation of large lateral stresses, then, relaxation of the triaxial constraints by the formation of voids, and finally, growing of the void and strain hardening of the adjacent polymer ligaments while alignment of the molecules continues. The initiated craze structure becomes steady in this fashion, and if the proper stress conditions are present, the craze can then propagate. It is evident that the stress increase present in the initial step, which promotes more shear deformation, will suppress the development of a craze nucleus (Kausch, 1983).

A craze may be distinguished from other localized types of plastic deformation in polymers, including shear bands, by its fibril structure. The load-bearing components of the craze are the tiny fibrils. The fibrils, however, can decompose to create substantial voids, which can then develop into sub-critical fractures and cause sudden fracture (Kramer, 1984). Therefore, the mechanisms of craze fibril creation and breakdown, which is given schematically in Figure 2.25, are crucial for determining how the polymer would fracture in the end.

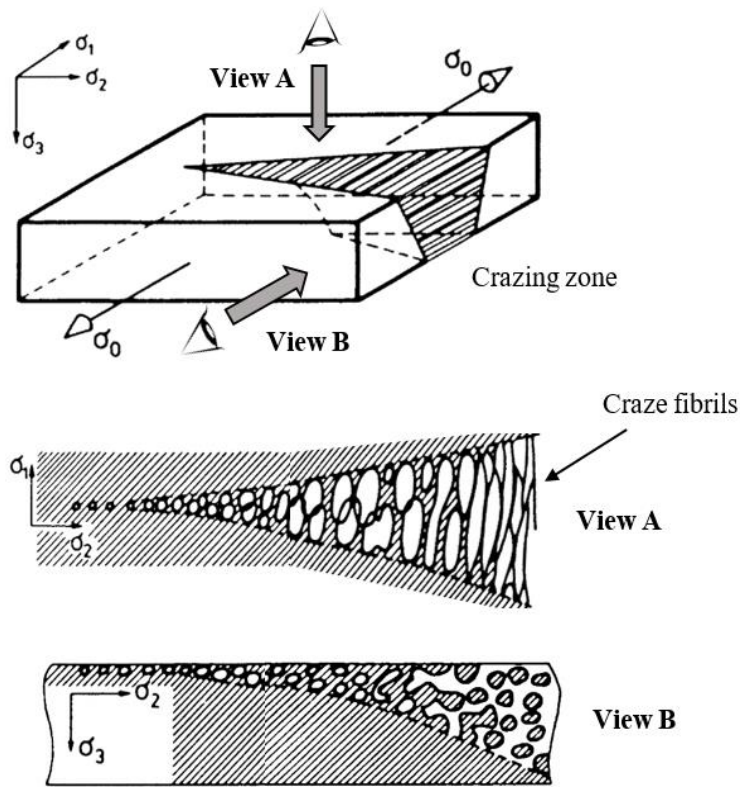


Figure 2.25 Schematic representation of craze formation by convolution-based craze generation in an amorphous polymer, which results in the void/fibril craze structure (Kausch, 1987)

Fibrils are formed at the same time at the crack tip while the craze grows in areal range, and at the bulk/craze interfaces as the width of the craze increase (Plummer, & Donald, 1990). The stress-whitening phenomena results from intense light scattering from the fibril structured crazes is a visual distinguishing feature of craze deformation (Kausch, 1987). The crazing behaviour of glassy polymers is influenced by the characteristics of the entanglement network. Because, stress induced instability of the entanglement structure, which are trapped during the glass transition, govern the onset of inherent crazes. Higher molecular weights result in larger coils and an increase in the total number of entanglements in each coil. This increases fracture resistant and strength of the fibrils due to disentanglement or slippage. Furthermore, strain hardening, which takes place in later stages of crazing, due to the molecular reorientation in fibrils, significantly strengthens and stabilizes the craze framework (Kinloch, 1995).

In a highly entangled polymer glass such as epoxy, the generation of new surface is necessary for craze fibril formation. For this process to operate, it is geometrically necessary for some strands of the entanglement network to be lost. Chain scission is now widely accepted as a major process of entanglement loss, especially at low temperatures, despite the possibility that some of it still happens because of chain disentanglement. In the attempt to generate a surface that is greater than the van der Waals surface energy for highly entangled polymers, the requirement for chain scission results in an additional work term. The stress for crazing increases in comparison to that for shear deformation due to the extra surface energy (Kramer, 1984).

Lilley & Holloway, (1973) has investigated different epoxy systems all of which included unmodified DGEBA epoxy resin. They reported that they encountered craze-like structures in the areas close to the crack tip in their work conducted with Araldite epoxy resin polymer systems that were fully cured with anhydride hardener. Lilly et al. state that craze can occur in fully cured epoxy structures (Lilley, & Holloway, 1973).

Gledhill et al., (1978) have investigated crack propagation behaviour of DGEBA epoxy resin cured with triethylenetetramine (TETA) thermosetting system. They pointed out that crack propagation in the epoxy polymer system is caused by craze formed in front of the crack. They claim that shear yielding rather than craze occurs at the crack tip in fully cured epoxy systems, although there is evidence of small craze formation in partially cured epoxy resin systems (Gledhill, Kinloch, Yamini, & Young, 1978).

Multiple crazing in polymers generally can result in yielding and serve as a process for toughening. It is a common method to specifically prepare polymers containing a second soft or hard particle phase where the multiphase polymer ensure that it is possible for polymer to benefit from this toughening process (Kinloch, & Young, 1995).

2.3.3 Shear Yielding

Shear yielding that involves the creation of micro shear bands is essential for the formation of cracks. Localized mechanisms that dissipate plastic and viscoelastic energy usually appear adjacent to the crack tip during even brittle crack growth in polymers. As with crazing, shear yielding is also a micro mechanism in the material that often serves as the primary source of energy absorption (Kinloch, 1995).

Strain softening is a property of all isotropic glassy polymers due to shear bands in the material although some that orientate and rapidly strain harden subsequently. Therefore, all these polymers have a tendency to produce shear bands when the factors that favour crazing are suppressed. Many polymers exhibit the orientation or strain hardening, where the true stress increases after yield and any strain softening has taken place. It is known as orientation hardening because this increase happens at high stresses when the polymer chains have already started to become orientated (Haward, & Young, 1997).

Nearly all glassy polymers undergo inhomogeneous deformation after the tensile yield point in the absence of crazing and fracture. The resulting strain is localized neck formation, in the classical tensile tests. The development and coalescence of inclined shear zones accompany neck formation, as shown in Figure 2.26. At the maximal load or nominal yield stress, a single macroscopic shear band rapidly transforms into an accumulated shear fields with almost axial symmetry (Stokes, & Bushko, 1995).

The constraint that the nearby material exerts on the deforming area determines the forms of strain inhomogeneity that may emerge. The deformation occurs in plane strain, which means the structure is usually constrained in two dimensions around the crack tips within the body of a solid. For an isotropic material, assuming the volume is constant, the deformation is a simple shear deformation of a band with an angle of 45° , and this band is referred to as a micro-shear band (Kinloch, 1995).

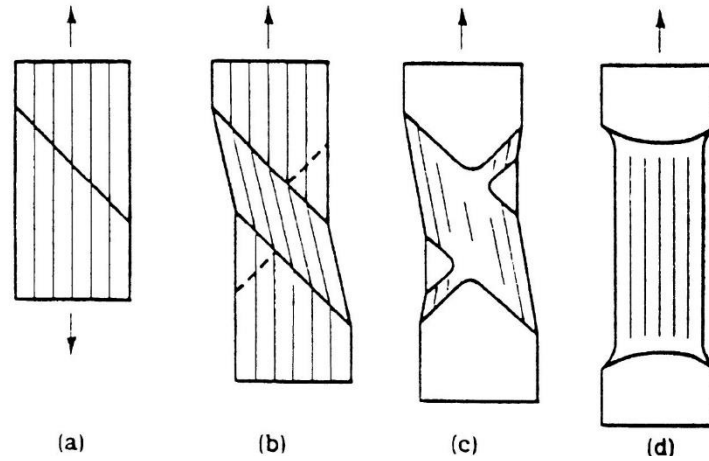


Figure 2.26 Schematic representation of neck formation under tension (Stokes, & Bushko, 1995)

Diffuse shear zones, in addition to micro-shear bands, are another type of shear band seen in many polymers. The strain in diffuse shear zones is comparatively low and they have a viscoelastic nature as opposed to a plastic one. In contrast to the micro-shear bands, nevertheless, their contribution to the total strain rate is very high (Kramer, 1975). Micro-shear bands and these fine deformation bands are not independent but interconvertible during deformation. Compared to diffuse shear zones, slip bands are substantially more localized. Wu and Li (1976), in their study on deformation of polystyrene, observed that a shear fracture was created when a piles of micro-shear bands propagated over the material, although the failure was basically brittle because of the little total plastic strain. In contrast, when the conditions were favourable for a diffuse shear zone, consisting of fine deformation bands, spreading throughout the specimen, a significant overall plastic strain was produced, resulting in a significant kink, and as a result, a ductile fracture was observed (Wu, & Li, 1976).

Many researchers have thought about the possibility that micro-voids formed at the intersections of the shear bands might initiate cracks. In essence, it is proposed that polymer imperfections operate as stress concentrations and allow micro-shear bands to be created by the shear stress. Chain disentanglement or scission preferentially take place in the over stressed material at the micro-shear band intersection locations, creating micro-voids that serve as the initiating places for crack formation (Argon, 1975; Wu, 1976).

Chain molecules cannot slide at temperatures below roughly 80% of the T_g because the molecular bonds are too strong, and the specific volume is too small. Upon loading, the molecules become viscoelastically straightened, and failure occurs, mostly resulting in the breakage of the intermolecular bonds (Rösler, Harders, & Bäker, 2007).

Crazing and localized shear yielding are essentially competing processes in brittle tensile fracture. Both are clearly favoured by the polymer, which exhibits a strain-softening behaviour and hence highly localization of plastic strain. In the cross-linked polymers, macromolecules are generally linked by covalent bonds, which inhibits crazing and causes brittle fracture by a localized shear yielding process (Donald, & Kramer, 1982).

It should be emphasized that localized shear yielding and crazing are not always mutually exclusive micro mechanisms. Interactions can occur between them in certain polymers where both can be seen concurrently. These interactions could be crucial in providing multiphase polymers a high degree of toughness. When shear bands initiate at the craze tip, they acts as a craze terminator, blinding the craze. On the contrary, when an advancing craze encounters a previously formed shear band, it cannot relieve the stress at the craze tip (Donald, Kramer, & Kambour, 1982; Andrews, 1978; Bucknall, Partridge, & Ward, 1984).

Another potential toughening mechanism that might produce ductile polymers is a multiple crazing mechanism triggered by shear yielding. Gross shear yielding may be accompanied by multiple crazing.

Although there are many theories about plastic deformation in amorphous structures, such as Eyring theory, Rouse-Zimm theory, Dislocation theory by Bowden and Raha, and Robertson theory, which explain shear yielding in molecular terms, the Argon theory, which is consistent with tests performed at low temperatures below T_g with many amorphous polymers, is mostly accepted (Haward, 1997). Although the mathematical analysis of the theory is rather complicated, the final equations predicting the link between the shear yield stress τ and shear modulus G are very simple (Kinloch, 1995).

The most definitive and important information on the shear yielding process is that intermolecular forces are the source of the resistance to plastic deformation after the yield point. Argon (1973) suggests that the elementary process of deformation includes the formation of a pair of folded knees or kinks of the chains. According to his theory, the glassy polymer is made up of a network of smooth chain molecules that are interpenetrating one another in a zigzagging pattern at random, resulting in an initially isotropic distribution of the orientations of the molecular segments. Then he provides a convincing molecular theory of local strain creation, which is seen in Figure 2.27 and involves rotating of a chain segment from originally random orientations into a direction parallel to the main tensile stretch.

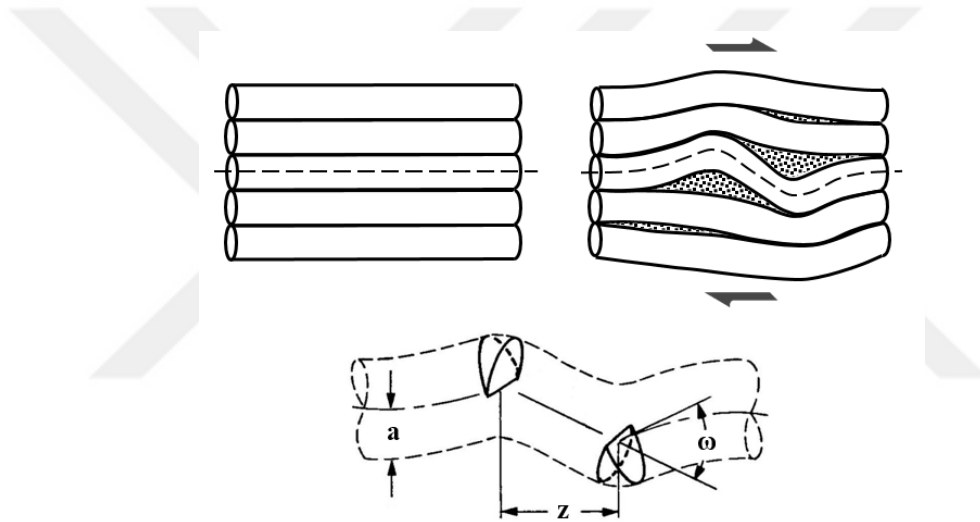


Figure 2.27 Schematic representation of parallel chains deforming under the effect of increasing plastic strain caused by a pair of kinks in a polymer structure (Argon, 1973)

The process of segment rotation involves creating two kinks along the chain, spaced apart by z , bending angle ω of 115° which is the bond angle between C-C-C atoms. Twisting neighbouring backbone bonds equally but opposite displacements results in the formation of the kink pair. The resulting strain is proportional to $a^2\omega^2z$, where (a) is either the radius of a single chain or the radius of a group of chains that are collaboratively deforming. Argon determines the net energy ΔU of a kink pair with the size of z resulting from elastic deformation of the surrounding environment with shear modulus G and Poisson ratio ν , decreased by work produced by the applied stress τ (Argon, 1973).

2.3.4 Shear Yielding vs. Crazing

The equilibrium of crazing and shear is particularly sensitive at room temperature. For polymers with very high entanglement densities, which is the density of strands in the entanglement network like polycarbonate (PC), shear is dominant while for polymers with low entanglement densities like polystyrene (PS), crazing is always seen.

Polymers that are strongly entangled and require significant stress to craze through scission tend to have high T_g . Consequently, their intermolecular friction coefficient is high at ambient temperature. As a result, disentanglement is difficult to achieve, which will increase the stress associated with crazing. Because of this reason shear yielding is usually associated with the highly entangled polymers (Legrand, 1969; Pitman, Ward, & Duckett, 1978).

Berger and Kramer (1988) studied with crosslinked PS of various strand densities to investigate the dominant type of fracture depending on the temperature and cross-link density. Figure 2.28 shows a plot of deformation modes depending on the two changing parameters.

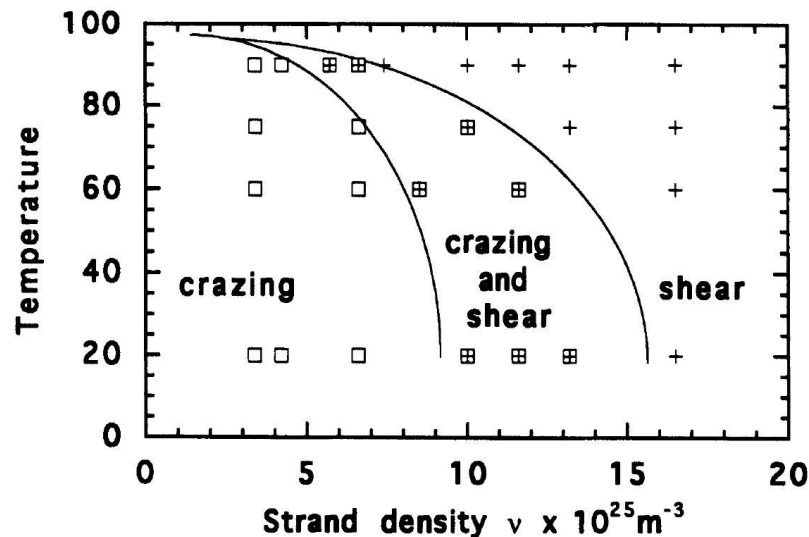


Figure 2.28 Results show the primary plastic deformation modes seen in crosslinked PS depending on the temperature and strand density (Berger, & Kramer, 1988)

Shear involves only local segmental motion. In contrast, crazing is strongly affected by the strand density and surface energy to create micro voids. Therefore, shear at low temperatures turns into crazing at high temperatures. Because this parameter directly affects the energy barrier for scission, the transition is dependent on the crosslink density (Haward, & Young, 1997).

At room temperature, scission processes for a polymer like PS actuate crazing, but as the temperature rises, disentanglement starts to play an important role. PS is a low-density entanglement polymer and increasing cross-link density may have tendency for shear, which leads to a less damaging deformation mechanism. Therefore, it makes sense to consider that intentionally generating high level of crosslinks to increase strand density might be beneficial. Epoxy polymers like other thermosets are considered brittle. But an increase in shear can be observed by decreasing the crosslink density. As a result, altering the crosslink density allows for a wide range of responses. For instance, as being in the epoxies, decreased strand density from its very high value may promote shear deformation, which leads to improved mechanical properties. Glad and Kramer (1991) in their micro-deformation study conducted with epoxy thin films, concluded that epoxies with high strand density favour shear deformation over crazing (Glad, & Kramer, 1991). On the other hand, since they worked with thin epoxy films, crack initiation and propagation occurred in plain stress mode. Since the crazing deformation mechanism mostly prefers the plain strain mode as being in the bulk materials, it may not be correct to generalize the results they found to the structures that show plain strain behaviour.

2.4 Linear Elastic Fracture Mechanics (LEFM)

The definition of a fracture is the development of surfaces within a solid. In a brittle fracture, this definition is clear, but not as much in a ductile fracture where crack propagation is accompanied with blunting. Fracture in a structure occurs as a result of breaking the atomic cohesive bonds that provide structural integrity at atomic scale when forced more than they can withstand. A material's theoretical cohesive strength is approximately equal to E/π , although for brittle materials, experimental fracture strengths are often ~ 3 orders of magnitude lower than this value (Anderson, 2017). Griffith (1920) first claimed that the differences between the real strengths of brittle

materials and theoretical predictions were caused by defects or flaws in these materials. As a result, the imperfections must decrease the overall strength by increasing local stress.

The study area of fracture mechanics is the creation of mathematical rules that determine the amount of stress required for the propagation of a pre-existing crack in the material. Linear elastic fracture mechanics (LEFM) methodology is used to determine the correlation between applied stress and crack size.

Since the thermosets essentially have linear elastic stress-strain behaviour and are frequently brittle, which is the prerequisite for the application of the method, LEFM and test methods can be applied for these group of the material (LeMay, & Kelley, 1986).

The energy criteria and the stress intensity technique are two main alternative methods for fracture analysis. Both of these are actually comparable in some situations. According to Griffith (1920) fracture may happen when a crack develops and releases enough stress field energy to meet the demands of the new fracture surfaces. The elastic or potential energy of the loading system is the source of the released energy. Crack propagation is only possible when the available energy is enough to surpass the material resistance. This energy dissipation may be provided by surface energy, plastic deformation, or another sort of crack propagation-related energy dissipation mechanism. Therefore, this approach gives an estimate of the energy needed to grow a crack throughout the unit area, which is designated as fracture energy and is represented by G_{ic} (Kinloch, 1986).

Irwin (1957) and Orowan (1949) modified the Griffith's definition to express for the materials which can be plastically deform, whereas Griffith's model involved just ideal brittle material such as inorganic glasses (Anderson, 2017).

Despite the fact that the energy balancing approach offers valuable conceptual and practical techniques to guide design choices, its limitations provide a great deal of uncertainty when determining the risk of component failure. An elastic theory-based stress analysis provides a more comprehensive and versatile method for addressing the

fracture of components with flaws. Westergaard (1939) and Irwin (1968) developed a crack tip certain stress-function solution associated with the three major loading modes shown in Figure 2.29, which associate the localized stress concentration at the crack tip to the applied stress σ . Keep in mind that these modes include various crack surface displacements (Hertzberg, 2013).

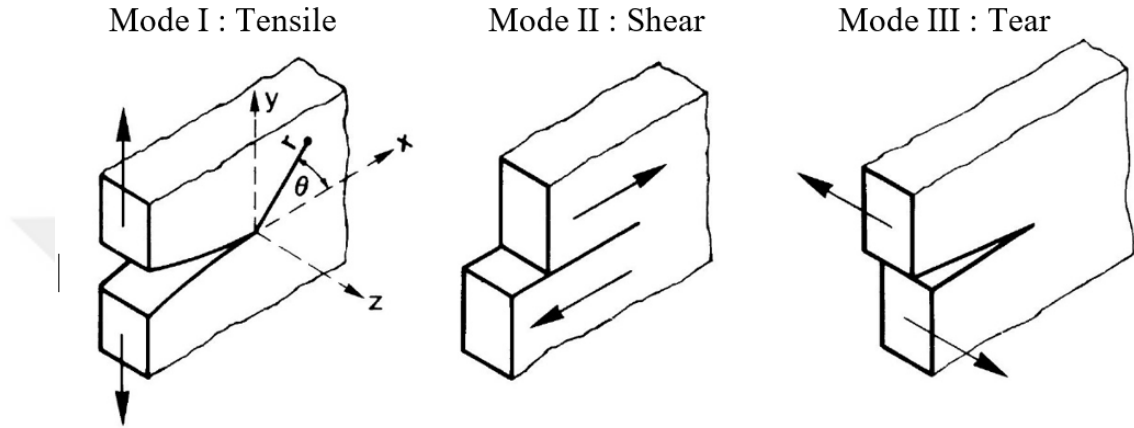


Figure 2.29 The three different loading situations that might be used for a crack, which are Mode I: crack opening, Mode II: sliding, and Mode III: tearing mode (Kausch, 1987)

Figure 2.30 depicts a sharp crack in an infinite, unidirectionally stressed plate (plane stress condition), assuming Hookean behaviour and finite strains. The solutions near the crack tip have the format of equation 2.5

$$\sigma_{ij} = \frac{K}{\sqrt{2\pi r}} f_{ij}(\theta) \quad (2.5)$$

where σ_{ij} are part of the stress tensor at a certain location, r and θ are the polar coordinates of the location, based on the crack tip.

According to Irwin (1968), the stress intensity factor, K , is a measure that may be used to describe the stress field surrounding a sharp crack in a linear elastic material. This factor turns into K_{Ic} where the subscript I indicates that a crack is stressed in Mode I, tensile opening mode. He claimed that when the value of K surpasses a specific critical value, K_{Ic} , fracturing develops. As a result, K_{Ic} is commonly known as the

fracture toughness, which is a measure of a material characteristic while K_I is a stress field parameter that independent of the material (Kinloch, 1986).

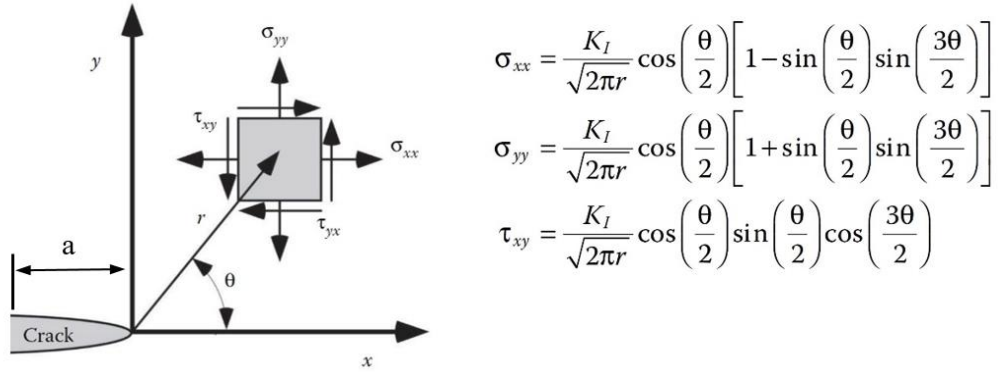


Figure 2.30 Set of the coordinate axis in front of a crack tip and stress fields for Mode I cracks in elastic materials after the crack tip (Anderson, 2017)

Due to the similarity of the stress field in the area at the crack tip because of the singularity of the stress field near the crack tip, the stress distributions for different geometries may then be deduced from the results of the investigation of one geometry (Rösler, 2007).

Essentially, K acts as a scale factor to determine the size of the stress field at the crack tip. Irwin (1968) states that $K=f(\sigma, a)$ where the functionality depends on the way in which the stresses are loaded and the configuration of the cracked component. Consequently, the stress intensity factor K_I can be characterized employing the external stress σ , crack dimension, and the loading geometry as given with the Equation 2.6.

$$K_I = \sigma\sqrt{\pi a}Y \quad (2.6)$$

where (a) is half length of a sharp crack on a plate, and Y is a geometry factor that considers various geometries. If the load increases and hence the stress intensity factor K_I , the crack would eventually propagate when K_I reaches a threshold value of the fracture toughness K_{Ic} . Consequently, since fracture toughness is a feature of the material, Equation 2.7 provides the failure criteria for Mode I loading.

$$K_{Ic} = \sigma_c\sqrt{\pi a}Y \quad (2.7)$$

where σ_c is the critical stress that will cause a crack with an initial length of $2a$ to propagate.

As a result of the crack tip distance (r) entering the denominator, the stress functions are unique. Figures 2.31 shows an example of the stress fields at the crack tip of 10 mm length where a plate is loaded with 100 MPa stress.

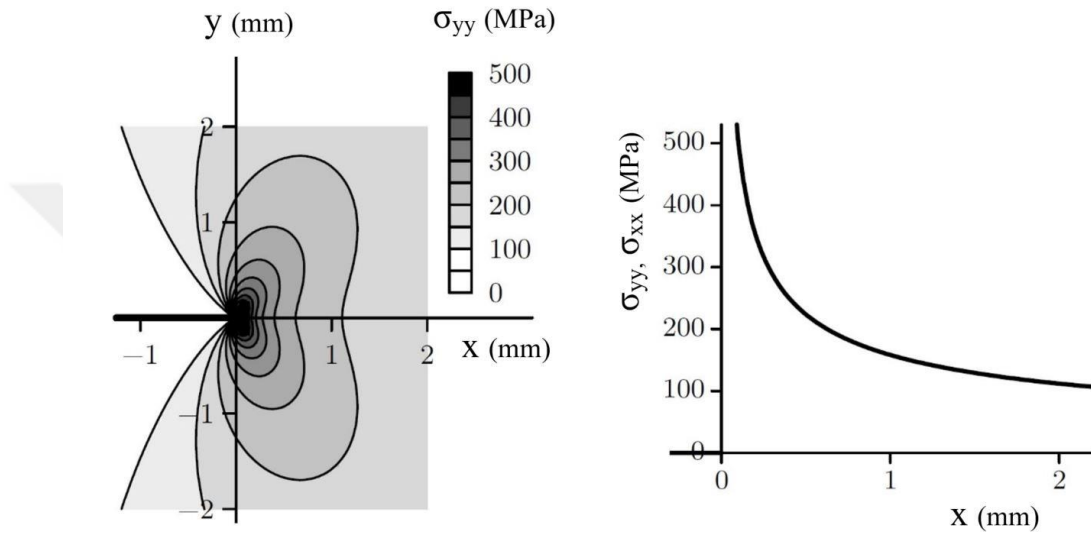


Figure 2.31 Stress fields at the tip of a sharp crack. The crack length $2a=10$ mm and loaded stress $\sigma=100$ MPa. a) Stress distribution field. b) Stress distribution along the y axis where $\theta = 0$. On the x axis, σ_{xx} and σ_{yy} are identical (Rösler, 2007)

A primary objective of LEFM is to establish fracture criteria, such as G_{Ic} and K_{Ic} , that are of the geometry independent (Kinloch, 1986). The relation between G_{Ic} and K_{Ic} can be defined by using energy balance equations as given in Equation 2.8 and Equation 2.9 for plain stress condition and plain strain condition, respectively, where E is modulus of elasticity, and ν is Poisson's ratio (Rösler, 2007).

$$G_{Ic} = \frac{K_{Ic}^2}{E} \quad (2.8)$$

$$G_{Ic} = \frac{K_{Ic}^2}{E} (1 - \nu^2) \quad (2.9)$$

LEFM predicts infinite stresses around the tip of crack. However, because radius of the crack tip should be finite, stresses at the crack tip should also be finite in real materials. The toughness of a material is known as the resistance to growth of the crack through the absorbed energy during the crack growth process. In brittle materials, toughness emerges from the breaking chemical bond energy on the crack surface, but in tough materials such as polymers, bond breaking has only a small impact in preventing crack propagation because the majority of the fracture energy occurs at the crack tip due to plastic flow. The observed fracture energy is a function of both the elastic and plastic energy required to detach the two crack surfaces. A significant factor in the way that materials fracture is the plastic energy, which is correlated to the degree of plastic deformation. It is a common knowledge that the high stresses caused by concentrated severe stresses at the crack tip leads to the local plastic deformation at the tip. Crack tip stresses may also be relaxed as a result of inelastic material deformation like crazing in polymers.

As the crack tip plastic zone grows, the elastic stress analysis becomes progressively incorrect. To establish the boundaries of the plastic zone at the crack tip in the case of a considerable crack tip yielding circumstance, basic modifications to LEFM are possible. The size of the yielding zone at the crack tip can be defined by two methods, which are the Irwin model, where elastic/plastic boundary estimation is done using the elastic stress analysis, and Dugdale approach that is generally known as the strip yield model. In both models, simple crack tip yielding adjustments are incorporated into the solution (Irwin, 1965; Dugdale, 1960). Since the plastic zone shape predicted by the strip yield model proposed by Dugdale is very similar to the crack tip craze zones for many polymers, this model is better suited to polymers. The strip yield model superimposes two elastic solutions to simulate the elastic-plastic behaviour. A whole crack under distant tension and the same crack with proximate stresses at the crack tip are superimposed to define the elastic-plastic zone in the strip yield model approach (Anderson, 2017).

It is possible to define the boundaries of the plasticity at the crack tip for all θ angles by applying von Mises yield criterion given with the Equation 2.10 to the stress field equations given in Figure 2.30.

$$\sigma_e = \frac{1}{\sqrt{2}} \left[(\sigma_1 - \sigma_2)^2 + (\sigma_1 - \sigma_3)^2 + (\sigma_2 - \sigma_3)^2 \right]^{1/2} \quad (2.10)$$

where σ_e is the effective stress, and σ_1 , σ_2 , and σ_3 are the three principal normal stresses. Considering the yielding occurs when σ_e equals to yield strength σ_{ys} according to the von Mises criterion, the plastic zone radius $r_y(\theta)$ as a function of θ in the Mode I loading condition can be obtain as Equation 2.11 for plane stress, and as Equation 2.12 for plane strain, where ν is Poisson's ratio.

$$r_y(\theta) = \frac{1}{4\pi} \left(\frac{K_I}{\sigma_{ys}} \right)^2 \left[1 + \cos \theta + \frac{3}{2} \sin^2 \theta \right] \quad (2.11)$$

$$r_y(\theta) = \frac{1}{4\pi} \left(\frac{K_I}{\sigma_{ys}} \right)^2 \left[(1 - 2\nu)^2 (1 + \cos \theta) + \frac{3}{2} \sin^2 \theta \right] \quad (2.12)$$

Equations 2.11 and 2.12 can be plotted as in Figure 2.32, which define the approximate boundary between elastic and plastic behaviour. It should be noticed the Mode I plastic zones of plane stress and plane strain differ significantly in size and form. The plain strain condition suppresses yielding, which results in a smaller plastic zone for a given K_I value (Anderson, 2017).

Amorphous polymers have an apparently homogeneous deformation behaviour of the entanglement network in the elastic region during the deformation. Anyway, beyond the yield point or at the beginning of the fracture, a localized and heterogeneous deformation of the entanglement network is produced. Localized plastic deformation can also be seen in very brittle polymers. In amorphous polymers, crazing and localized shear yielding are very similar in terms of local plastic deformation. Both entail inhomogeneous plastic deformation because of the localized stress concentrations, and strain softening properties of the structure.

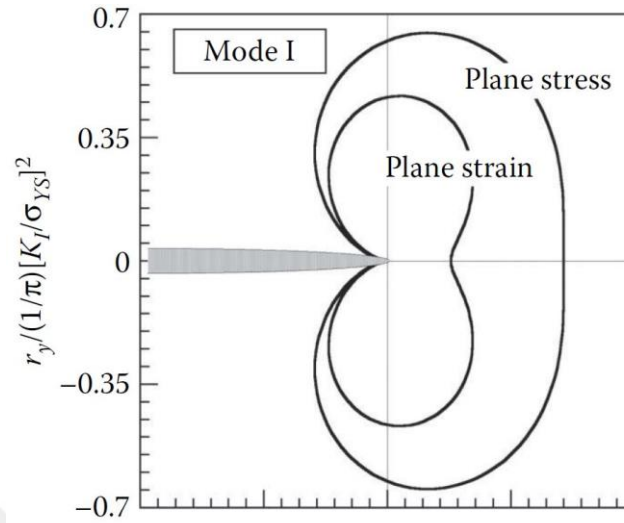


Figure 2.32 According to the von Mises yield criteria and crack tip plastic zone forms determined from elastic solutions under Mode I loading conditions (Anderson, 2017)

Conversely, when they are severely localized, it may result in brittle fracture. Dugdale's strip yield plastic-zone model is appropriate for crazes and shear yielding deformation fields in specific conditions. At the onset of the fracture, there is a small plastic zone in front of the crack tip, and once macromolecules are stretched, then chain scission and consequently crack propagation occur in a small volume. The amount of energy dissipation in this zone almost entirely corresponds to the energy absorbed by such a polymer during fracture. On the other hand, breaking of fibrils that leads to crack initiation and propagation plays an important role for controlling the fracture process (Michler, & Calleja, 2012).

2.5 Particle Reinforced Epoxy Composites and Toughening Mechanisms

Despite its many advanced and outstanding properties in industrial usage, neat epoxy thermosets have some significant drawbacks such as severe brittleness, low impact strength and fracture resistance due to their high crosslinked matrix in case of full-cure production. Several techniques are used to increase the fracture toughness properties of the cured resin. The traditional approaches of modifying curing chemistry have involved chemically changing an existing rigid epoxy structure to a more flexible one based on the structure and property relationships. This involves either reducing

the activity of the curing hardener or increasing the molecular weight of the epoxy resin in order to decrease the crosslink density. which may also create some drawbacks such as low T_g and decreased tensile strength (Sue, Puckett, Bertram, & Walker, 2000). Another common approach to toughen epoxy thermosets without sacrificing some degree of other mechanical properties is to incorporate a second phase in the epoxy matrix. Incorporating soft rubber particles into the epoxy matrix is frequently the most effective way to increase toughness, however, the major disadvantages of using such modifiers are the decrease in modulus of elasticity and T_g (Liang, & Pearson, 2010). When loading, rubber particles can cause the formation of micro voids that may lead to substantial amount of energy dissipation in the plastic zone near the crack tip. Other soft mediums as toughening agent are reactive liquid rubbers, core-shell rubber particles, and self-organizing block copolymers. On the other hand, rigid filler particles, such as titanium dioxide (TiO_2), aluminium oxide (Al_2O_3), calcium carbonate ($CaCO_3$) or silica (SiO_2), as contrary to rubber particles, have been proved to be effective thermoset resin toughening modifiers without sacrificing modulus of elasticity and T_g (Wetzel, Rosso, Hauptert, & Friedrich, 2006). Besides, most rigid particles which are often utilized to increase the matrix's modulus, increase performance at high temperatures, minimize friction and shrinkage, lower the matrix's permeability, or improve flame retardancy. They can also be used to improve wear and abrasion resistance and surface hardness (Michler, 2012). Even though rigid particles do not significantly improve toughness compared to rubber particles, they boost substantially greater strength and modulus of elasticity. This part of review concentrates on the use of SiO_2 particle fillers to modify the thermal and mechanical properties as well as fracture toughness of epoxy resin at various particle sizes and filler contents. There are two main factors influencing toughness of the particle filled epoxy composites, which are particle size, and amount of particle content.

2.5.1 Effect of Particle Size and Filler Content on K_{Ic} and G_{Ic}

The impact of silica particle size on the fracture characteristics of epoxy resin composites was investigated by Nakamura et al. using angular shaped silica particles with varying sizes between 2 μm to 47 μm and filler content of 55 wt% and 65 wt% by SENB test method. They found that both G_{Ic} and K_{Ic} increase with increasing silica

particle size and increased particle content. The increase of fracture toughness was attributed to larger damage zone at the crack tip for the epoxy filled with largest particles, crack path deflection around the large particles and fracture of some large silica particles (Nakamura, 1992).

McGrath et al. reported comparable results in their study conducted with two different type DGEBA epoxy composite filled with alumina (Al_2O_3), mean particle size ranging from 2 μm to 20 μm with the filler content up to 50 vol%. They reported increased K_{Ic} with increasing particle size for both epoxy systems. Besides, fracture toughness increased monotonically with increasing filler content. According to SEM images, the toughening mechanism is crack pinning for the epoxy system with 18 μm particle size and 10 vol% filler content (McGrath, 2008).

Lange and Radford (1971) also studied the particle size effect of on the fracture energy of hexahydrophthalic anhydride (HHPA) cured DGEBA epoxy thermoset composite system reinforced with alumina trihydrate (ATH, $\text{Al}(\text{OH})_3$) powder with the particle sizes of 1, 8, and 12 μm and up to 43 vol% filler content. They concluded that for a given interparticle spacing, the fracture energy was greater for the composite containing the larger particles, and crack pinning was the dominant toughening mechanism (Lange, & Radford, 1971).

It has been shown that the fracture toughness of composites with micron-sized particles strongly depends on the particle size and filler content. The fracture toughness also increases with increase in the particle size. On the other hand, a distinctive effect is seen when the particle size is in the nano-size range. Adachi et al. (2008) investigated the effect of particle size and content of spherical silica particle on Mode I fracture toughness of DGEBA epoxy resin cured with methyl tetra hydro phthalic anhydride (MTHPA). The volume fraction varied from 0 to 35 vol%, while the particle sizes varied from 240 nm to 1.56 μm . They reported that the as the volume fraction increased and the particle sizes decreased, the fracture toughness significantly increased (Adachi, 2008).

Zang et al. (2008) studied epoxy composite filled with 25 nm particle sized silica nanoparticles up to 15 vol% content. They reported that the K_{Ic} of the epoxy matrix

was enhanced when the amount of nanoparticles was increased. The fractographic investigation supported the reasonable strong particle-matrix adhesion. The increased toughening effect was most likely caused by the increased local plasticity caused by nanoparticles around the crack tip (Zang, 2008).

Jajam and Tippur (2012) investigated the effects of nano- and micro-size and filler content of spherical rigid silica particles on the quasi-static and dynamic fracture behaviour of DGEBA epoxy composites cured with amine-based hardener. They used 20 nm and 35 μm size of silica particle filler content of 3 vol%, 5 vol%, 7 vol%, and 10 vol%. They concluded that both nano and micro particles improved fracture toughness of epoxy under quasi-static loading with the increasing particle content. For each given volume fraction, the quasi-static K_{Ic} of nanocomposites was much greater than that of micro size particle loaded epoxies. In comparison to their micro-filler counterparts, nanocomposite specimens with 10 vol% volume fraction filler showed the greatest improvement in fracture toughness (by roughly 78%). When compared to neat epoxy, dynamic fracture toughness for both nano and micro fillers consistently increased with filler volume fraction. Contrary to quasi-static fracture tests, the nanocomposites showed considerably lower dynamic crack initiation toughness than those filled with microparticles having the same amount of fillers. They attributed enhanced dynamic fracture toughness of micro size composite to the increased surface roughness of the fracture surface. Comparing micro-filler composites to their nano-filler equivalents, surface roughness caused by fracture was substantially greater in the former (Jajam, & Tippur, 2012).

This comprehensive review demonstrates how particle size and filler content may have a significant impact on the toughness of filled epoxies. Modifying the particle size can improve or decrease toughness depending on the size range involving micron or nano dimension. It appears that there is a certain particle size above which toughness increases with increased particle size. But when the particle size is under some critical level, it is shown that reducing particle size results in an increase in fracture toughness. These findings can be explained by considering the various toughening mechanisms based on by these two different particle size ranges.

2.5.2 Toughening Mechanisms for Silica Filled Epoxy Composites

Unmodified epoxy is usually single phase and brittle. Although crazes frequently precede brittle fracture, they do not always compromise a polymer's crack resistance. A significant amount of local energy is absorbed by the material as a result of massive plastic strains produced by crazes and shear bands. However, compared to the overall volume of the test specimen, such micro-mechanisms are frequently highly localized and concentrated in a very small volume. As a result, the overall plastic energy absorption is frequently low. To produce a tougher polymer, it is essential to make sure that the volume in which these energy dissipative deformations take place is reasonably large. Consequently, it could be necessary to activate systems that restrict craze growth to avoid early craze deformation and accordingly crack initiation. Initiating crazing or shear yielding deliberately from many places in the composite has proven to be a highly effective and frequently used method for meeting these objectives. Therefore, significantly more of the material than just the area near around the crack tip is subject to energy dissipative deformations. One of the most efficient way to achieve this multiple deformation process is to add a second phase of dispersed particles to the matrix polymer in order to increase toughness (Haward, 1997).

To explain the increased toughness of silica filled epoxy resin composite system, a number of different toughening mechanisms have been suggested. These mechanisms are crack deflection (Faber, 1983), crack pinning mechanism (Lange, 1970; Evans, 1972), crack bridging mechanism (Budiansky, Amazigo, & Evans, 1988), microcracking mechanism (Ritchie, 1988; Evans et al., 1985), and debonding/shear banding mechanism (Lee, & Yee, 2000). Even though much of these mechanisms may emerge in micron-sized composites, however only a handful are accountable for the improved toughness in nano silica filled epoxy composites. Some significant features of these toughening mechanisms are discussed in the following review.

2.5.2.1 Crack Deflection Mechanism

The toughening caused by the crack path deflection process in the particle reinforced composites was proposed by Faber and Evans (1983) using a fracture mechanics approach. According to the deflection theory, the second phase inclusion causes a nonplanar propagating crack by deviating its route away from its initial plane. The local activity of the crack tip consists of an initial tilting and then twisting, as given schematically in Figure 2.33. The tilted crack tip creates a mixed stress state involving Mode I and Mode II, which are opening and sliding, respectively. Besides, the twisted crack causes a mixed mode condition of I and III, which are opening and tearing. The fracture process requires more energy overall as a result of this mode combination, which improves fracture toughness. According to Johnsen et al. (2007), the particle size has a significant impact on the crack deflection (Johnsen et al., 2007).

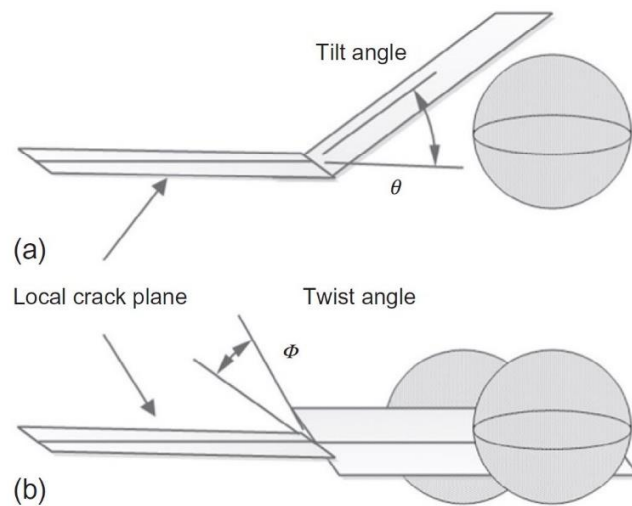


Figure 2.33 Schematic representation of crack tip plane deflection amongst the hard particles, a) tilting, b) twisting (Faber, 1983)

In general, high fracture surface roughness is a good indicator for crack deflection mechanism. As the crack propagates, it is constantly deflected by the particles in the matrix then the surface roughness of the fracture increases. Surface roughness effect has been widely studied by Kinloch and Taylor (2006), and Kitey and Tippur (2005). An improvement in toughness for a robust filler/matrix interaction is attributed to the crack deflection behaviour. In contrast, when weakly bounded interfaces are present, twisting the filler and subsequent blunting from total debonding occur. When a crack

is locally blunted, it requires more energy to initiate it again, which has a greater effect on the increase of the toughness than the indicated tilting and twisting (Kitey, 2005).

2.5.2.2 Crack Tip Pinning Mechanism

For the first time, Lange (1970) described the presence of the crack-pinning process in micro-sized hard particle reinforced polymers. The fundamental concept presented out by Lange is that a progressing crack front has not enough energy to break or cut hard and tightly bound particles. Preferably, hard particles cause the crack to pin and bow out between the particles, leading to many secondary crack pathways. Secondary cracks have a tendency to combine after passing a particle to generate fracture steps that are visible as a tail (Lange, 1970; Pearson, 1993). The crack pinning is represented schematically in Figure 2.34.

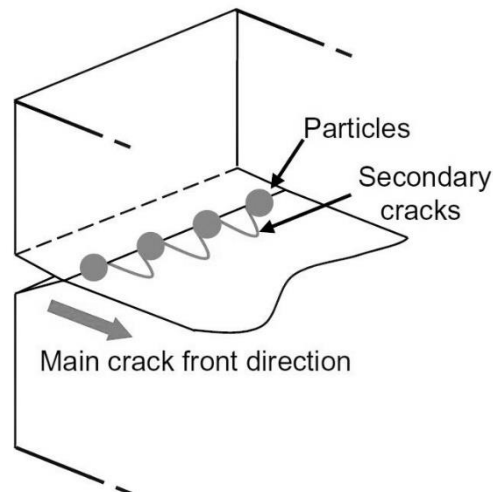


Figure 2.34 Occurrence of subsequent semi-circular cracks during the pinning step (Lange, 1970)

The crack pinning mechanism was thoroughly detailed by Lange et al. (1971) in their investigation using an epoxy composite reinforced with alumina trihydrate. During the fracture, a moving crack front is temporarily pinned at inhomogeneity locations during fracture in the brittle epoxy matrix. Because of this interaction, the crack front bows out in between the pinning points, increasing the overall crack length. The crack front leaves behind discernible steps on the fracture surface after parting from these pinning points. The crack front overlaps as it bows between the dispersed particles, creating these stages. According to Lange et al. (1971), increasing the strain

energy is necessary to increase the crack front length, which in turn increases the fracture energy of the material. Regardless of the particle size, his mathematical model indicated that decreasing the distributed particle spacing should increase the fracture energy which corresponds to an increased filler content. The fracture energy does increase with decreasing particle spacing. But, when dispersed particles become too close together to interact with the fracture front effectively, a maximum energy condition is achieved. According to their results, before the fracture energy threshold, the energy increase is influenced by both particle size and interparticle spacing. The stress fields of crack front must overlap as it passes between and around the particles for the pinning positions to be effective. Since the size of the stress fields is inversely proportional to the crack tip (Figure 2.30), the size of the particles that separate the crack front segments should have an impact on how much bowing occurs before the crack front leaves. Therefore, compared to bigger particles, fine particles are less effective as pinning sites. Consequently, the composites containing the greater particles should have a higher fracture energy for a given interparticle spacing (Lange et al., 1971).

Evans (1972) also reported that the crack pinning contribution attenuates with increasing rigid particle size. According to Johnsen et al. (2007), crack pinning is unlikely to occur in the case of using nano-silica fillers because of their comparatively small dimensions. Therefore, fracture pinning is not anticipated for particles with all diameters at the nanoscale (Johnsen et al., 2007).

2.5.2.3 Crack Bridging Mechanism

Crack bridging occurs at a wake just rear of the crack tip, where the connecting particles bind the crack surfaces. These bridge particles toughen the brittle material by applying additional pressure during the fracture opening, which reduces the stress intensity at the crack tip (Figure 2.35). Crack bridging is often represented as a set of serial distributed springs that are attached to the crack faces at both ends and apply a closing force (Budiansky et al., 1988; Rose, 1987). This mechanism is also conventional in case of soft particle usage such as rubber filler for toughening the brittle polymer matrix such as epoxy. According to Pearson and Yee (1991), the

toughening with tiny soft particles significantly contributed to the creation of voids and shear banding. They claimed that the only rubber particles effective of bridging the crack faces are those that are greater than the matrix plastic zone (Pearson, & Yee, 1991).

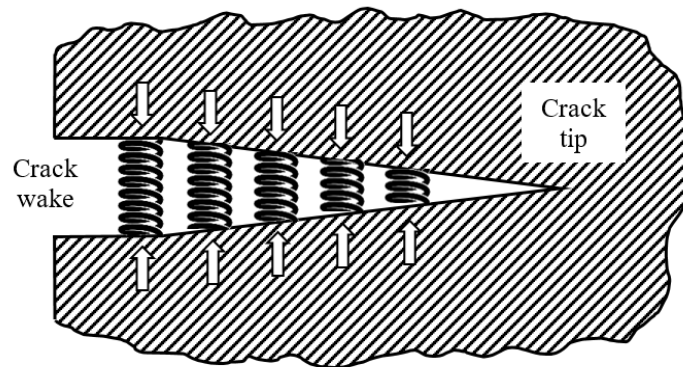


Figure 2.35 Crack bridging where the rigid particles were modelled by springs (Budiansky, 1988)

Fracture toughness improvement of fiber reinforced composites was studied extensively by Kim and Mai, (1991). When brittle short fibres are used for bridging, interfacial shear stresses increase until the particles either fracture or debond from the matrix. Whether the short fiber will fracture or debond is directly dependent on the adhesion strength formed at the matrix interface. If the interface adhesion strength is higher than the fiber fracture strength, the increase in toughness of the composite is determined by the fiber fracture strength. On the other hand, pull-out is responsible for the increase in composite toughness when the adhesion strength is low. In this case, it can be concluded that higher interfacial adhesion strength will result in higher toughness. The interfacial debonding and subsequent frictional pulling-out process have a significant impact on the toughness of the material (Kim, & Mai, 1991).

The trans-particle fracture mechanism, which is evident from the transversely fractured large silica particles that can be seen in the SEM images in the current dissertation, is a special form of the crack bridging mechanism. Silica particles with large aspect ratio have a bridge function in the crack propagation plane and resist crack propagation until they break without debonding due to high interface adhesion,

consequently contributing to the increase of toughness of the composite structure. The schematic diagram of trans-particle fracture mechanism is given in Figure 2.35.

It is well known that carbon nano tubes (CNT) have the capacity to bridge cracks in polymeric composites. Small bridge field may be form in the wake of the crack since these nanostructures often have sufficient overall lengths. A bridging model was presented by Mirjalili and Hubert (2010) to determine the fracture toughness of epoxy polymer incorporated with CNTs. This model takes into account a critical embedded length that governs if CNT break or pulling out happens (Mirjalili, & Hubert, 2010).

2.5.2.4 Microcracking Mechanism

According to Evans (1985), microcracks appear in the shape of debonding at the loosely bonded particle/matrix interface in particle-reinforced polymers. Microcracking or crazing of the matrix is a non-linear deformation mechanism. The shrinkage difference between the matrix and rigid particles creates a residual mismatched strain, which causes residual tangential tensile stresses. Due to the increased tangential tensile stress caused by the applied load, matrix microcracking between particles is therefore possible to occur. These microcracks would reduce any residual stress and be prone to recurrent opening (Evans, 1985). Schematic representation of microcracking mechanism is given in Figure 2.36.

In general, two types of crack shielding phenomena are involved in microcrack toughening: the first is induced by the material's decreased elastic modulus within the microcrack process zone as a result of microcracking; the second, which is more significant form, is due to dilatation driven by the volume that the microcrack displaces. Only very brittle materials, such as epoxy resins can be toughened by this mechanism because the amount of energy that can be absorbed owing to surface energy is restricted (Rühle, & Evans, 1989).

2.5.2.5 Debonding and Shear Banding Mechanism

Rigid or soft particle debonding in the matrix is a crucial mechanism which enables plastic void formation in the composite. When silica nanoparticles are present, stress concentrations develop in the area between the particles, which leads to debonded

particles at the particle/matrix interface. The level of interfacial adhesion achieved at the particle/matrix interface is a key factor in this process. Although some energy may be dissipated during the creation of voids or debonding of nanoparticles, the most significant effect of this process is that it permits plastic void formation in the matrix, which leads to more energy being dissipated and enhances fracture resistance (Zhang, 2008; Dittanet, 2013; Johnsen et al., 2007).

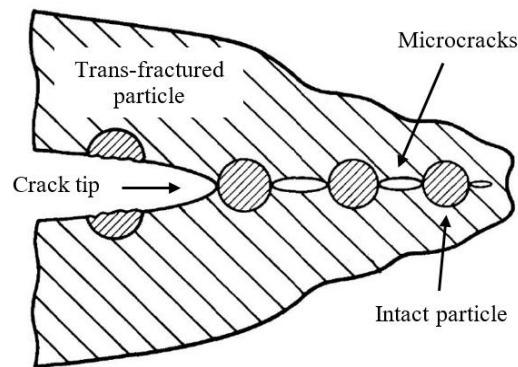


Figure 2.36 Schematic diagram illustrating both crack bridging and microcracking mechanisms (Rühle, 1989)

The primary intrinsic source of the toughness in polymers is thought to be matrix plastic deformation. The plastic response of the composite arises from the local plastic deformation, crazing, or microcracking of the matrix (Kinloch, 1995). Stress concentrations created by the hard or soft particles in amorph polymers induces the transition from a condition of uniaxial stress to triaxial stress, which encourages shear yielding of the matrix. If the interface adhesion is low, debonding at the particle/matrix interface can occur. In this case, voids are developed, which decreases the degree of triaxial stress in the surrounding matrix and promotes the further growth of shear bands. Shear bands form at an angle of approximately 45° to the applied maximum principal stress. Additional plastic yielding is confined within the shear band after it has developed. As the loading increases, the shear bands combine the cavities, which is also called dilation bands (Kinloch, & Taylor, 2006; Lauke, 2008). These two mechanisms are represented schematically in Figure 2.37.

The fracture toughness of epoxy matrix was examined by Dittanet and Pearson (2012) in relation to the impact of silica nanoparticles with diameters of 23, 74, and 170 nm. According to their SEM micrographs, the primary cause of toughening in silica filled epoxy nanocomposites is the creation of plastic voids. Liang and Pearson (2009) and Hsieh et al. (2010) carried out similar detailed investigations on nano silica and epoxy composites. They presented graphical proof of void growth and shear banding from SEM micrographs.

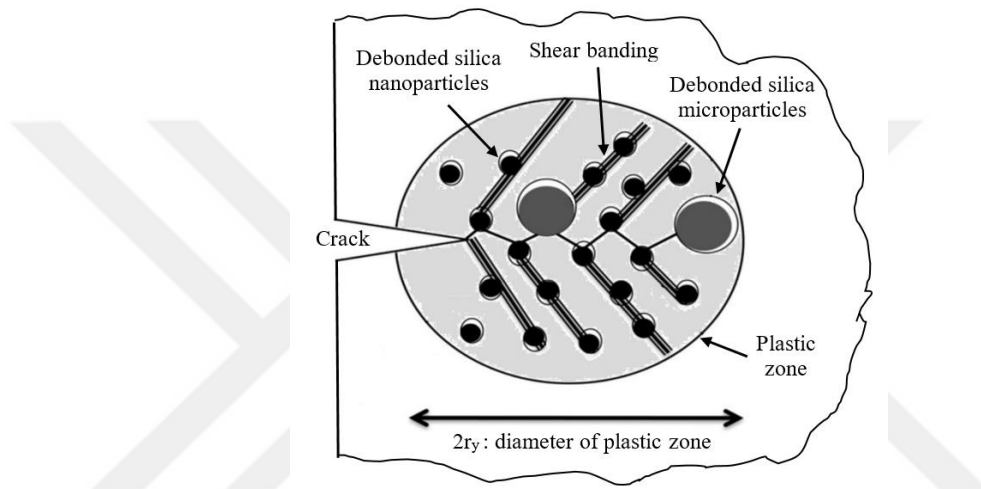


Figure 2.37 Schematic diagram illustrating the debonding and shear banding toughening mechanisms involving the fracture of silica filled epoxy containing bimodal particle size distribution (Dittanet, 2013)

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

3.1.1 Materials for TTT Diagram

Araldite CY 225, a diglycidyl ether of bisphenol A (DGEBA) resin, and Aradur HY925, methyl tetra hydro phthalic anhydride (MTHPA) as curing agent constitute the epoxy system under examination. Both of the ingredients were supplied by Huntsman AG (Switzerland). Angular shaped silica particles (SiO_2) prepared by crushing natural raw silica with the mean diameter of $36.7\text{ }\mu\text{m}$ as a filler supplied by Sibelco (Belgium) is added to mixture. This epoxy system is used mainly in indoor electrical insulators for medium and high voltage applications such as a switchgear devices, bushings, or overmolding of vacuum components. The resin and hardener were mixed in a stoichiometric ratio of 100:80 parts by weight each, while the quartz particles were mixed in at a ratio of 270 parts by weight. Silica content was 60 wt%. Mixing of all the components performed under 10 mbar vacuum condition for one hour to eliminate air entrapment into the mixing formula. All these operations are performed at room temperature.

3.1.2 Materials for Mechanical Tests

Same resin of DGEPA and hardener of MTHPA with the stoichiometric resin-to-hardener mixing ratio of 100:80 ppw were used to produce epoxy composite mechanical test samples. Angular shaped silica particles with three different particle sizes were used as a filler. Mean particle sizes of the fillers were 280 nm, $1.1\text{ }\mu\text{m}$ and $36.7\text{ }\mu\text{m}$. Particle distribution of the silica is given in Figure 4.15. Molding parameters and material configurations regarding the silica particle sizes and filler contents are given in Table 3.1.

Table 3.1 Molding parameters and material configurations

Filler content (%wt) 36.7 μm	30%	40%	60%
Curing temperature $^{\circ}\text{C}$	160	160	160
Curing time (min)	180	180	180

Filler content (%wt) 1.1 μm	20%	30%	40%
Curing temperature $^{\circ}\text{C}$	160	160	160
Curing time (min)	180	180	180

Filler content (%wt) 280 nm	2%	5%	8%	10%
Curing temperature $^{\circ}\text{C}$	160	160	160	160
Curing time (min)	180	180	180	180

3.1.3 Materials for Coefficient of Thermal Expansion (CTE) Measurements

CTE samples were prepared from tensile test specimens after completing mechanical tensile tests. Square parts with the dimension of 10 x 10 x 3.2 mm were cut from the bottom side of the tensile test specimens. Resin to hardener stoichiometric mixing ratio of 100:80 ppw was kept the same. Particle size of silica and filler contents are the same since the samples were taken from tensile test specimens and material configurations are given with the Table 3.1.

3.2 Time Temperature Transformation (TTT) Diagram

3.2.1 Isothermal Curing for TTT Diagram

TTT diagram of current epoxy composite system was formed by using isothermal curing of the prepared epoxy mixture. Classical method to determine a TTT diagram is based on measurements of post-curing behaviour of the composite. Differential Scanning Calorimeter (DSC) method was used to cure samples in a specific temperature for predetermined times. The samples were cured in DSC for different times at isothermal reaction temperature, then rapidly cooled to a temperature below the glass transition temperature (T_g). T_g values after curing at the respective temperature and time configuration were measured according to the Standard of ASTM D3418.

Calorimetric measurements were performed using Mettler Toledo DSC823 (Giessen, Germany) differential scanning calorimeter equipped with an intercooler unit. The device calibration was performed with high purity indium and zinc standard test samples previously. Graph showing the relationship between the temperature and the heat capacity (dH/dT) indicates an endothermic step shift during the glass transition in a DSC dynamic experiment. As a function of temperature, the change in specific heat capacity is measured then glass transition temperature (T_g) is considered as the midpoint of this transition. Figure 3.1 depicts cross-section of a DSC furnace and the results of an endothermic step shift in heat capacity during the glass transition. The glass transition temperature for a thermoset polymer evolves from a starting point, T_{g0} , which corresponds to no crosslinking, to a maximum value, $T_{g\infty}$, which corresponds to the completely cured structure.

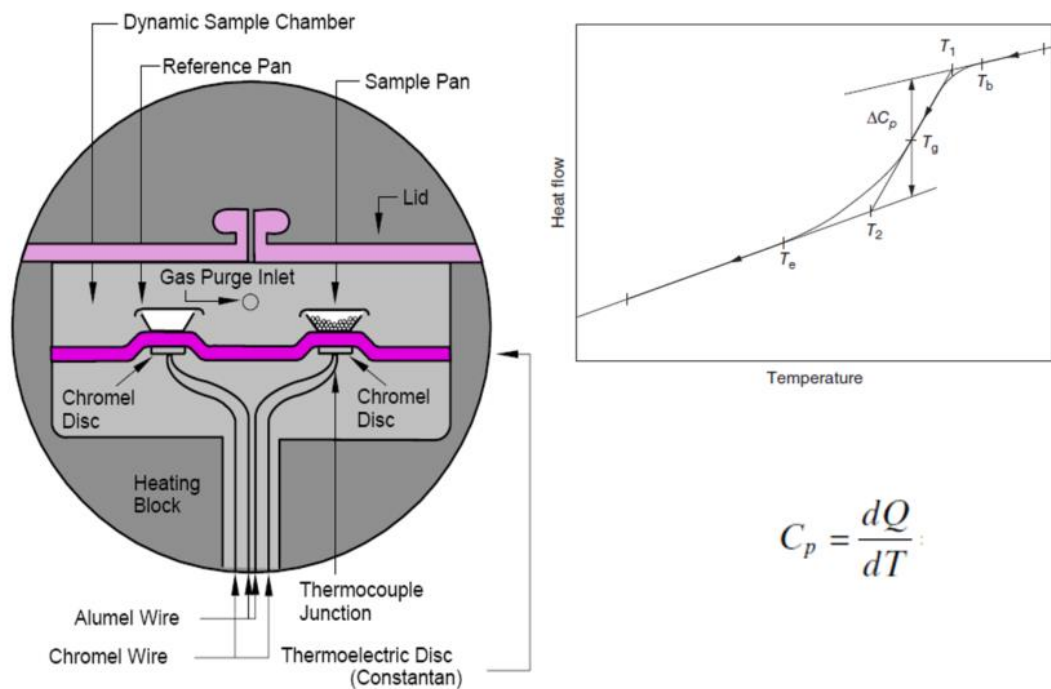


Figure 3.1 Schematic cross-section of a DSC furnace and an endothermic major shift in heat capacity at the glass transition can be seen from the output (Wunderlich, 2005)

After mixing the resin, hardener, and silica with the stoichiometric ratio under the vacuum for 1 hour, 20 mg samples were encapsulated in aluminium DSC pans and

then kept under -40°C till the performing the T_g tests. Photos of DSC device and aluminium pans are given in Figure 3.2.

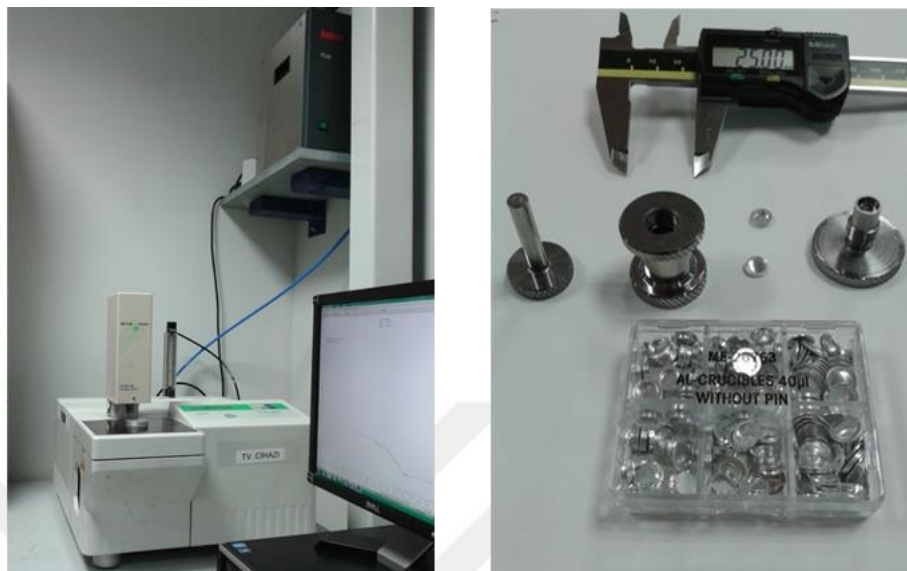


Figure 3.2 DSC device with intercooler unit and aluminium pans for the curing tests

Experiments were carried out in dynamical and isothermal regimes. Runs between 30 and 170°C were carried out at a constant heating rate. The isothermal cure regime was maintained at varying times starting from 5 to 4320 minutes depending on the curing temperature. In first step, sample was heated to the target curing temperature with the rate of $20^{\circ}\text{C}/\text{min}$. Target curing temperatures were chosen as $30, 60, 80, 100, 120, 140,$ and 170°C to construct TTT diagram of epoxy composite. Every sample was kept at this target temperature for the predefined times of $5, 10, 20, 40, 90, 360, 600, 2160,$ and 4320 minutes in order to allow epoxy to polymerize from partially to full structure. All samples were promptly cooled to 25°C with a cooling rate of $200^{\circ}\text{C}/\text{min}$ following the isothermal run. After the samples were heated to 160°C at a rate of $20^{\circ}\text{C}/\text{min}$, a dynamic scan was performed to measure the glass transition temperature (T_g) and residual enthalpy. All composites were prepared using the same resin to hardener ratio; hence all fillers were regarded as inert (nonreactive) ingredients. As an example of DSC isothermal curing and T_g measuring route of 170°C set is given in Table 3.2. Graphically visualizing of this table is given in Figure 3.3 for 170°C temperature set. Same curing times given in the table were used for other curing

temperature sets to form a T_g mesh to form TTT diagram. Table 4.1 was created by using measured T_g values depending on the curing temperature and time sets, which is the heart of the TTT diagram of the studied epoxy composite system. The T_g values for the 8640 hours curing time were extrapolated from the previous data because of the remarkably long curing time.

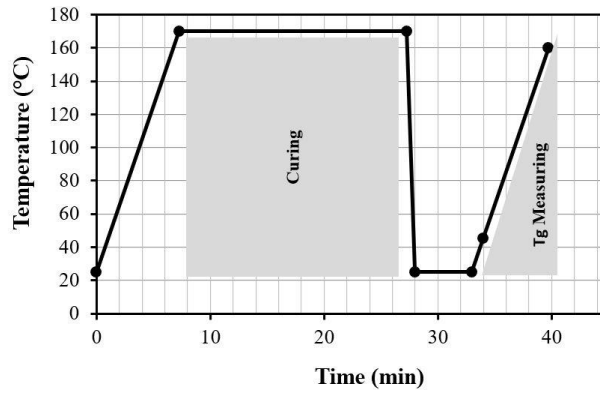


Figure 3.3 DSC isothermal curing and T_g measuring route of 170°C and 20 min curing set

Table 3.2 An example of DSC isothermal curing and T_g measuring route of 170°C set

Curing times for 170°C (min.)	Dynamic heating	Isothermal curing	Dynamic cooling	Wait	Dynamic heating	T_g Measuring
20	25→170°C, 20°C/min	170°C, 20 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
40	25→170°C, 20°C/min	170°C, 40 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
90	25→170°C, 20°C/min	170°C, 90 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
360	25→170°C, 20°C/min	170°C, 360 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
600	25→170°C, 20°C/min	170°C, 600 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
2160	25→170°C, 20°C/min	170°C, 2160 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min
4320	25→170°C, 20°C/min	170°C, 4320 min.	170→25°C, 200°C/min	5 min.	25→45°C, 20°C/min	45→160°C, 20°C/min

3.2.2 Gelation Study for TTT Diagram

Gelation of the epoxy polymer system occurs at a specific moment depending on the applied temperature and time. The time when gelation takes place is known as the gel time. Gel-timer may be used effectively to measure this time. In gelation tests, gelation times is measured as the function of the different curing temperatures. Gelation tests were performed with the gel-timer device by Gel Instrumente AG (Switzerland) accompanied by thermoregulated oil bath furnace with the maximum heating temperature of 210°C by Julabo GmbH (Germany). Outlines of thermoregulated oil bath device and gelation instrument are given in Figure 3.4.



Figure 3.4 Outlines of gelation instrument and thermoregulated oil bath device

At the beginning of the test, the glass tube filled with prepared epoxy material is placed in a thermo regulated oil bath. While a measuring stamper moves reciprocally in the glass tube, gelation times corresponding to specified temperatures are measured. The gelation device has a switch-off mechanism that reacts to pressure. The measuring stamper encounters a specified reaction force in the activated epoxy resin when the gelation time limit is achieved due to an abrupt increase of the viscosity. When the change in viscosity is reached, a built-in timer is stopped, and the gelation time can be read off for the predefined curing temperature. Amplitude of stamper is 13 mm and frequency of the reciprocal movement is 6 cycle/min. Same epoxy composite mixture which was used for the isothermal tests previously was used for the gelation tests. 100 gr epoxy mixture was put in a glass tube then placed in the thermoregulated oil bath. Oil bath temperatures were set to 30, 60, 80, 100, 120, 140, and 170°C as the same for the isothermal curing tests to define gelation tests regarding temperatures. Reciprocal stamper run in the epoxy then stop time was recorded automatically when the gelation was reached. Gelation times regarding the gelation temperatures are given in Table 3.3.

Table 3.3 Gelation times as a function of temperature

Gelation temperature (°C)	Gel time (min)
170	2
140	7
120	21
110	36
100	53
80	149
60	227
30	938

3.2.3 Conversion Study

The dependence of glass transient temperature on the conversion or crosslink density can be measured by post curing. It is possible to confirm the presence of a correlation between T_g and conversion degree (α) that is irrespective of the temperature of isothermal cure. As a reliable conversion indicator, T_g can be employed in this manner.

From a practical standpoint, this represents a significant advantage because T_g can be measured more readily and accurately than conversion. This is apparent particularly at high conversions where T_g rises even while the residual heat readout on the calorimeter remains unchanged. Nielsen, (1969) reported a modified form of the empirical DiBenedetto equation given with the Equation 3.1, which gives the correlation between T_g and α (Nielsen, 1969; Teil, 2004).

$$T_g(\alpha) = \frac{\lambda \cdot \alpha \cdot (T_{g\infty} - T_{g0})}{1 - (1 - \delta) \cdot \alpha} + T_{g0} \quad (3.1)$$

where T_{g0} is the glass transient temperature of the uncured epoxy monomer, $T_{g\infty}$ is the highest glass transition temperature for the completely cured material that was determined experimentally, and λ is assumed to be a variable, structure-dependent factor ranging from 0 to 1.

The residual enthalpy (H_r) of the partially crosslinked resin and the overall enthalpy of reaction (H_t) associated to sample without curing treatment, as mixed one, may be used to determine the conversion degree (α) of the curing process, which is given with the Equation 3.2. Here, (H_r) and (H_t) were determined by numerical integration of the area enclosed under the exothermic peak in the thermograms of T_g measurements.

$$\alpha = 1 - \frac{\Delta H_r}{\Delta H_t} \quad (3.2)$$

The 40 μ L aluminum crucibles were filled with 20 mg of the mixture and sealed. They were then stored at -40°C until they were measured. Before the measurement, the samples were held at 140°C for different periods to be cured to different extend. After the partial curing at the same isothermal temperature with different times, samples were cooled rapidly to -25°C . The DSC measurement was performed from -25°C to 220°C at $10^\circ\text{C}/\text{min}$. for every samples. DSC isothermal curing and T_g measuring route at 140°C with 20 min time duration is given with the Figure 3.5.

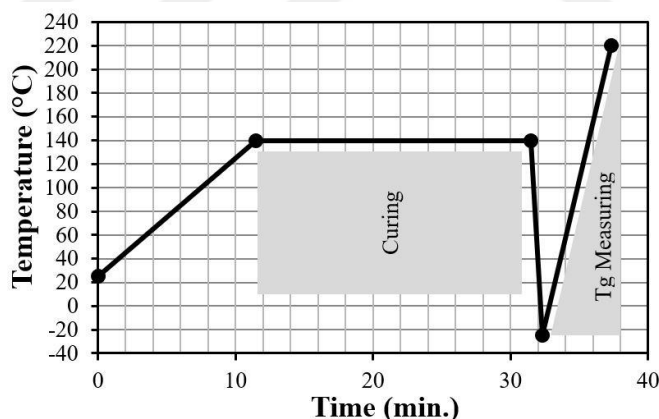


Figure 3.5 DSC isothermal curing and T_g measuring route at 140°C with 20 min time duration

3.3 Mechanical Tests

3.3.1 Material Preparation

At the beginning of the molding, required material was weighted according to the hardener to resin stoichiometric ratio. The stoichiometric mixing ratio for the resin-

hardener was set at 100:80 parts per weight to achieve complete conversion during epoxy curing reactions. The highest cross-linking density at a stoichiometric composition, which is the consequence of full transformation, suggests that anhydride reactants were used to cross-link the majority of the resin chain ends. The untransformed portion of the components in the structure may cause fracture toughness to decrease to some extent. Therefore, complete conversion of the epoxy is required in order to properly interpret the net effect of filler size and amount on the fracture properties of the composite. Required quantities of resin, hardener, and silica are given in Table 3.4, Table 3.5, and Table 3.6 depending on the silica filler % content by weight. Overall, 800 gr of material was prepared for one shut molding.

Table 3.4 Molding required quantities of resin, hardener, and 36.7 μm particle sized silica

800 gr of total molding	36.7 μm			
	60%	40%	30%	0%
Silica (gr)	480.0	320.0	240.0	0.0
Resin (gr)	177.6	266.4	311.2	444.5
Hardener (gr)	142.4	213.6	248.8	355.5
Hardener/Resin	80%	80%	80%	80%

Table 3.5 Molding required quantities of resin, hardener, and 1.1 μm particle sized silica

800 gr of total molding	1.1 μm			
	40%	30%	20%	0%
Silica (gr)	320.0	240.0	160.0	0.0
Resin (gr)	266.4	311.2	355.2	444.5
Hardener (gr)	213.6	248.8	284.8	355.5
Hardener/Resin	80%	80%	80%	80%

Table 3.6 Molding required quantities of resin, hardener, and 280 nm particle sized silica

800 gr of total molding	280 nm				
	10%	8%	5%	2%	0%
Silica (gr)	80.0	64.0	40.0	16.0	0.0
Resin (gr)	400.0	408.8	422.4	435.2	444.5
Hardener (gr)	320.0	327.2	337.6	348.8	355.5
Hardener/Resin	80%	80%	80%	80%	80%

Particle size distributions of the silica fillers were investigated by Zeta-Sizer for 1.1 μm and 280 nm particle sizes and by Beckman Coulter size analysers for 36.7 μm particle sizes. Filler shape, size, and distribution are important parameters affecting the final mechanical properties of cured polymer systems. Silica filler was dried for 2 hours at 90°C to remove moisture. Silica tends to absorb moisture from the air and moisture in the silica structure inhibits curing reactions and decreases the T_g temperature to some extent.

After drying, the resin and hardener were poured into the mixer. Silica was gradually added to the resin system, which was stirred slowly to prevent agglomeration. All the three ingredients were mixed under 10 mBar vacuum conditions at 40°C for 2 hours. Vacuum mixing is required to eliminate the air bubbles that are formed during the mixing process, which may cause air entrapment during the molding operation. During the mixing process, mold release agent was applied slightly to the mold surface to prevent the adhesion of the epoxy. The mold was then mounted between the plates of a hydraulic press equipped with an internal resistance heating system. The temperature of the plates was set to 160°C and kept constant by a PID temperature control system. External heat source is required for curing reactions to start and continue. When the final mixing was completed, mold was filled with the prepared material through the runner by using air pressure of 5 bar. At the end of 3 hours curing time at 160°C mold was taken from the heater plates of the machine and disassembled. Afterwards, specimens were extracted from the mold carefully. Finally, specimens were kept between two flat insulator plates during the cooling time to prevent any distortion.

3.3.2 Test Procedure

Tensile tests were carried out with Shimadzu standard tensile testing machine with 50 kN load capacity at room temperature (23°C) according to ASTM-D638 standard. The main dimensions of the dog-bone shape tensile specimen were 160x13x3.2 mm (LxWxT). The tensile deformation rate was 5 mm/min. Modulus of elasticity was measured by a camera extensometer attached to the tensile testing machine. The mean values and standard deviations were calculated from the five measured results of tensile strength, modulus, and elongation at break.

The use of linear elastic fracture mechanics (LEFM) is one of the most practical methods for investigating the propagation of cracks in epoxy resin thermosets. The prerequisites for applying LEFM are easily met by thermosets since they typically exhibit very linear elastic deformation behaviour with limited plastic deformation. Linear elastic fracture mechanics concept provides information about the fracture toughness of brittle materials regardless of sample geometries. Therefore, ASTM-D5045 standard was used to determine Mode-I fracture toughness (K_{Ic}) and critical strain energy release rate (G_{Ic}) in single end notch bending (SENB) test configuration. The dimensions of the test specimen and test conditions are given in Figure 3.6. The dimensions of the test specimen meet plain strain criteria which are compulsory in the standard. Initially, a sharp and deep notch, with 0.3 mm width, was machined on the specimen. Next, a sharp razor was slid along the root of the notch, creating a natural sharp crack. This process was repeated with five fresh razor blades for each sample consecutively due to the razor blunting effect of the hard silica particles in the structure.

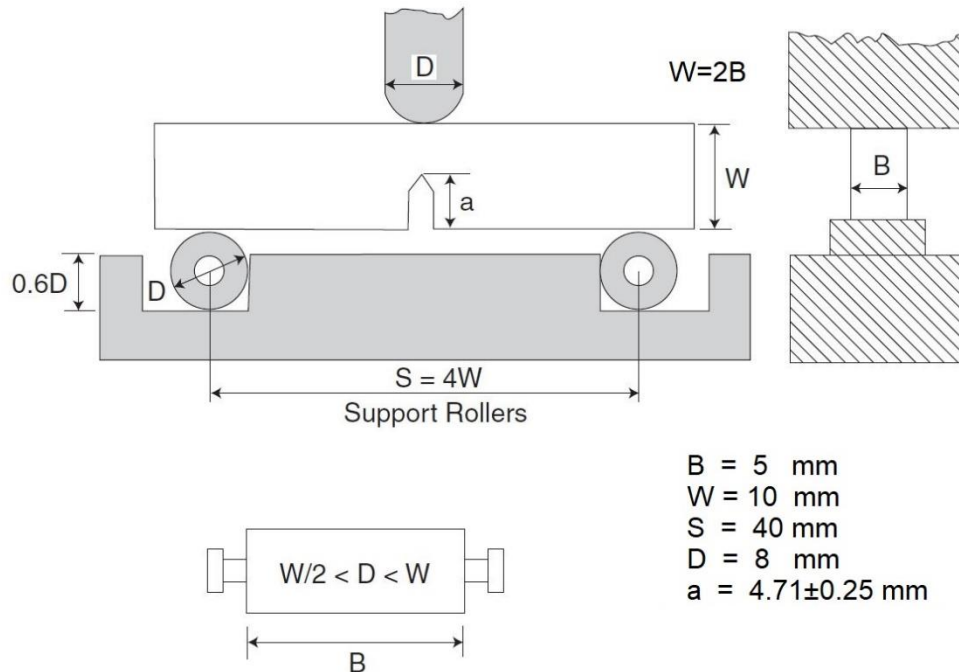


Figure 3.6 The dimensions of the SENB test specimen

The total crack length (a) was measured from the fractured surfaces by using a light microscope, which was coupled with an electronic micrometre. The crack lengths of the samples were kept between 0.45W and 0.55W. SENB specimens were used for the three-point bending tests, which were performed by the same Shimadzu tensile testing machine with the 10 mm/min crosshead speed at ambient room temperature. K_{Ic} values were determined using Equation 3.3 with the unit of $\text{MPa.m}^{1/2}$:

$$K_{Ic} = \frac{P_c}{BW^{1/2}} f(x) \quad (3.3)$$

where

$$f(x) = 6x^{1/2} \frac{[1.99 - x(1 - x)(2.15 - 3.93x + 2.7x^2)]}{(1 + 2x)(1 - x)^{3/2}} \quad (3.4)$$

$$x = \frac{a}{W} \quad (3.5)$$

P_c : maximum load at break (kN)

B : thickness of specimen (cm)

W : width of specimen (cm)

a : length of crack (cm)

3.3.3 Tensile and Fracture Tests

Mechanical properties such tensile strength, modulus of elasticity, and elongation at break were determined by tensile test. Fracture behaviour of the epoxy composites were investigated by SENB test. Specially designed and machined aluminium alloy mold was used to produce Tensile and SENB test specimens in the study. Aluminium alloy was chosen as the mold material due to its high thermal conductivity properties, which is necessary to supply heating energy effectively on the curing epoxy system. Figures of the specimens were machined on both sides of the middle mold plate. Two aluminium plates were used as covers to create a full molding specimen cavity. The

mold was so designed that five identical samples in every molding cycle can be produced to evaluate the results statistically. The outline of the mold, material mixing and feeding system is given in Figure 3.7 as a 3D design. Figure 3.8 and Figure 3.9 depict 3D design of the mold in open position showing both side cavities of tensile and SENB test specimens, respectively. Same cavities can be seen on both side of the machined aluminium mold as given in Figure 3.10 and Figure 3.11.

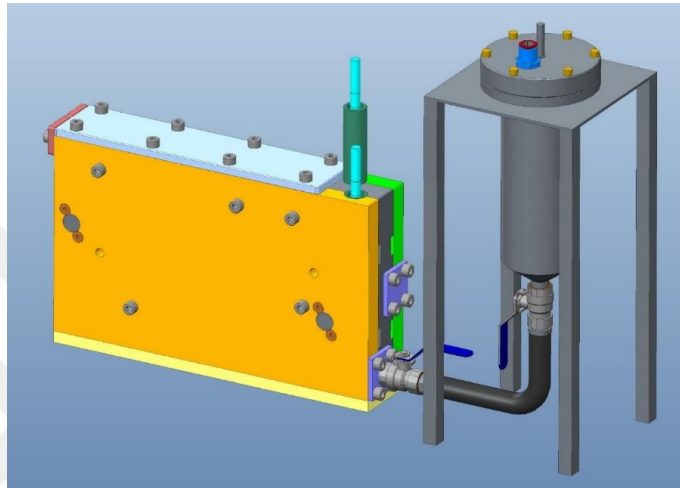


Figure 3.7 3D design of mold and mixer system

3.4 Thermal Properties

3.4.1 Glass transient temperature (T_g) Measurements of Specimens

The glass transition temperature (T_g) of the cured material is a good measure of the degree of transformation of the epoxy polymer system at the end of polymerization. The measured maximum T_g temperature of the cured polymer system corresponds to the maximum conversion of the curing reactions, which also determines the final fracture properties of the material. Rahul and Kitey (2016) explained the relationship between molecular weight, cross-link density, and fracture toughness in their work. In their study, the maximum glass transition temperature with the maximum crosslink density and consequently the minimum molecular weight was obtained, while the K_{Ic} value was minimum at the stoichiometric mixing condition (Rahul, & Kitey, 2016).

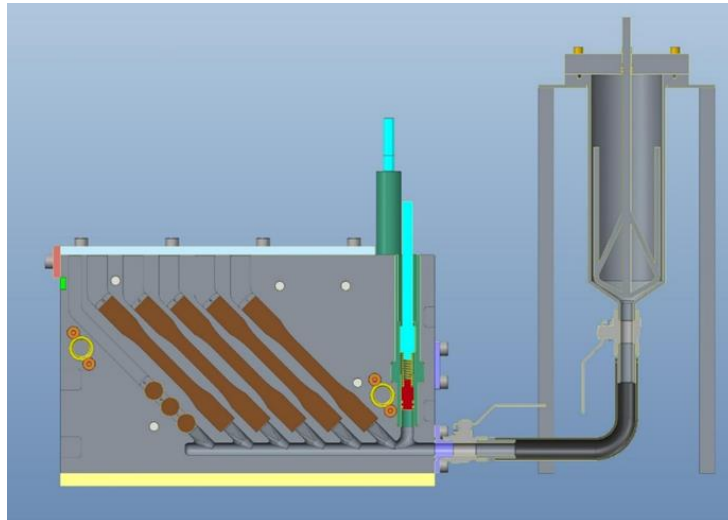


Figure 3.8 3D design of mold in open position showing the cavity of tensile test specimens

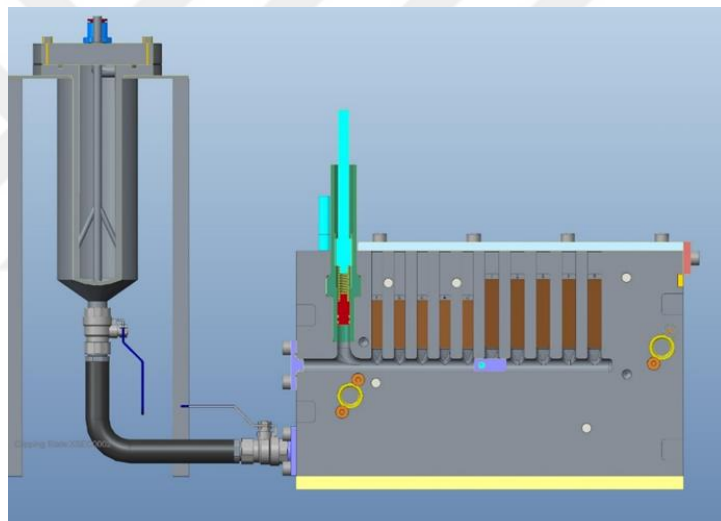


Figure 3.9 3D design of mold in open position showing the cavity of SENB test specimens

Therefore, T_g measurements were conducted to verify the transformation degree of the curing system. Mettler Toledo DSC823 differential scanning calorimeter equipped with an intercooler unit was used for the T_g measurements. The device was calibrated previously with high purity zinc and indium standard test samples. Measurements were carried out according to ASTM D3418 standard procedure. In the method, the change in specific heat capacity as a function of temperature is measured and the characteristic glass transition temperatures are determined from the midpoint of the obtained curves. 10 mg of test epoxy samples were taken from the runner of the molded parts for T_g

measurements. Samples were placed in aluminium pans and heated at a rate of 10°C/min from 40°C to 160°C.



Figure 3.10 Machined aluminium mold in open position showing the cavity of tensile test specimens



Figure 3.11 Machined aluminium mold in open position showing the cavity of SENB test specimens

3.4.2 TGA/DTA Analysis

The aim of this part is to investigate the effect of the different contents of silica particles on the thermal stability of the epoxy polymer composites. Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to

investigate thermal stability parameters. Thermal analysis of TGA is a technique in which a sample's mass is determined as a function of time and temperature. This method offers details regarding chemical processes like thermal oxidation, reduction, or oxidation as well as physical processes like absorption, desorption, adsorption, and phase transitions. Many polymers show a characteristic decomposition path during the pyrolysis. The pyrolysis process is the thermal decomposition of polymers at elevated temperatures in an inert atmosphere. As pyrolysis progresses, the sample's weight decreases gradually before experiencing a rapid decrease across a narrow temperature range. As the reactant runs out, the slope eventually returns to zero. The kinetic factors of the pyrolysis, such as activation energy and reaction sequence, control form of the curve.

DTA is a thermo analytic technique which is theoretically similar to DSC. In DTA, similar thermal cycles are applied to the sample being studied and an inert reference, (i.e., same heating or cooling program). Any temperature differences between the sample and the reference are monitored during the heating cycle. Then, the temperature difference is shown versus temperature (DTA curve, or thermogram) or against time. Compared to the inert reference, changes in the sample, whether exothermic or endothermic, can be found. DTA curve therefore gives information on the transformations, such as crystallization, glass transitions, melting, or sublimation.

In current study, thermal stability parameters, which were investigated to compare polymers, are initial decomposition temperature (IDT), temperature of maximum rate of mass loss (T_{max}), decomposition activation energy (E_a), integral procedure decomposition temperature (IPDT), char yield, and silica contents of epoxy composites (Saavedra, 2008).

The IDT parameter is determined by detecting the temperature corresponding to a certain amount of mass loss (5%) in the heating regime. T_{max} is the temperature at which the maximum mass loss rate occurs. E_a is a measure of the rate of degradation of that reaction. In other words, higher activation energy means lower reaction rate. Therefore, the decomposition activation energy can be used to compare the thermal stability of different silica filled composites. Horowitz and Metzger (1963) derived a simple approximate integral method to determine the activation energy by inspecting

the raw TGA data (Horowitz, & Metzger, 1963). Horowitz-Metzger method was used to determine E_a of silica filled epoxy composites using TGA data according to the following equation:

$$\ln[\ln(1 - \alpha)^{-1}] = \frac{E_a}{RT_{\max}^2} \theta \quad (3.6)$$

where α is the decomposition ratio given with the equation of $(w_i - w)/w_i$ where w_i is initial weight and w is the weight at any t time with increasing temperature. $T_{\max}$ is the temperature at the maximum rate of weight loss, $\theta = (T - T_{\max})$, E_a is the activation energy for decomposition, and R is the gas constant (8.3145 J/mol.K). The activation energies E_a for decomposition were calculated from the slope of the straight line from the plots of $\ln[\ln(1 - \alpha)^{-1}]$ versus θ .

The comparison of composites based on the thermal stability is not easy due to their possible different behaviours. Anderson (1961) showed that epoxy resins decompose in more than one decomposition steps. Doyle (1961) estimated thermal stability of polymers by using TGA in his work. He put these different behaviours on a common numerical basement by using arbitrarily defined integral procedural decomposition temperature (IPDT), which was derived from the weight loss vs. temperature plot. Weight loss was assigned to a single temperature which was the IPDT. Thus, this temperature could be represented as a rectangle restrained by the residual weight fractions of 100% and 0% in vertical axis, and between initial temperature (T_i) and final temperature (T_f) in horizontal axis, at the area under the TGA curve given in Figure 3.12. Thus, it was postulated that all volatilized material between T_i and T_f assigned to a single temperature.

In order to estimate the intrinsic thermal stability of polymeric materials, Doyle (1961) introduced the IPDT, which correlates the volatile components of polymeric materials. IPDT was calculated from the TGA graphs by using Equation 3.7.

$$\text{IPDT} = A * K * (T_f - T_i) + T_i \quad (3.7)$$

$$A^* = (S1 + S2) / (S1 + S2 + S3) \quad (3.8)$$

$$K^* = (S_1 + S_2) / S_1 \quad (3.9)$$

where A^* is the area ratio of the total experimental curve divided by the total TGA thermograph, K^* is the coefficient of A^* , T_i is the initial test temperature, which was 35°C in the study, and T_f is the final test temperature which was 800°C. S_1 , S_2 , and S_3 are areas of the three zones obtained from the dividing of the TGA graph as shown in Figure 3.12.

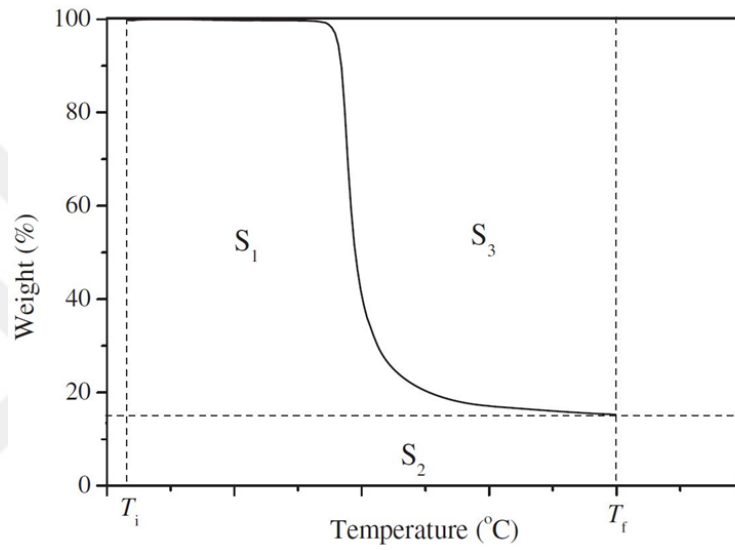


Figure 3.12 Schematic representation of S_1 , S_2 , and S_3 zones

In the IPDT calculation, to determine the real effect of silica filler on thermal stability of the composites, the remaining silica amount at the end of 800°C in TGA measurements was mathematically subtracted from total residue with the assumption that there would be no change in silica mass at this temperature. Thermal stability parameters of IPDT and IPDT* were calculated as uncorrected and the corrected from the TGA curves.

In the study, TGA/DTA analysis was conducted using a Shimadzu DTG-60H/TA-60WS simultaneous thermal analyser. 10-20 mg samples were prepared from the K_{ic} test specimens for TGA and DTA tests. Heating regime was started from 30°C with 10°C/min rate to 800°C. Heating atmosphere was nitrogen with the 100 ml/min rate.

3.4.3 Coefficient of Thermal Expansion (CTE) Measurement Study

The coefficients of thermal expansion of unfilled epoxy and its silica filled composites were obtained by using a thermomechanical analyser (TA Instruments Inc., TMA 400). A standard expansion probe is placed on the sample and the sample is heated according to a temperature program. While the size changes under heat application, probe movement records contraction or expansion of the sample. The analyses with expansion mode were made from -30°C to 120°C at a ramp of $5^{\circ}\text{C}/\text{min}$.

3.5 Fracture Surface Analysis

Scanning electron microscopy (SEM) was used to investigate the fracture surfaces of SENB specimens and consequently to explain the fracture behaviour of the composite filled with different size and content of the silica subsequent tests.

SEM is one of the most common analytic methods to investigate the morphology of the fracture surfaces. In the process, the sample surface is scanned by a small high energy electron beam. Because of the interaction between the electron beam and the sample a series of radiation is produced. Two types of radiation are used for image formation in the application, which are primary backscattered electrons and secondary electrons. Backscattered electrons provide information about the compositional and topographic structure of the sample while secondary electrons generate a depth of field that shows images of the surface topography. Images are seen in CRT by the signal modulation of these two types of radiation, which provides the surface topology, morphology, and composition of the sample surface.

In this study, the fracture surfaces were examined by using JEOL JSM-6060 instrument. Three main fracture mechanisms were described, which are crack pinning, crack deflection and trans-particle fracture mechanisms depending on the particle size and filler content.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Establishing of TTT Diagram of Epoxy Polymer Composite

4.1.1 Isothermal Curing Graphics

Measured T_g values obtained from the isothermal temperatures at defined isothermal time durations by DSC tests were given in Table 4.1. All vitrification and decomposition fields of the TTT diagram of given epoxy system are depicted by using these data in Figure 4.1, in which T_g of the material can be obtained depending on a specific isothermal curing temperature and curing time, can be constructed by using Table 4.1.

Table 4.1 T_g values obtained from the isothermal temperatures at defined time durations

T_g (°C)	Curing time (min)										
Curing temperature (°C)	5	10	20	40	90	360	600	1,200	2,160	4,320	8,640
170	79.2	97.0	104.2	105.4	106.9	109.6	110.6	110.3	108.7	102.7	90.5
160	52.0	75.3	96.0	102.0	107.1	110.0	110.7	110.6	109.5	103.5	91.3
140	28.0	55.8	79.3	101.8	108.7	111.1	111.3	111.6	111.0	105.7	94.8
130	0.0	13.0	52.0	84.0	104.0	110.3	110.8	111.3	111.1	107.2	99.4
120	0.0	0.0	24.8	62.0	92.9	109.1	110.1	110.6	111.0	108.8	104.6
110	0.0	0.0	0.0	18.0	64.0	106.3	107.0	108.3	109.7	110.8	109.6
100	0.0	0.0	0.0	0.0	33.4	93.0	104.2	108.0	109.7	110.0	111.5
90	0.0	0.0	0.0	0.0	0.0	66.0	89.0	104.0	108.0	110.0	111.8
80	0.0	0.0	0.0	0.0	0.0	24.8	56.5	80.0	98.0	102.0	106.0
60	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

T_g values under the curing temperature of 80°C could not be measured for the maximum curing time of 8640 minutes. Main reason for non-occurrence of T_g at low temperatures is low reactivity of the epoxy-hardener system that chosen. Due to long shelf-life demand for the industrial usage, resin-hardener couples used in the study have low reactivity at lower temperatures.

It can be clearly seen from the Figure 4.1 that, T_g of the cured material is the function of the isothermal curing temperature and curing time. That means a specific

T_g value of the material can be reached either with a low curing temperature using a higher curing time or with a high curing temperature with a lower curing time.

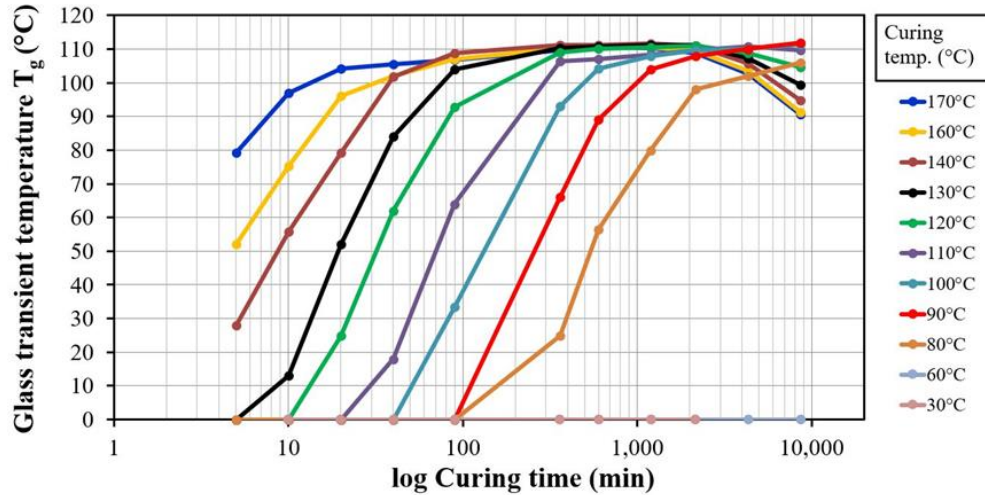


Figure 4.1 Glass transient temperature (T_g) of the composite as a function of isothermal curing temperature and curing time

For example, if we need to reach a T_g value of 105°C for the epoxy material system, there are two different processes, which are 80 minutes curing time is enough at 160°C curing temperature, while 600 minutes curing time is needed at 100°C curing temperature. This kind of behaviour of the epoxy system has two practical significant consequences which are production productivity and manufacturability. Same epoxy material system can be used for coreless epoxy molding products and for the products with iron cores such as electric transformers with different production parameters of time and temperature. Productivity concern is effective with the coreless system at higher curing temperatures while it is nearly impossible for iron cored transformer molding products to produce higher than 100°C curing temperature for current material system due to high coefficient of thermal expansion between iron core and epoxy material above the temperature of 100°C as can be seen in Figure 4.2, (Huntsman, 2008). If we increase the curing temperature to shorten the production time of the iron cored product, the coefficient of thermal expansion of epoxy increases drastically, generating a huge internal stress between iron core and epoxy due to cooling shrinkage and causes cracking of the epoxy material. Thus, low curing temperature and elevated curing time is a must for iron cored epoxy systems. On the other hand, coreless or aluminium cored epoxy systems allow higher curing

temperatures with shorter production times without any risk of cracking due to low coefficient of thermal expansion, which means the increased productivity.

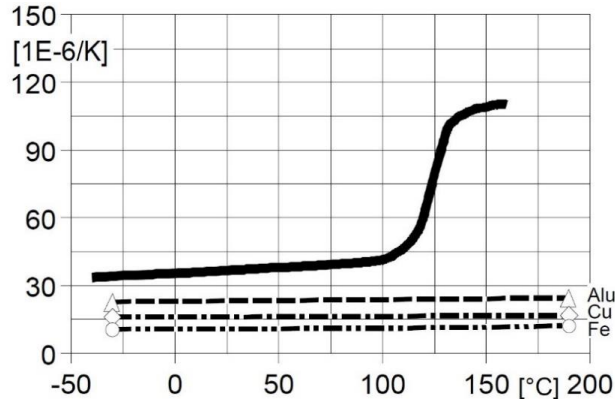


Figure 4.2 Coefficient of linear thermal expansion (CTE) as a function of temperature, $f(T)$, for current epoxy system of Araldite CY225-Aradur HY925-SiO₂, (Huntsman, 2008)

TTT diagram of the current epoxy system was constructed by modifying Figure 4.1. The independent variable of log Time axis was kept the same while dependent Y axis was replaced with the curing time of the process. In addition to isothermal curing graphs, gelation, vitrification, and decomposition graphs are also required to build the specific regions, which have different physical properties, for a complete TTT diagram.

4.1.2 Gelation

Gelation is the characteristic feature occurred during network formation in the presence of a critical transition and it entails a sudden transition from a liquid-like to a solid-like characteristic. At gel point, viscosity becomes infinite and insoluble gel fraction suddenly appears while the elastic modulus starts to build-up. Gel times with logarithmic scale are given in Figure 4.3 regarding the curing temperatures. Gel time is directly the function of curing temperature. Elevated curing temperature causes an abrupt gelation while very low curing temperature causes very elongated gel time. In order to construct a gel zone, curing temperatures that chosen in the previous isothermal tests were used to find out gel times. In Figure 4.3 the zone under the curve is liquid epoxy which allows the molding process. Upper zone of the curve reflects the infinite viscosity which does not allow the epoxy to propagate in the mold during the mold filling process. During the mold filling process, gelation must be prevented

before the final product is shaped for the given epoxy formulation in a molding production. Key success factor for appropriate mold filling is to stay below the curve of gel points constructed with the couples of gel times and regarded curing temperatures.

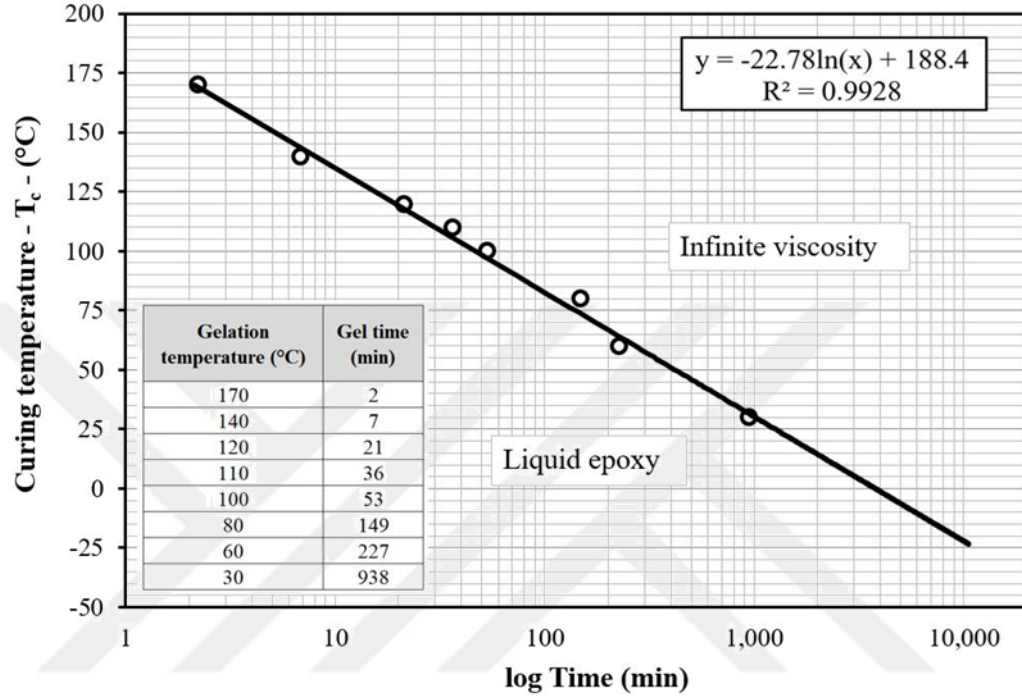


Figure 4.3 Gelation times regarding the curing temperatures measured by Gel-timer

Figure 4.4 shows mold filling process section of the time-temperature curve regarding the curing temperature limits of 140 and 170°C. Practically, epoxy production with the mold temperature of 150°C allows just lower mold filling times of 5.3 minutes. Exceeding this mold filling time for this mold curing temperature will cause pre-solidification of epoxy during the filling process, which leads to unfilled epoxy final part at the end of full curing phase. Therefore, gelation phase is a crucial part in determining mold filling parameters of current epoxy system.

Appropriate mold filling times, which should be less than gel time (t_{gel}), can be calculated by modifying Figure 4.4 as a function of mold curing temperature (T_c). Figure 4.5 was obtained by exchanging the axis of Figure 4.4, which gives the equation of mold filling time limits as a function of curing temperature. The function is given with the linear Equation 4.1, where t_{gel} is gel time in minute and T_c is curing

temperature in °C. Equation 4.1 is valid between the curing temperatures of 140 and 170°C.

$$t_{\text{gel}} = -0.154T_c + 28.4 \quad (4.1)$$

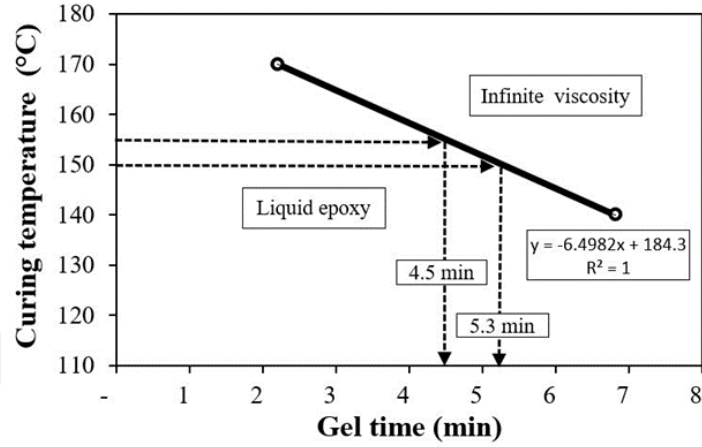


Figure 4.4 Mold filling gel time limits regarding the curing temperature in the mold

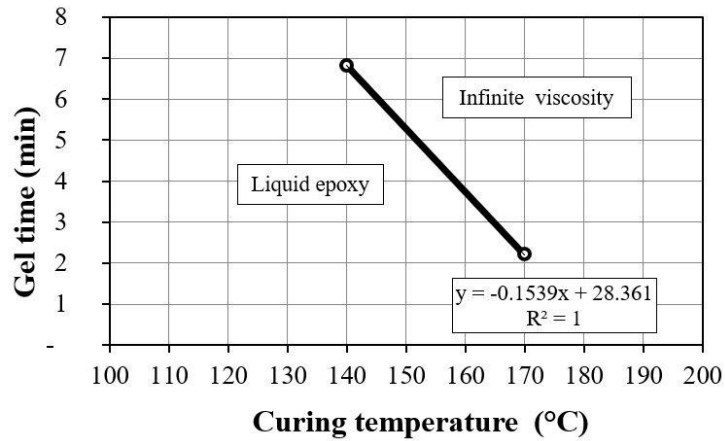


Figure 4.5 Mold filling gel time limits regarding the curing temperature in the mold

4.1.3 Vitrification

If the glass transition temperature of the formulation is equal to or increases above the curing temperature, vitrification may occur during the polymerization of the epoxy system. Table 4.1 was modified to construct vitrification zone of the TTT diagram and Table 4.2 was created. With the help of this table, the vitrification zone was

constructed as given in Figure 4.6. Curing times at which the glass transient temperature equals to the curing temperature were calculated by regression. To form an accurate spline, 75, 105, and 107°C curing temperatures were added to the table and regarding glass transient temperatures were calculated by regression. Since the epoxy system gets into glassy state in vitrification zone, formation of covalent bonds during polymerisation is severely retarded.

Table 4.2 The times when vitrification occurs

T _g (°C)	Curing time (min)										
Curing temperature (°C)	5	10	20	40	90	360	600	1,200	2,160	4,320	8,640
170.0	79.2	97.0	104.2	105.4	106.9	109.6	110.6	110.3	108.7	102.7	90.5
160.0	52.0	75.3	96.0	102.0	107.1	110.0	110.7	110.6	109.5	103.5	91.3
140.0	28.0	55.8	79.3	101.8	108.7	111.1	111.3	111.6	111.0	105.7	94.8
130.0	0.0	13.0	52.0	84.0	104.0	110.3	110.8	111.3	111.1	107.2	99.4
120.0	0.0	0.0	24.8	62.0	92.9	109.1	110.1	110.6	111.0	108.8	104.6
110.0	0.0	0.0	0.0	18.0	64.0	106.3	107.0	108.3	109.7	110.8	109.6
107.0	0.0	0.0	0.0	12.6	54.8	102.3	106.2	108.2	109.7	110.6	110.2
105.0	0.0	0.0	0.0	9.0	48.7	99.7	105.6	108.2	109.7	110.4	110.6
100.0	0.0	0.0	0.0	0.0	33.4	93.0	104.2	108.0	109.7	110.0	111.5
90.0	0.0	0.0	0.0	0.0	0.0	66.0	89.0	104.0	108.0	110.0	111.8
80.0	0.0	0.0	0.0	0.0	0.0	24.8	56.5	80.0	98.0	102.0	106.0
75.0	0.0	0.0	0.0	0.0	0.0	11.4	41.3	64.0	83.3	87.3	91.3
60.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

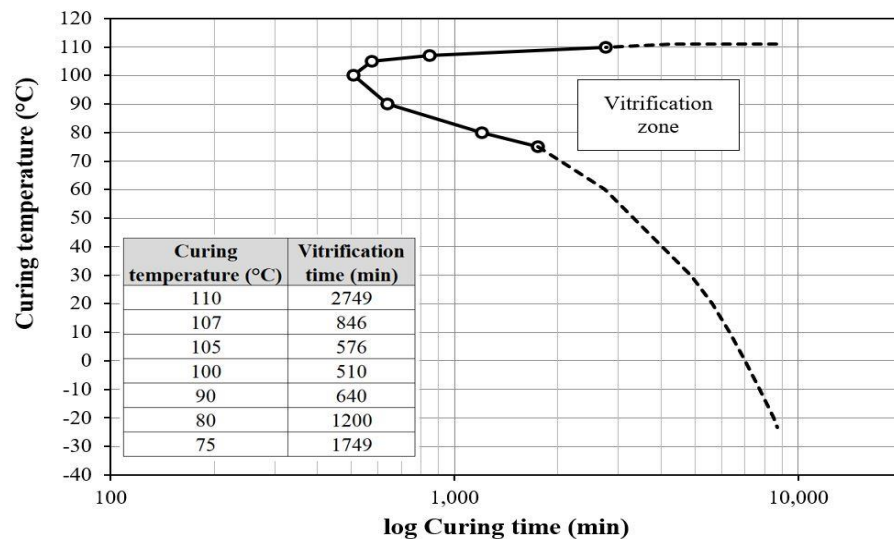


Figure 4.6 Vitrification zone depending on curing temperature and time

Vitrification zone has two significant industrial importance due to this aspect. Processing of products at low temperatures with elongated times such as iron cored

transformers should not be cured in vitrification zone. Due to retardation of polymerisation kinetics final structure of the product does not meet expected mechanical and electrical properties. So, process parameters of curing time and temperature should be defined out of vitrification zone to obtain proper final epoxy structure. Another aspect of this zone is to allow longer shelf life of partially reacted epoxy system. In this way, unreacted epoxy systems may be safely stored in the glassy state provided that curing temperature is lower enough than glass transient temperature to avoid any significant propagating in the polymerization reaction.

4.1.4 Decomposition

Decomposition of the curing epoxy system starts when the glass transition temperature tends to decrease for the given curing temperature. During the curing process at high temperatures for elongated times, non-curing reactions may cause degradation. Main reason of degradation is devitrification while T_g decreases through the isothermal temperature due to formation of plasticizing materials in the structure or reduction of cross-linking density.

There is a competition between cure and thermal degradation reactions in high T_g systems. Therefore, high temperature polymers should be processed in low temperatures (Gillham, 1986). Decomposition zone was constructed with the graphic of glass transient temperatures and curing times between 360- and 4320- minutes in Figure 4.7. This curing time interval was chosen because onset of T_g decrease occurs in this interval for the curing temperatures of 170, 160, 140, 130, and 120°C. Since decomposition or char formation starts when the T_g begins to decrease, curing times which correspond to starting of T_g decrease were determined by using Figure 4.7. Decomposition zone was constructed by using these curing times regarding curing temperatures, which is given in Figure 4.8. Char formation starts at the 170°C after 1000 min, or 120°C after 1900 min. Char formation was not observed under the curing temperature of 110°C for the maximum curing time.

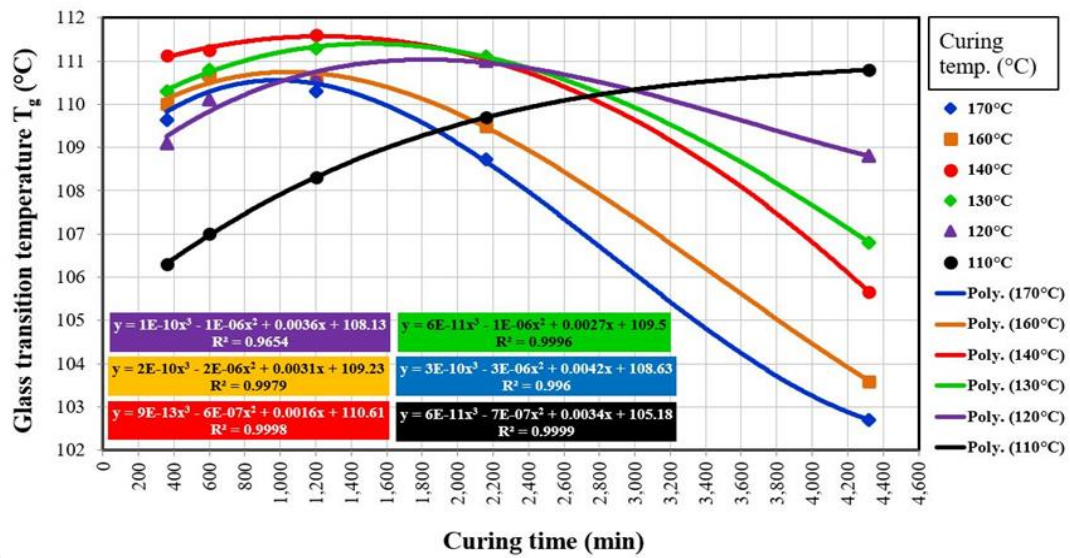


Figure 4.7 Onset time of T_g decrease depending on the curing temperature

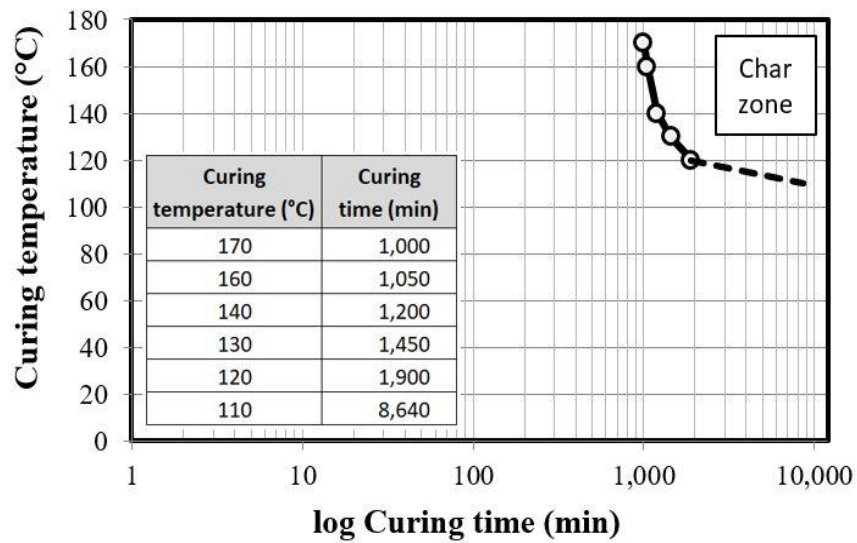


Figure 4.8 Decomposition zone of the epoxy system

4.1.5 Isothermal Curing Curves on the TTT diagram

Interpolation from the Table 1 is used to obtain the required curing parameters such as temperature and time for a specific T_g value. Table 4.3 summaries interpolation couples for the T_g of 105°C as an example. By using these interpolated data, Table 4.4 was established, which gives the process parameters to obtain T_g value of 105°C.

Table 4.3 Interpolation table for a specific T_g value of 105°C

T_g (°C)	Curing time (min)										
Curing temperature (°C)	5	10	20	40	90	360	600	1,200	2,160	4,320	8,640
170	79.2	97.0	104.2	105.4	106.9	109.6	110.6	110.3	108.7	102.7	90.5
160	52.0	75.3	96.0	102.0	107.1	110.0	110.7	110.6	109.5	103.5	91.3
140	28.0	55.8	79.3	101.8	108.7	111.1	111.3	111.6	111.0	105.7	94.8
130	0.0	13.0	52.0	84.0	104.0	110.3	110.8	111.3	111.1	107.2	99.4
120	0.0	0.0	24.8	62.0	92.9	109.1	110.1	110.6	111.0	108.8	104.6
110	0.0	0.0	0.0	18.0	64.0	106.3	107.0	108.3	109.7	110.8	109.6
100	0.0	0.0	0.0	0.0	33.4	93.0	104.2	108.0	109.7	110.0	111.5
90	0.0	0.0	0.0	0.0	0.0	66.0	89.0	104.0	108.0	110.0	111.8
80	0.0	0.0	0.0	0.0	0.0	24.8	56.5	80.0	98.0	102.0	106.0
60	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 4.4 Process temperatures and times for the T_g of 105°C

T_g (°C)	Curing temperature (°C)	Curing time (min)
105	168.7	40
105	132.1	90
105	109.0	360
105	102.9	600
105	92.5	1,200
105	87.0	2,160
105	83.8	4,320
105	79.0	8,640

In this way, all curing temperature-time couples corresponding to a specific T_g value can be obtained. Isothermal T_g curves of 60, 80, 90, 100, 105, 107, 108, 109, 110, and 111°C are given in Figure 4.9. The lowest acceptable T_g value in electromechanical epoxy applications is 105°C, and this value is obtained in 40 minutes, which is the lowest curing time, and at a curing temperature of 170°C. In terms of high production productivity, it is necessary to produce at the lowest possible time to obtain the required minimum T_g value. Therefore, it is necessary to keep the curing temperature at the highest value. Full cure is obtained with the T_g 111 curve, and the minimum time required for the maximum T_g value of 111°C is 360 minutes at the curing temperature of 140°C. Iso-conversion curves are almost parallel the gelation line since the gelation is regarded to be an iso-conversion state.

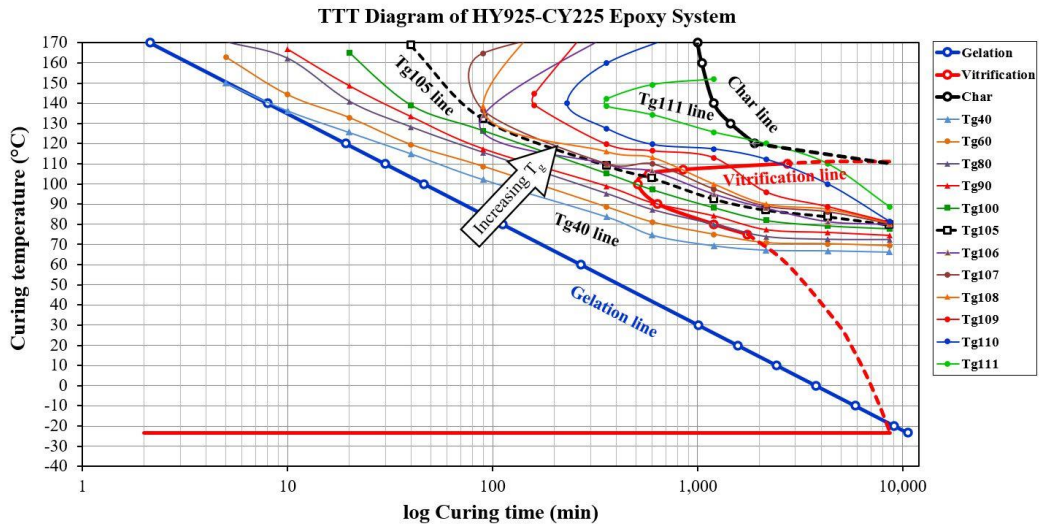


Figure 4.9 Specific isothermal T_g curves of the studied epoxy system

4.1.6 TTT Diagram of Studied Epoxy System

The TTT diagram of studied epoxy system summarizes the times to gelation, vitrification, thermal degradation, and full cure depending on the temperature of cure (T_c). The diagram given in Fig 4.10 summarizes separate regions of matter which were formed during the curing of thermoset system. These regions are called liquid, sol/gel rubber, gel rubber, sol/gel glass, sol glass, and char. The diagram includes three critical temperatures of T_{g0} , $_{gel}T_g$ and $T_{g\infty}$. T_{g0} is glass transient temperature of uncured reactants and was measured as -23.4°C which is given in the next chapter. $_{gel}T_g$ is the temperature where vitrification and gelation concur and was calculated as -17.9°C . $T_{g\infty}$ is the maximum glass transient temperature of curing system and was measured as 111°C .

At the beginning of the curing reaction, the material is in the liquid condition and has low molecular weight under the $T_{g\infty}$ temperature and Gelation line. With the increase of curing temperature and time, gelation begins over the Gelation line and the sol/gel rubber zone is reached. In this zone infinite molecular weight gel and finite molecular sol mixture is formed. When T_g reaches to curing temperature, vitrification begins to occur on the Vitrification line. Vitrification of the system in the Vitrification zone decreases the molecular mobility causing retardation of chemical reactions. The

prior to elastomer formation. In this condition, from above to below in the TTT diagram, T_g of the material decreases (Gillham, 1986).

Automatic pressure gelation process (APG) is widely used as an epoxy thermoset molding process to produce medium and high voltage electrical components such as switchgears, bushings, and voltage and current transformers. Mold filling, curing, and post-curing are the three main phases of the manufacturing process (Nowak et al., 2006). TTT diagram can be used conveniently to optimize the process parameters. For instance, if the curing temperature in the mold is set to 150°C, as can be seen from Figure 4.11, the maximum filling time of the mold at this temperature should not exceed 5.3 minutes.

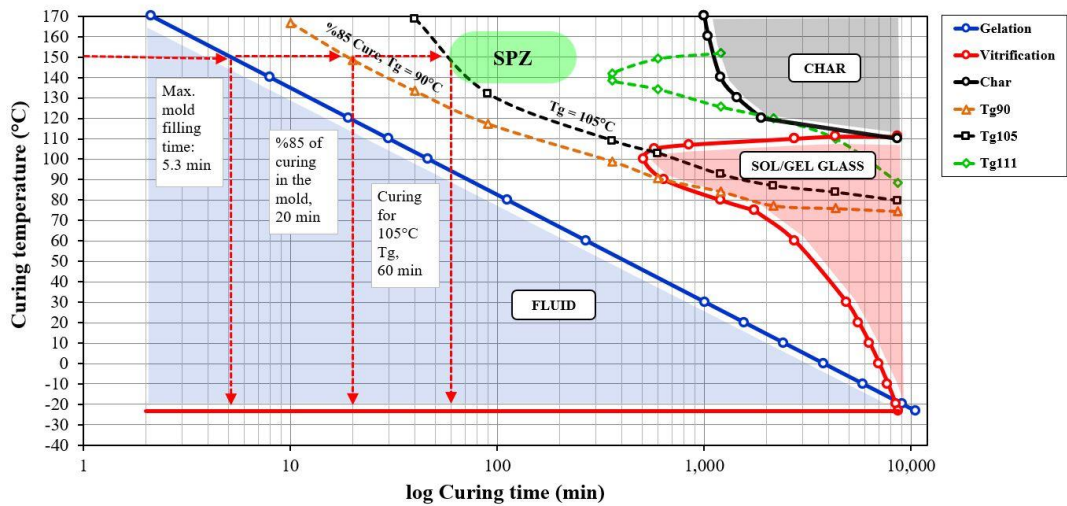


Figure 4.11 Important process parameters for the studied epoxy system. Optimum process parameters can be set in the safe process zone (SPZ)

Otherwise, since the gelation line will be passed, solidification begins before the filling is completed and a complete molded product cannot be produced at the end of the curing cycle. On the other hand, in order to use the molding machine and mold productively in mass production, the curing time in the mold should be kept as minimum as possible. According to general industrial acceptance, after 85% of curing is completed in the mold, the part can be easily removed from the mold without any deformation. As discussed in the next section, Chapter 4.2, with the aid of the DiBenedetto equation, the T_g must reach about 90°C during the curing process in the

mold to achieve a conversion degree of 85%. To obtain $T_g=90^{\circ}\text{C}$ at a curing temperature of 150°C , the minimum time required to cure in the mold is determined as 20 minutes. Final T_g of the molded product should be greater than 105°C according to design requirements. By using Tg105 isothermal curve depicted in Figure 4.11, the total required minimum curing time can be obtained as 60 minutes at 150°C curing temperature. Since the heat transfer to the epoxy part during the post-curing process in the furnace will be by convection, instead of conduction as in the mold, it should be considered that some extra time is required to reach the desired temperature in the furnace.

As a result, a safe process zone (SPZ) can be set over the Tg105 isothermal curve, as can be seen in Figure 4.11, which meets the required quality requirements, allows optimum time consumption, and can be produced with optimum energy expenditure.

4.2 Conversion Degree

The molecular weight and T_g increase during isothermal polymerization below $T_{g\infty}$, and eventually T_g will reach T_c . Provided that T_c is greater than T_g , maximum T_g of the curing system will reach $T_{g\infty}$, and dependently maximum conversion degree is also reached. T_g of the epoxy thermoset is a property which depends on the conversion degree (α) value. Increasing crosslinking density of the system decreases the mobility of the chains and consequently T_g increases.

Conversion degree can be calculated with total enthalpy change (ΔH_t) and residual enthalpy change (ΔH_r) by using DSC measurements. Figure 4.12 gives a residual enthalpy of the system cured at 140°C for (a) 0.1 and (b) 90 minutes by integration of the curves.

Specific enthalpy values measured by the integration of heat flow for predefined curing times at 140°C are given with the Table 4.5.

In the uncured condition T_{g0} was measured as -23.4°C , and the total specific enthalpy ΔH_t was calculated as 327.6 J/g . Specific enthalpy values other than ΔH_t are residual enthalpies ΔH_r at the table and conversion degrees $\alpha(\%)$ were calculated for

every curing time by using Equation 3.2 given in Chapter 3.4. Since the T_g of the cured system is the function of α , both can be plot in the same graphic with the common time axis to investigate correlation, which is given in Figure 4.13. It can be seen clearly from the graphic that T_g and α are fully correlated depending on the time.

Table 4.5 Conversion degree α values by DSC measurements

$T_{\text{cure}} (^{\circ}\text{C})$	Cure time (min)	$T_g (^{\circ}\text{C})$	Integral (mJ)	Weight (mg)	Specific enthalpy (J/g)	α (%) experimental
uncured	0	-23.4	6780.69	20.7	327.6	0.0%
140	0.1	8.5	5336.62	19.7	270.9	17.3%
140	10	55.8	2059.89	21.0	98.1	70.1%
140	20	79.3	900.48	18.1	49.8	84.8%
140	40	101.8	932.59	20.6	45.3	86.2%
140	90	108.7	437.81	16.8	26.1	92.0%
140	180	109.3	634.71	24.4	26.0	92.1%
140	360	111.1	406.72	18.0	22.6	93.1%
140	720	111.3	467.03	21.2	22.0	93.3%

Since a network structure is related with one conversion, thus one conversion coincides to one T_g . As a result, a direct relationship between α and T_g can be established. The most used characteristic equation for expressing T_g as a function of α for a thermosetting system is the DiBenedetto equation which was given in Chapter 3.4 as Equation 3.1. With mathematical intermediate operations, the DiBenedetto equation can be expressed as Equation 4.2 where α can be calculated as a function of T_g .

$$\alpha(T_g) = \frac{1}{\left(\frac{111.3 - T_g}{T_g + 23.4}\right)^{0.57} + 1} \quad (4.2)$$

Calculated α values from the DiBenedetto equation and experimentally measured α values with the integrations of residual enthalpies by DSC application depending on the T_g values are given with the Table 4.6. By fitting Equation 3.1 with the experimental data, λ , an adjustable parameter was calculated as 0.57 with a good coefficient of correlation, which is also consistent with Teil's results (Teil, 2004).

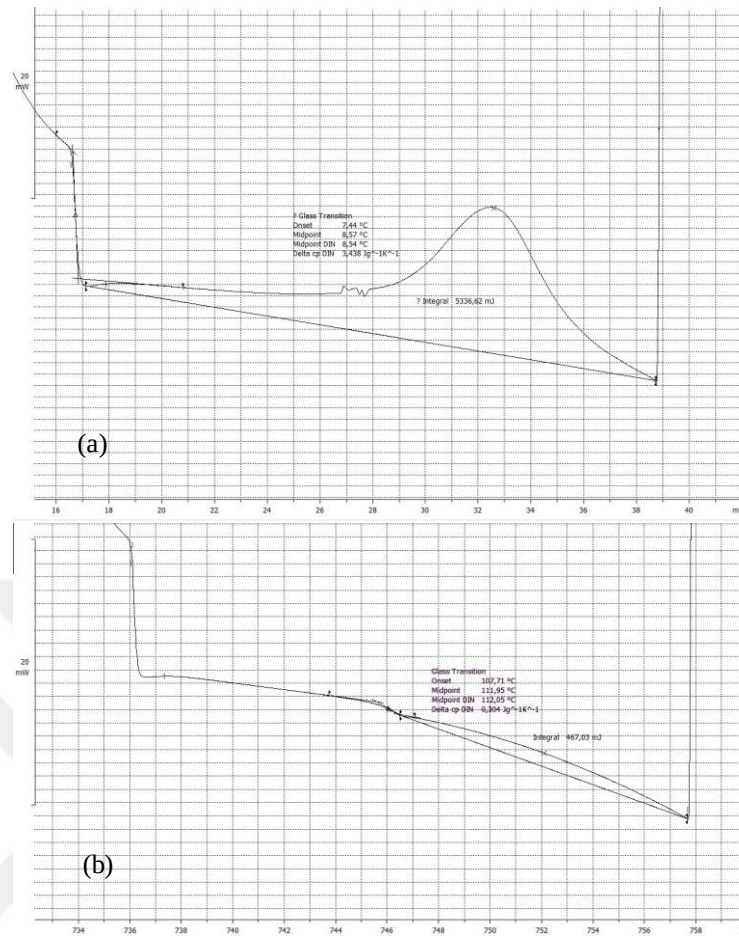


Figure 4.12 DSC thermograms displaying the total ΔH from a steady temperature. Cured at 140°C for (a) 0.1 and (b) 90 minutes

When the experimental α is compared with the α calculated by the DiBenedetto equation, it is seen clearly that the experimental one is 6.2% lower on average. The calculation method with the DiBenedetto equation only considers the polymerization reaction of epoxy resin and hardener but does not allow the effects of reinforcement additives such as SiO₂ and plasticizer. It is well known application of addition of plasticizers to improve flexibility and crack resistance and fillers to increase stiffness of the thermoset structure. It is well documented in the literature that these kinds of modifiers have strong decreasing effects on T_g values (Bakar, 2007; Simon, 2000; Thomson, 1984; & Liu, 2012).

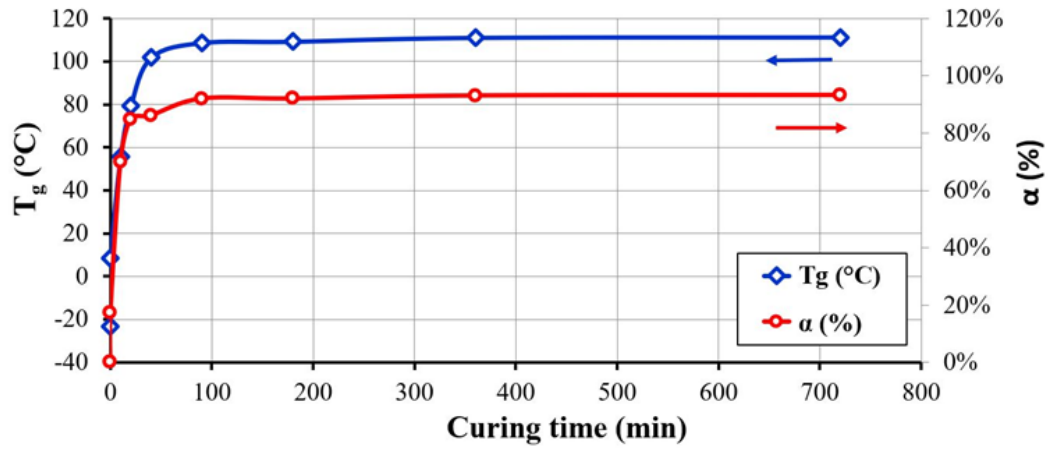


Figure 4.13 Correlation of conversion degree α with the T_g by DSC study

Table 4.6 Conversion degrees given by the DiBenedetto equation

Delta (λ) 0.57					
T_g (°C)	α (%) experimental	α (%) DiBenedetto	Difference	α (%) corrected (6.2%)	Mean error (%)
-23.4	0.0%	0.0%	0.0%	0.0%	0.0%
8.5	17.3%	35.3%	18.0%	29.1%	-68.0%
55.8	70.1%	71.5%	1.4%	65.2%	6.9%
79.3	84.8%	84.9%	0.1%	78.7%	7.2%
101.8	86.2%	95.9%	9.7%	89.6%	-4.0%
108.7	92.0%	98.9%	6.8%	92.7%	-0.7%
109.3	92.1%	99.1%	7.1%	92.9%	-1.0%
111.1	93.1%	99.9%	6.8%	93.7%	-0.7%
111.3	93.3%	100.0%	6.7%	93.8%	-0.6%
			6.2%	mean	0.05%

This 6.2% decrease from the equation can be explained with 0.2% plasticizer and 60% SiO₂ addition to the epoxy structure. Consequently, the DiBenedetto equation was modified by subtracting the modifier effect of 6.2% to obtain exact equation defining real correlation between α and T_g for current epoxy system, which is given with the Equation 4.3.

$$\alpha(T_g) = \frac{1}{\left(\frac{111.3 - T_g}{T_g + 23.4}\right)^{0.57} + 1} - 0.062 \quad (4.3)$$

Experimental (α), DiBenedetto (α), and Corrected (α) conversion degree values are given with the Figure 4.14 as a function of T_g . It can be clearly seen from the Figure 4.14 that, modified α conversion degree is well correlated with the experimental results.

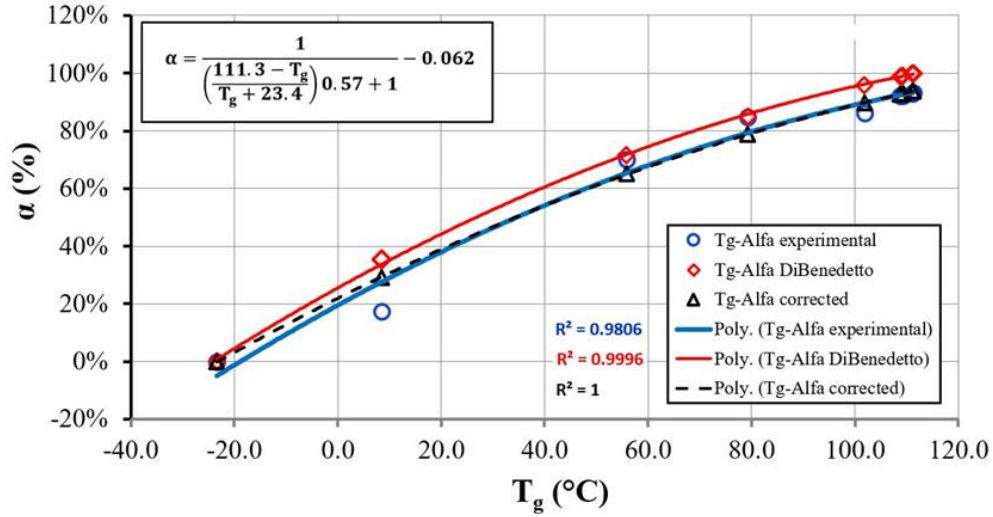


Figure 4.14 Conversion degree α correlation with the T_g given by the DiBenedetto equation

4.3 Mechanical Tests

4.3.1 Particle Distribution

Particle size distribution of the silica particles with 36.7 μm , 1.1 μm , and 280 nm are given in Figures 4.15 (a), (b), and (c) respectively. Silica particles with the mean size of 36.7 μm have a wide distribution span, while 1.1 μm and 280 nm particles accumulated around the 1 μm and 300 nm sizes respectively. Wide particle size distribution for the composite with 36.7 μm size has one advantage, which is the blocking effect of smaller particles on the sedimentation of the larger particles during the curing stage for the higher filler content. Large diameter distributions make high filler contents possible because the spaces between the large particles are filled with smaller particles. Suspended large particles have an enhancing effect on the fracture properties of the composite. On the other hand, nearly homogeneous particle distribution for the composite with 1.1 μm eliminates any sedimentation for all filler contents, which enables the composite superior on the one with larger particle size in terms of mechanical properties.

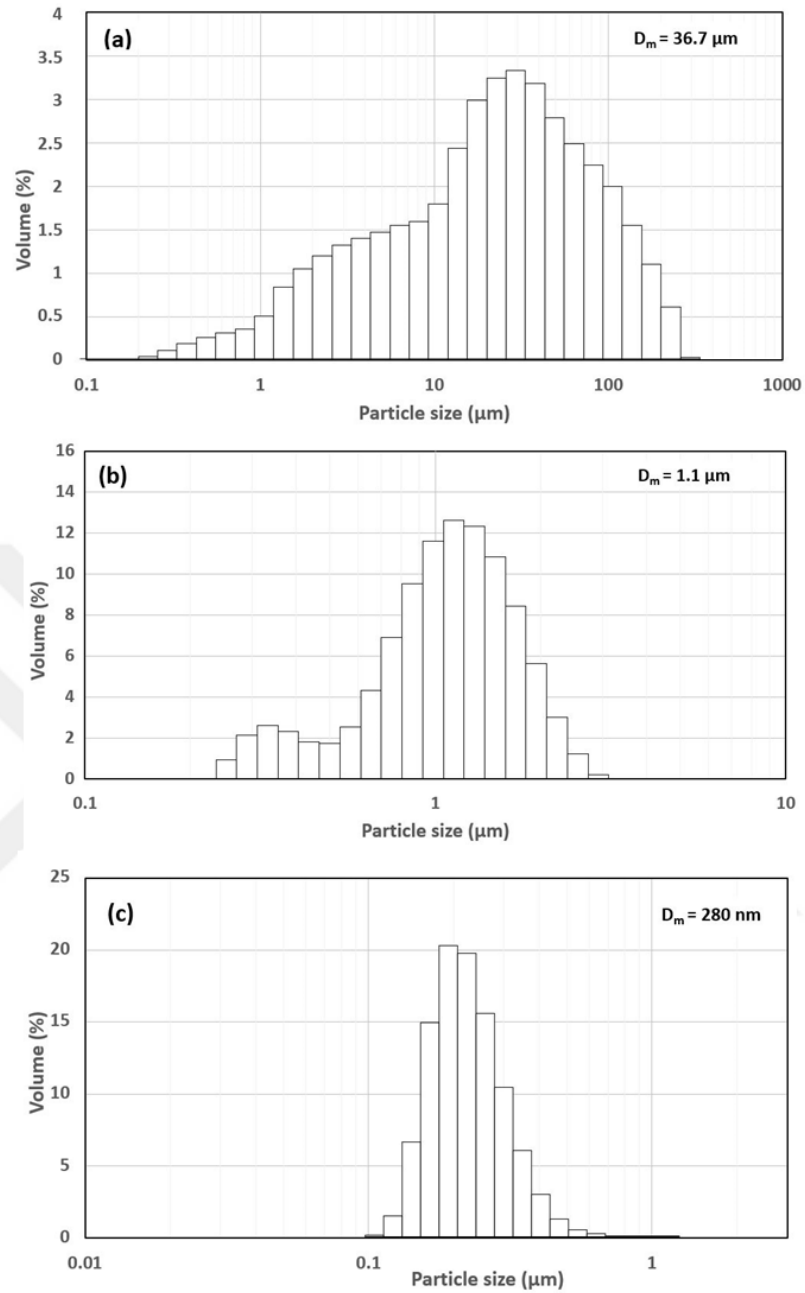


Figure 4.15 Particle size distribution of silica particles, (a) 37.7 μm size, (b) 1.1 μm and (c) 280 nm size

4.3.2 Tensile Properties

Mechanical test results are given in Table 4.7, in which standard deviations are determined based on the data obtained from five experiments, where E is modulus of elasticity, σ_y is tensile strength, ϵ is elongation at break, T_g is glass transient temperature, K_{Ic} is Mode I critical plain strain fracture toughness, G_{Ic} is plain strain

fracture energy release rate. The data from five experiments were used to calculate standard deviations. The tensile strength of the specimen with the silica size of 1.1 μm and with 30 wt% filler content shows the greatest value of 78 MPa among all configurations, including neat epoxy, as can be seen in Figure 4.16. The smaller particle size of silica is considered responsible for the increase of this tensile strength. Due to the higher specific surface area of 1.1 μm silica particles, the bonding strength between matrix and particles enhances, and this leads to an increase in tensile strength. Relatively high curing temperature of 160°C might have a positive effect on this increased bonding strength. The coefficient of thermal expansion (CTE) of the epoxy composite, which increases drastically with increasing curing temperature above 120°C, is nearly three times greater than the silica particle itself at 160°C (Huntsman, 2008; Liu et al., 2009).

Table 4.7 Mechanical test results

Particle size	Filler content (wt%)	E (GPa)	σ_y (MPa)	ε (%)	T_g (°C)	K_{Ic} (MPa.m ^{1/2})	G_{Ic} (kJ/m ²)
None	Unfilled	3.05 ± 0.21	74.70 ± 1.00	4.69 ± 0.15	118.1 ± 1.4	1.17 ± 0.06	0.511 ± 0.07
36.7 μm	30%	4.36 ± 0.49	62.44 ± 2.87	1.74 ± 0.21	115.1 ± 0.6	1.87 ± 0.12	0.860 ± 0.10
	40%	5.82 ± 0.10	59.71 ± 1.45	1.21 ± 0.04	114.7 ± 1.0	1.86 ± 0.08	0.763 ± 0.05
	60%	10.48 ± 0.61	72.79 ± 4.25	0.90 ± 0.15	113.4 ± 1.2	2.32 ± 0.15	1.024 ± 0.07
	20%	3.99 ± 0.21	76.13 ± 0.93	3.89 ± 0.10	117.0 ± 1.3	1.61 ± 0.14	0.709 ± 0.10
1.1 μm	30%	4.80 ± 0.13	78.13 ± 2.42	3.31 ± 0.14	115.9 ± 1.5	1.62 ± 0.13	0.630 ± 0.05
	40%	5.93 ± 0.24	74.88 ± 1.07	1.70 ± 0.10	113.3 ± 1.4	1.73 ± 0.04	0.664 ± 0.02
	2%	2.98 ± 0.08	71.98 ± 0.34	4.96 ± 0.03	119.8 ± 3.2	1.70 ± 0.23	1.006 ± 0.26
280 nm	5%	2.98 ± 0.23	73.29 ± 0.31	4.59 ± 0.25	118.4 ± 1.7	1.74 ± 0.15	1.090 ± 0.16
	8%	3.34 ± 0.11	75.05 ± 0.45	3.94 ± 0.23	114.1 ± 3.9	1.72 ± 0.16	0.977 ± 0.21
	10%				111.5 ± 3.7	1.57 ± 0.13	0.814 ± 0.15

This great mismatch on CTE at the high-temperature cure regime creates a squeezing pressure on the hard silica particles by the epoxy matrix after the cooling step of the composite due to shrinkage of the matrix, which then leads to mechanically enhanced bonding strength. However, both the maximum filler content and particle size have not a remarkable positive effect on the strength of the cured material. Vice versa, increasing of filler content of silica particles from 30 wt% to 40 wt% and particle sizes, decreases the tensile strength of composite for the silica size of 1.1 μm .

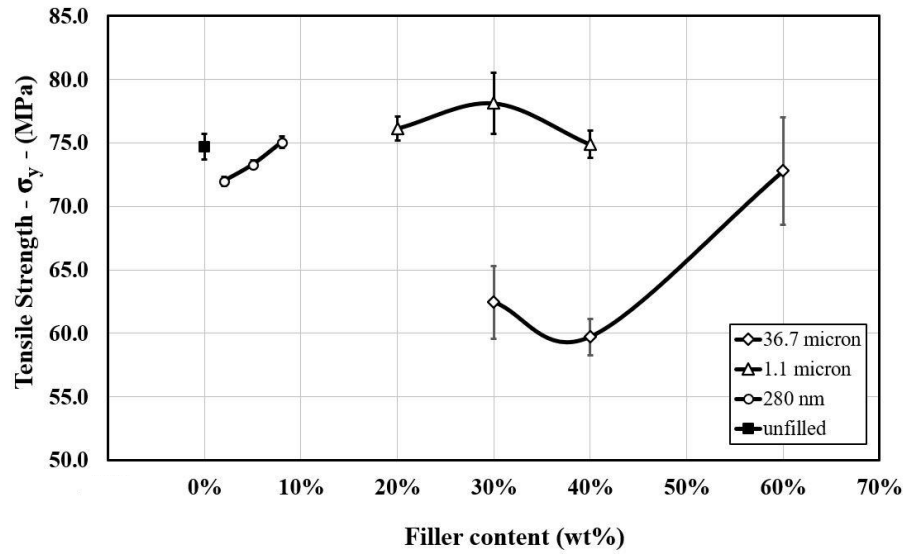


Figure 4.16 Relation between tensile strength (σ_y) and filler content

The strength of the composite depends on the weakest fracture route of the material. Increasing the filler content decreases the strength of the composite by weakening the structure because of stress concentration fields around the hard particles. This result is coherent with the literature (Young, & Beaumont, 1977; Mozco, 2004; Nakamura et al., 1992; Hojo et al., 1974). The reason for the increase in the tensile strength of the composite with 60% filler content and 36.7 μm particle size is considered due to the dominant fracture mechanism for this configuration, which is trans-fracture of larger particles in the structure. Trans-particle fracture mechanism will be detailed in the fracture surface analysis section extensively. Composite with the 280 nm silica shows increasing tensile stress values with increasing filler content. On the other hand, maximum tensile stress of the 280 nm silica filled epoxy composite with 8 wt% filler content was measured 75 MPa which is slightly above of the unfilled epoxy. Since the epoxy with 280 nm silica more than 8 wt% cannot fill the mold due to excessive viscosity, it is understood that the filling content above this ratio does not have a positive effect on tensile stress.

Modulus of elasticity of a composite can be enhanced easily by the addition of silica particles to the matrix. Therefore, the modulus of silica filled epoxy composite increased with the increase of filler content for the specimens with all sizes of the silica. This increase is due to the high load-bearing capacity of hard silica particles

since the fillers have much greater modulus than the matrix. Adhesion between the interface and the particles has not significant promotive effect on the increase of modulus (Dekkers, & Heikens, 1983; Sahu, & Broutman, 1972). Particle size has a positive effect on the modulus in the submicron dimension, while there is almost no meaningful effect over the micron size (Ji, Jing, & Jiang, 2002). It can be seen from Figure 4.17 that modulus was not affected significantly by the particle size. On the other hand, filler content has much more dominant effect on increasing the modulus. Modulus of the specimen, with 36.7 μm particle size and 60 wt% filler content, was measured as 10.48 GPa, which is a 244% improvement compared to the 3.05 GPa value of unfilled epoxy. Therefore, load bearing capacity of the composite can be increased easily by increasing the filler quantity.

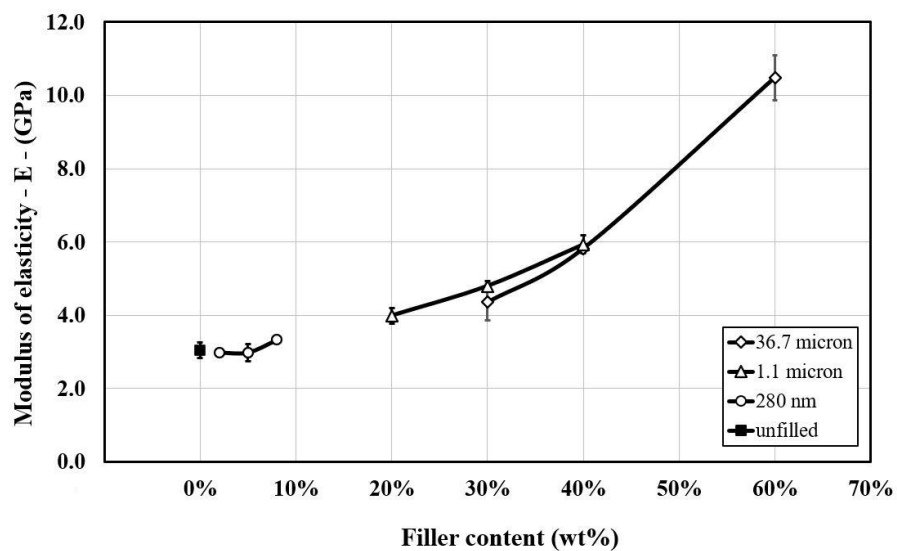


Figure 4.17 Relation between modulus of elasticity (E) and filler content

The filling of the matrix with the silica deteriorates the elongation at break for all of the particle sizes. Specimens with all particle sizes show a very sharp decrease in elongation at break with the increasing filler content compared to unfilled epoxy, Figure 4.18. Main reason for this decrease is the blocking of plastic shearing of the matrix by the silica particles. Thus, plastic deformation was very limited, which contribute to the deformation with minimum elongation. Material with the smaller particle size exhibits better elongation characteristics since small particle size has less

effect on the sharing of the matrix. On the other hand, since the increase in filler content by volume of 1.1 μm silica filled composite is greater compared to 36.7 μm , the $\epsilon\%$ elongation reduction is more sensitive for the 1.1 μm silica filler, which can be seen from the sharper decrease in slope of the curve. Silica filled specimens showed no necking during tensile tests, while the neat epoxy had an observable necking behaviour before the final fracture (Fu, Feng, Lauke, & Mai, 2008).

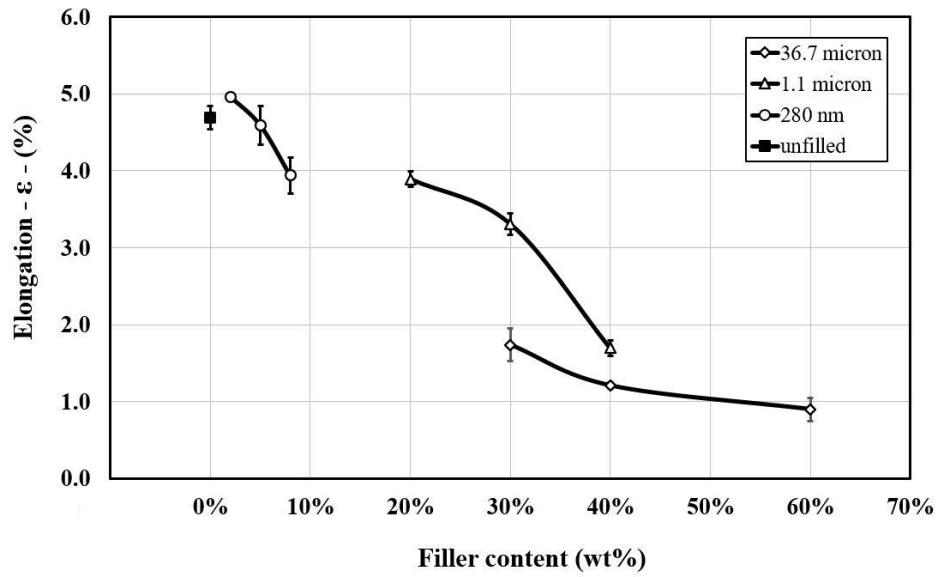


Figure 4.18 Relation between elongation at break (ϵ) and filler content

4.3.3 Fracture Properties

The fracture toughness (K_{Ic}) and critical energy release rate (G_{Ic}) properties of cured epoxy resin filled with the silica particles were studied. K_{Ic} and G_{Ic} values increased with increasing silica size and filler content for 1.1 μm , 36.7 μm , and 280 nm particle sizes compared to unfilled condition, as shown in Figure 4.19a and b. The fracture toughness increased from 1.17 $\text{MPa}\cdot\text{m}^{1/2}$ for the unfilled epoxy to 2.32 $\text{MPa}\cdot\text{m}^{1/2}$ for the epoxy with 36.7 μm particle size and 60 wt% of silica content, which is an improvement of %98. These results reveal that the improvement of the fracture toughness is proportional to the silica filler content and particle size for micron dimension. The G_{Ic} values of the silica filled specimens also enhanced with the silica content. Results are coherent with the results of Nakamura et al. (1992). On the other

hand, the composite with 280 nm silica content shows different fracture behaviour compared to larger particle sizes. Maximum K_{Ic} of 1.74 MPa.m^{1/2} was measured for 280 nm particle size with the 5 wt% silica content, which is also 49% improvement compared to unfilled epoxy. Increasing silica content for the 280 nm particle size inversely effects fracture properties after 5 wt% filler content in contrary to 1.1 µm and 36.7 µm particle sizes. Decreasing fracture properties with increasing silica filler content in sub-micron dimension might be due to over filler content of silica in terms of volumetric base, which can cause agglomeration of sub-micron silica particles.

Fracture energy G_{Ic} of the composite with 280 nm particle size is 1.09 kJ/m² for 5 wt% filler content, which is the greatest value compared to all other composite configurations. Similar improvement was not seen for K_{Ic} value of the same composite compared to 36.7 µm particle size. The reason for higher G_{Ic} is thought to be due to the extremely low modulus of elasticity of the 280 nm particle size composite structure with 5 wt% content. In Mode I crack formation for plain strain condition, G_{Ic} is inversely proportional with transverse elasticity modulus E , which is given with the Equation 4.4 where ν is Poisson's ratio. Relatively low modulus of elasticity is the reason for the higher G_{Ic} compared to K_{Ic} .

$$G_{Ic} = \left(\frac{K_{Ic}^2}{E} \right) (1 - \nu^2) \quad (4.4)$$

The higher fracture toughness compared to the unfilled matrix for the 1.1 µm and 36.7 µm particle sizes is due to a combination of some mechanisms such as trans-particle fracturing of some large silica particles in the matrix, crack path deflection around particles which leads to energy dissipation in the damage zone, and crack pinning depending on the particle size and filler content. On the other hand, dominant fracture mechanisms for the composite with 280 nm particle size are crazing of the matrix ahead of the crack tip for the initiation phase, and shear yielding and crack pinning for the crack propagation phase. Fracture mechanisms depending on the particle size and content are discussed in section 4.3.7 in detail.

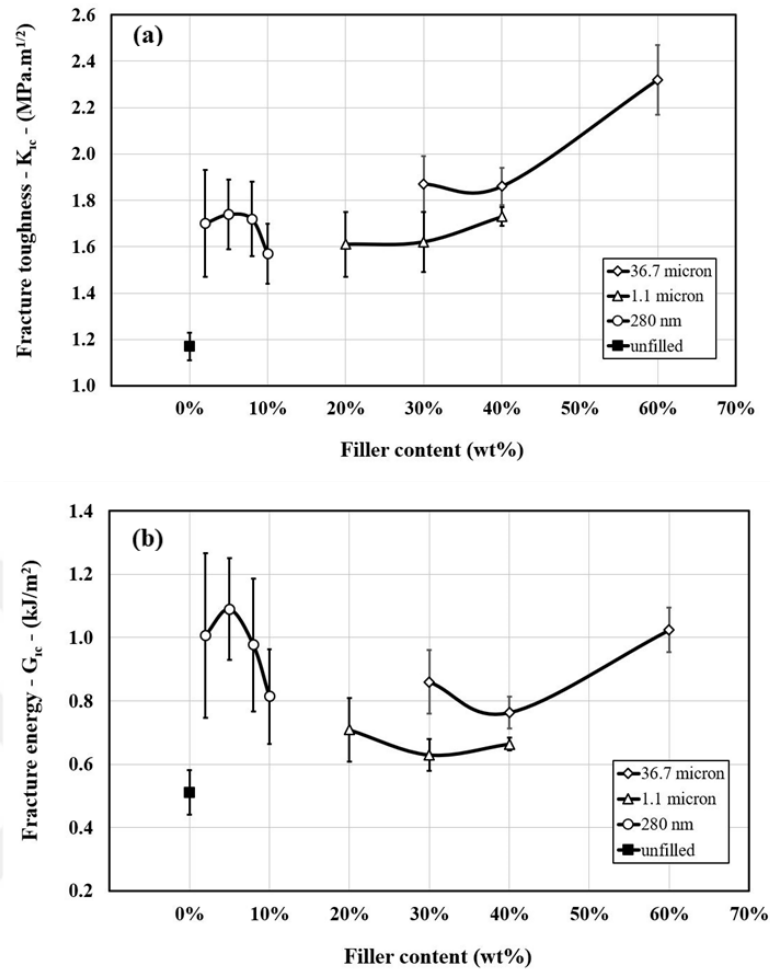


Figure 4.19 Relation between filler content and (a) plain strain fracture toughness (K_{IC}), (b) plain strain fracture energy release rate (G_{IC}).

Two important results were obtained from the SENB tests, depending on the particle size and the filler content: the behaviour of the fracture properties of the material depending on the grain size varies depending on whether the particle size is at the micro or nano level. While K_{IC} and G_{IC} values increase with increasing particle size in micron dimension, they decrease with increasing particle size in nano dimension.

Similar relationship is valid for silica particle content, depending on the particle size dimension. In other words, while increasing particle content in micron size, K_{IC} and G_{IC} values increase, on the contrary, increasing particle content in nano dimension worsens fracture properties. It is thought that the main reason for this is the high risk

of agglomeration at high volumetric loading of particle size in nano dimension (10 wt% ~ 63 vol% for 280 nm particle size).

4.4 Glass Transient Temperature

There is a slight decrease in T_g for both particle sizes, with 60 wt% and 40 wt% filled epoxies while the composite filled with 280 nm particle shows a drastic decrease after 5 wt% silica content compared to the unfilled one. T_g change depending on the particle size and filler content is given in the Figure 4.20. In the graphic, the averages of the measured values are represented by circles, triangles, and squares, while the standard deviations are shown by error bars. Maximum T_g decreases depending on the particle sizes with the maximum filler content are 4.7°C, 4.8°C, and 6.6°C for the composite with 36.7 μm , 1.1 μm , and 280 nm particle size, respectively, compared to unfilled epoxy.

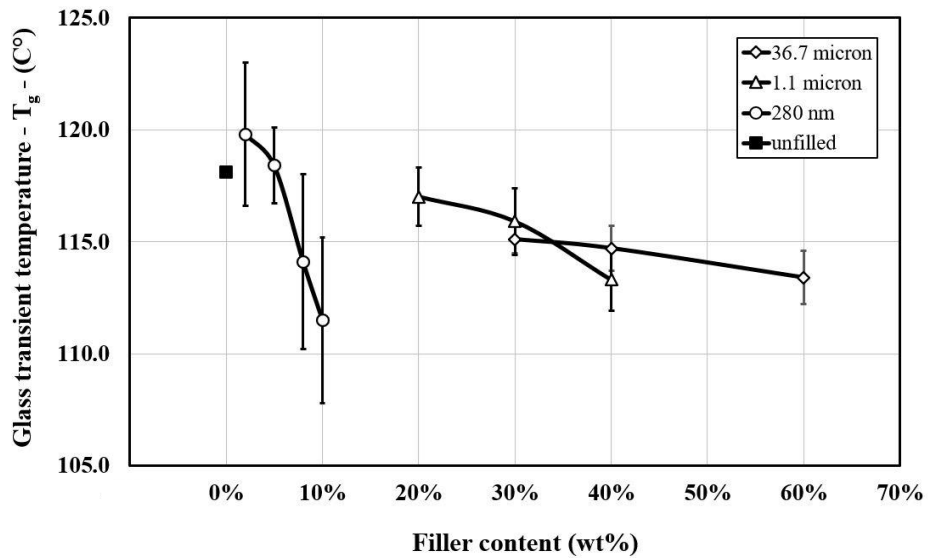


Figure 4.20 Relation between glass transient temperature (T_g) and filler content

The common result for each composite group is that the T_g value decreases with increasing particle content. In addition, as it can be easily seen from the increase in the slope of the curves, with decreasing of the particle size, the T_g value decreases more drastically as the particle size gets smaller. Due to the smaller particle size, the number of particles per unit volume and therefore the specific surface area increases drastically, especially for the nano dimension. Accordingly, this decrease in T_g is

thought to be due to the blockage of covalent bond formation in the final stages of the reaction due to the excessive number of particles in the structure. The structure that cannot complete the covalent bond formation in the final stages of the curing reaction due to the interaction with the smaller particles gives a lower T_g value. On the contrary, slightly higher T_g was measured for the composite with 280 nm particle size and 2 wt% particle content compared to unfilled epoxy. It is thought that the small amount of nano particles in the structure promotes the formation of more covalent bonds by creating nucleation sites in the initial stages of the curing reaction.

Harsch et al. (2007) found out in their study that the reaction activation energy of the epoxy was increased when inorganic silica particles were incorporated. The reactive monomers and rigid inorganic particles may have chemical or physical interactions. Chemical bonds can be formed between reacting molecules and the silica surface. Thus, some inhibition of the cure process between the hardener and resin might be maintained. That might give rise to the total conversion for the filled material is less than the neat resin. It is deduced from the study of Rahul and Kitey (2016) that, K_{ic} value of the cured neat epoxy is inversely correlated with cross-link density. Considering the T_g of the cured epoxy is directly the function of cross-link density according to DiBenedetto equation, decreasing T_g has a positive effect on the fracture toughness of the cured final structure (Pascault, 2002). Consequently, it is anticipated that the decrease of the T_g value of the specimens with the 60 wt% filler content brings about an improvement of K_{ic} values of the final structure. It can be estimated by a simple calculation from the study of Rahul (2016) that 4.7°C decrease of T_g value for 60 wt% filled specimens might cause just 3.2% improvement on K_{ic} value, which is insignificant compared to the overall improvement of 98% with respect to neat epoxy. As a result, a minor decrease in T_g of the final structure has a minor effect on K_{ic} while filler content and particle size play the greatest role in the improvement of the fracture properties of the final material. The composite with smaller particle size shows more drastic T_g decrease compared to larger particle size, due to the relatively increased interaction of much smaller particles with the reactants during the curing reactions. The maximum cross-link density at stoichiometric composition shows that anhydride reactants are primarily utilised to crosslink resin chain ends.

These findings show that the T_g of composites rises as nanoparticle size decreases. In general, the improvement in T_g is ascribed to strong adhesion between the polymer and reinforcement particle, allowing the nano size particle to limit segmental motion and therefore improve T_g . More contact area between the silica and the epoxy matrix is provided by smaller particles at a given SiO_2 concentration, which increases the interfacial force between the two components more than larger particles (Ou, & Shiu, 2010).

4.5 Thermal Stability Analysis by TGA/DTA

Thermogravimetric analysis results are summarized in Figure 4.21 to investigate the thermal stability of the silica reinforced epoxy polymer composites. The overall thermogravimetric curve patterns of the silica filled epoxy resins resembled those of the unfilled epoxy. This is rational due to the thermal weight loss of the composites comes from the organic part of the epoxy resin.

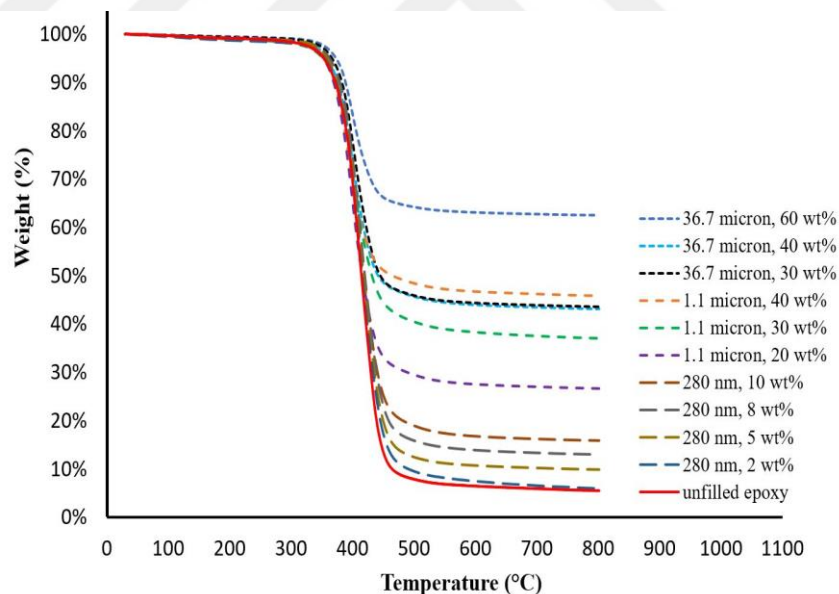


Figure 4.21 TGA thermograms of silica filled and unfilled epoxy composites

The degradation graphics of the composites show a two-stage process. The first stage takes place at the temperature between 30°C and 365°C, which was due to the breaking of unreacted part of epoxy resin or other impurities. In this step, homolytic chain scission of chemical bonds takes place. This influences the physical properties

but does not cause a large weight loss (Macan et al., 2005). The second stage occurs between 365°C and 413°C, which corresponds to thermal degradation char formation of the cured epoxy network (Jin, & Park, 2012). In this step, dehydration owing to the removal of the water molecule from the carboxyl group, -COOH, causes the first major weight loss in both oxidative and non-oxidative degradation of anhydride-cured epoxies. Then, subsequently formed double bonds continue to breakdown, leading to a total network degradation. It is clearly seen from Figure 4.21 that as the silica filler content ratio increases, the weight loss ratio increases accordingly. This increase is entirely due to inorganic silica filler residue that does not react with increasing temperature.

Thermal resistance of the polymer composites was predicted by taking into consideration of the thermal stability of all TGA weight loss curves with three parameters, which are integral procedure decomposition temperature (IPDT), initial decomposition temperature (IDT), and activation energy (E_a) of decomposition process. Parameters such as IDT, endothermic peak temperature, char yield, and weight loss of TGA tests are given in Table 4.8.

Table 4.8 TGA test results of silica filled and unfilled epoxy composites

Particle size	Filler content (wt%)	Sample weight (gr)	Weight loss (gr)	Weight loss (%)	Residue (gr)	Silica weight (gr)	Char yield (%)	IDT (°C)	Endothermic peak (°C)	IPDT* (°C)
Unfilled	0.0%	13.814	13.063	94.6%	0.751	0.000	5.4%	379	413	480
280 nm	2.0%	12.198	11.469	94.0%	0.729	0.244	4.1%	381	412	482
	5.0%	18.964	17.094	90.1%	1.870	0.948	5.1%	379	412	481
	8.0%	19.353	16.838	87.0%	2.515	1.548	5.4%	380	413	483
	10.0%	13.857	11.660	84.1%	2.197	1.386	6.5%	381	408	481
1.1 micron	20.0%	17.397	12.765	73.4%	4.632	3.479	8.3%	370	399	473
	30.0%	18.137	11.421	63.0%	6.716	5.441	10.0%	372	399	475
	40.0%	18.685	10.121	54.2%	8.564	7.474	9.7%	365	394	469
36.7 micron	30.0%	20.359	13.183	56.4%	7.176	6.108	7.5%	375	405	478
	40.0%	20.130	11.450	56.9%	8.680	8.052	5.2%	372	400	474
	60.0%	17.632	6.571	37.3%	11.061	10.579	6.8%	375	401	468

IPDT comprises initial decomposition, fast decomposition, and char formation (Haldera, Goyatb, & Ghoshc, 2015). In order to accurately compare the thermal

stability of the polymer composites, the corrected IPDT* obtained by subtracting the residual silica weight in the test results was used when calculating the corresponding integrals of the TGA curves. Corrected IPDT* results of silica added composites are also given in Table 4.8.

The highest IPDT* value was obtained with the composite of 280 nm particle size and 8 wt% filler composition, and its value was 483°C which is slightly greater than the unfilled epoxy. On the other hand, smallest decomposition temperature was obtained for the composite with the epoxy 36.7 μm particle size and 60 wt % of silica content. The IPDT* values of the composites depending on the particle size and filler content are given in the Figure 4.22. As can be easily seen from the Figure 4.22, in general terms, increasing particle content decreases the thermal stability of the epoxy composite with increasing temperature. In nano-dimension, 280 nm silica has better effect on the IPDT* compared to unfilled epoxy while decreasing particle size decreases the decomposition temperature in micro-dimension.

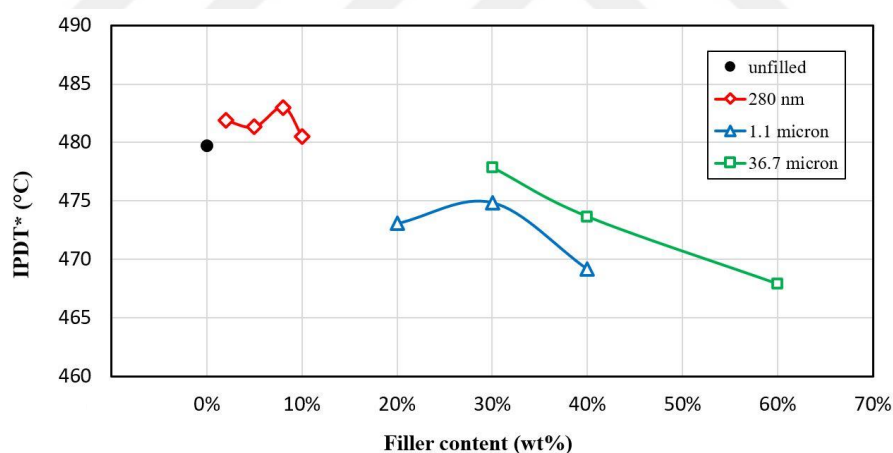


Figure 4.22 IPDT* change depending on the silica particle size and content

Particle size of 36.7 μm with 30 wt% and 40 wt% content shows better thermal stability compared to 1.1 μm particle size with the similar filler content. A similar change is seen in the char yield at the end of IPDT*. The highest char yield belongs to the 1.1 μm particle size composite while the 280 nm particle size composite shows lowest char yield compared to unfilled one, which means even 2 wt% nano-silica addition to composite improves thermal stability. The IDT value is slightly better for

the 280 nm particle size compared to unfilled epoxy, and in the micro-dimension it is worsen with decreasing grain size and increasing silica content. This is also consistent with the IPDT* results.

Activation energy (E_a) of the decomposition of the composites is also a good measure of thermal stability. Higher E_a means better thermal stability due to resistance to thermal degradation. E_a of the composites were obtained from the straight lines corresponding to the $\ln(\ln(1-\alpha)^{-1})$ versus temperature change (θ). All data of the slopes were given good correlation coefficients of R^2 , which were higher than 0.98. The slope graphs to be used to calculate the decomposition E_a of the composites are given in Figure 4.23, Figure 4.24, and Figure 4.25 for 36.7 μm , 1.1 μm , and 280 nm particle sizes, respectively. Calculated activation energies are given in Table 4.9, Table 4.10, and Table 4.11 for, 37.8 μm 1.1 μm , and 280 nm particle sizes, respectively. Change of decomposition activation energy depending on the silica particle size and filler content is summarized in Figure 4.26.

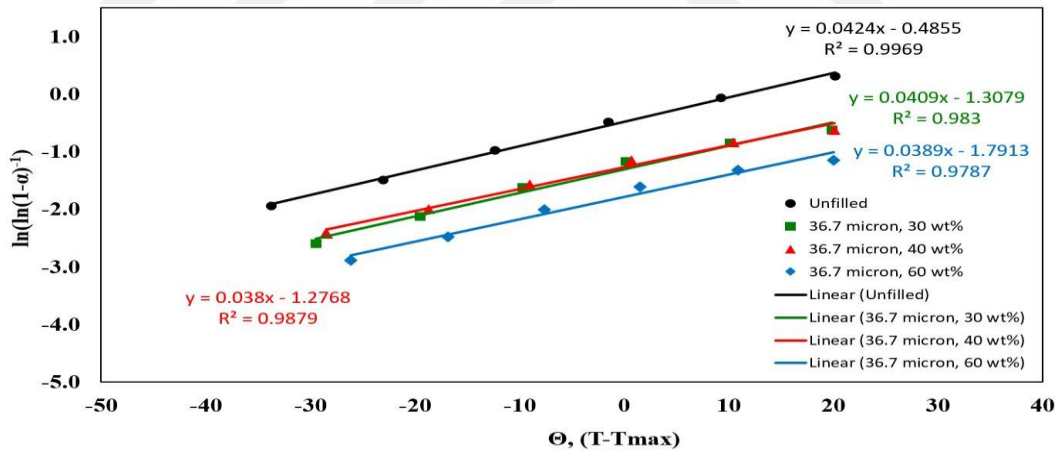


Figure 4.23 Plots of $\ln(\ln(1-\alpha)-1)$ vs. $(T-T_{\max})$ for the epoxy with 36.7 μm particle size

E_a change shows similar pattern with the IDP and IPDT*. Maximum E_a of 169 kJ/mol belongs to the composite with 280 nm particle size and 8 wt% filler content while the composite with 1.1 μm particle size and 30 wt% filler content has 134 kJ/mol. In similar manner, decreased particle size and increased filler content lead to lower activation energy of decomposition in micron size dimension, which worsen the thermal stability of the composite.

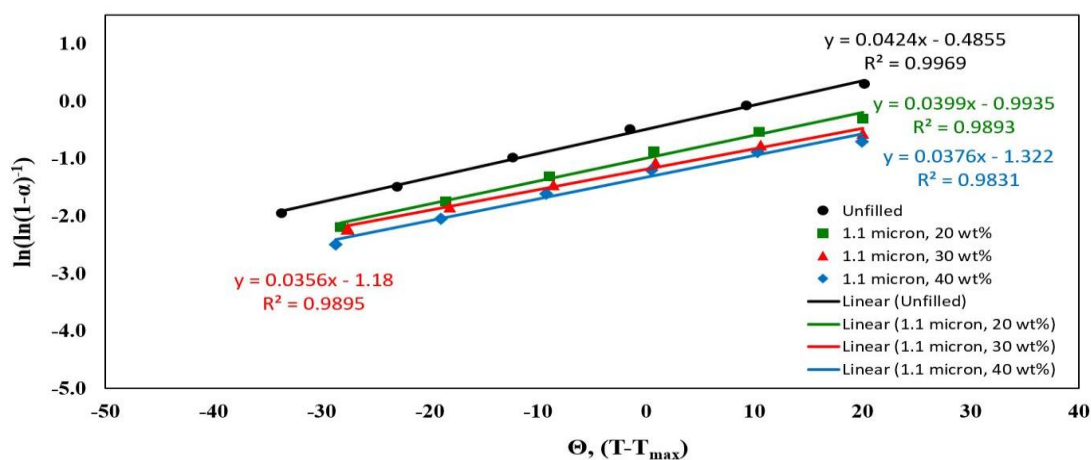


Figure 4.24 Plots of $\ln(\ln(1-\alpha)-1)$ vs. $(T-T_{\max})$ for the epoxy with 1.1 μm particle size

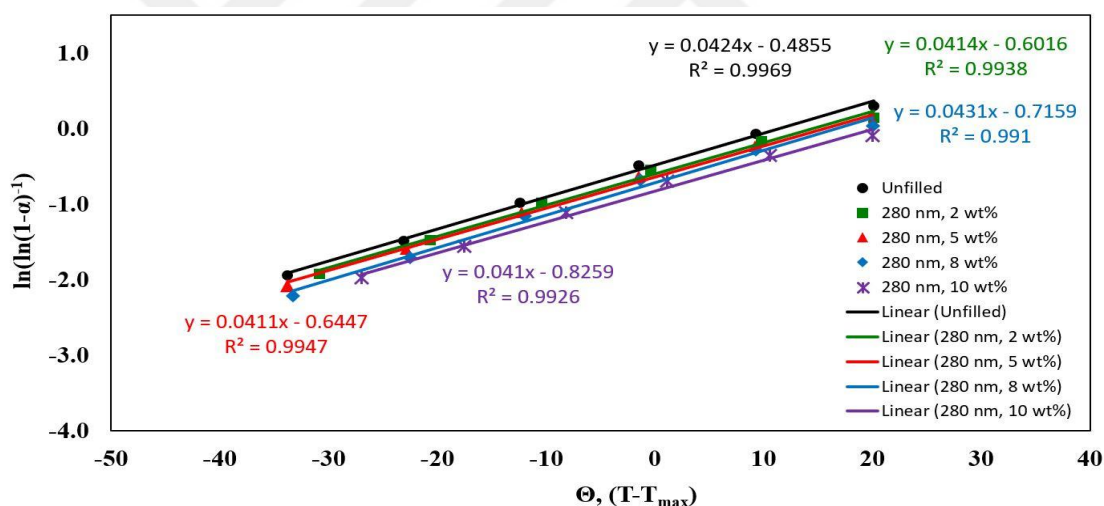


Figure 4.25 Plots of $\ln(\ln(1-\alpha)-1)$ vs. $(T-T_{\max})$ for the epoxy with 280 nm particle size

The crosslink density, curing agent structure, and monomer structure all affect thermal stability and flammability of the epoxy composites. Dehydration of the secondary alcohol, which results in the creation of vinylene ethers, is the first step in the thermal degradation of epoxy composite. The final allylic ether C-O bond is thermally less stable compared to the original C-O, which causes chain scission to occur mostly at the allylic position. On thermal degradation of epoxy resins that have been anhydride-cured, a significant amount of phthalic anhydride is formed. In the

later stages of the decomposition, aliphatic chain ends produce various hydrocarbons, allyl alcohol, acetone, and light combustible gases (Levchik, Edward, & Weil, 2004).

Table 4.9 Activation energies for the decomposition of composites with 36.7 μm particle size depending on the filler content

Particle size	Filler content (wt%)	$\ln(\ln(1-\alpha)^{-1})$	Θ ($T-T_{\max}$)	$E_a/RT_{\max}^2$	E_a (kJ/mol)	$T_{\max}$ ($^{\circ}\text{C}$)
36.7 μm	Unfilled	-1.943	-33.763	0.0424	166	413.3
		-1.490	-23.068			
		-0.979	-12.386			
		-0.485	-1.511			
		-0.070	9.251			
		0.302	20.127			
36.7 μm	30%	-2.596	-29.437	0.0409	156	404.8
		-2.132	-19.523			
		-1.622	-9.697			
		-1.178	0.189			
		-0.853	10.113			
		-0.630	19.882			
36.7 μm	40%	-2.422	-28.459	0.0380	143	400.4
		-1.998	-18.678			
		-1.575	-9.019			
		-1.157	0.666			
		-0.836	10.401			
		-0.622	20.100			
36.7 μm	60%	-2.890	-26.167	0.0389	147	401.2
		-2.477	-16.837			
		-2.007	-7.668			
		-1.609	1.510			
		-1.327	10.885			
		-1.147	20.004			

Higher char yield at the end of a high temperature decomposition leads to higher thermal stability of the composite material. Vankrevelen (1975) showed that the charring performance of epoxy resins is associated with their OI (limiting oxygen index) (Vankrevelen, 1975). Although E_a and IPDT* are high in nano-silica added epoxy composite, the reason for the low char yield is thought to be due to the large quantity of phthalic anhydride being regenerated during thermal decomposition

Table 4.10 Activation energies for the decomposition of composites with 1.1 μm particle size depending on the filler content

Particle size	Filler content (wt%)	$\ln(\ln(1-\alpha)^{-1})$	Θ ($T-T_{\max}$)	$E_a/RT_{\max}^2$	E_a (kJ/mol)	$T_{\max}$ ($^{\circ}\text{C}$)
1.1 μm	20%	-2.191	-28.317	0.0399	150	398.84
		-1.741	-18.554			
		-1.302	-8.953			
		-0.876	0.660			
		-0.535	10.457			
		-0.302	19.981			
1.1 μm	30%	-2.218	-27.598	0.0356	134	399.31
		-1.837	-18.153			
		-1.451	-8.613			
		-1.068	0.843			
		-0.762	10.599			
		-0.559	20.030			
1.1 μm	40%	-2.488	-28.707	0.0376	139	394.19
		-2.039	-18.998			
		-1.612	-9.251			
		-1.194	0.501			
		-0.888	10.289			
		-0.696	19.961			

The low char yields of the epoxy resins based on nano-silica filler further indicate that this particle may act as a char protector rather than a char generation promoter. On the other hand, significant improvements in the OI index and thermal stability of nano-silicon doped epoxy composites are available in the literature (Wu et al., 2002). Conversely, Peterson et al. (1973) and Saavedre et al. (2008) demonstrated that

inorganic micro fillers such as alumina or silica, accelerate the thermal decomposition of epoxies because of their catalysis properties. Kinetic proof of the catalytic action of some metallic additives such as Zn, Cu, and Al in epoxy resin composites was provided by Sanchez et al. (1993) and Saavedra et al. (2008).

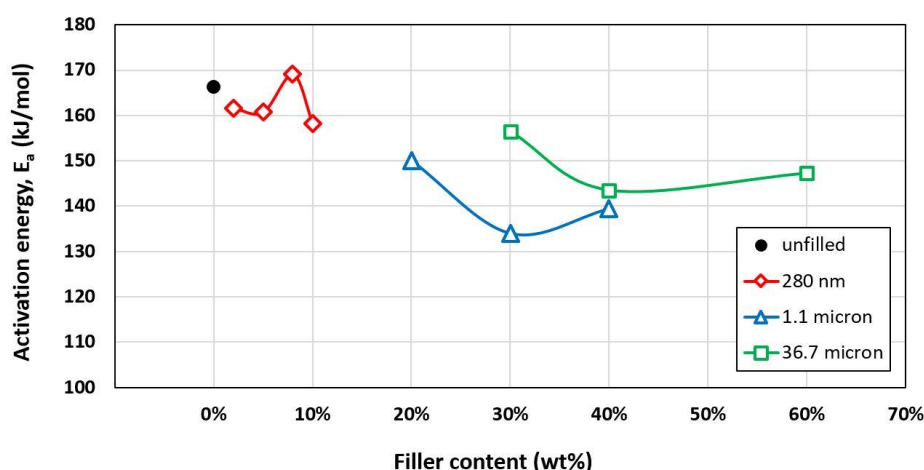


Figure 4.26 Activation energy of decomposition depending on the particle size and content

DTA plot of the composites given in Figure 4.27 also gives some information about the route of the decomposition reactions. Clear glass transition pattern can be seen from the change of the slope of the curves between 100°C and 120°C for all composites. First decomposition reaction starts at 370°C due to the breakdown of ether linkages for the composite with 1.1 μm particle size and 30 wt% filler content (Sickfeld, & Mielke, 1984). Weight loss beyond 399°C, which is the endothermic peak for the same composite, is attributed to the burning of the carbon residue from the decomposed composite. Endothermic peak is the temperature (T_{max}) that the maximum weight loss occurs. Endothermic peaks take place between 399°C and 413°C temperatures for other composites depending on the particle sizes and filler content. T_{max} of the nano-size composites almost equal to the unfilled epoxy, which is greater than the micron-size composites.

The isomerization of the epoxy groups to carbonyl groups is responsible for the exothermic peak seen between 450°C and 500°C. The first process of decomposition is bond scission, which results in a radical with an unbroken epoxy group. This radical is then isomerized to a radical with a carbonyl group. An essential step in the pyrolysis

of epoxide resins is the isomerization of an epoxy group to a carbonyl. Thermochemical studies have shown that the conversion of ethylene oxide to acetaldehyde is very exothermic (Joshi, You, Barckholtz, & Wang, 2005). Free radical mechanism of the thermal decomposition of epoxy resins proposed by Anderson (Anderson, 1961). According to Anderson, the quick isomerization reaction might produce enough heat in a moment to start a variety of free radical reactions, which would then cause the resin to decompose thermally.

Table 4.11 Activation energies for the decomposition of composites with 280 nm particle size depending on the filler content

Particle size	Filler content (wt%)	$\ln(\ln(1-\alpha)^{-1})$	Θ ($T-T_{\max}$)	$E_a/RT_{\max}^2$	E_a (kJ/mol)	$T_{\max}$ (°C)
280 nm	2%	-1.926	-30.822	0.0414	162	411.7
		-1.477	-20.624			
		-0.979	-10.417			
		-0.541	-0.348			
		-0.168	9.828			
		0.146	20.094			
280 nm	5%	-2.085	-33.737	0.0411	161	412.2
		-1.592	-22.833			
		-1.111	-12.222			
		-0.629	-1.498			
		-0.233	9.245			
		0.095	20.037			
280 nm	8%	-2.220	-33.252	0.0431	169	413.3
		-1.710	-22.485			
		-1.155	-11.922			
		-0.677	-1.328			
		-0.285	9.253			
		0.039	20.014			
280 nm	10%	-1.982	-26.959	0.0410	158	407.8
		-1.561	-17.496			
		-1.116	-8.156			
		-0.700	1.167			
		-0.359	10.577			
		-0.093	19.979			

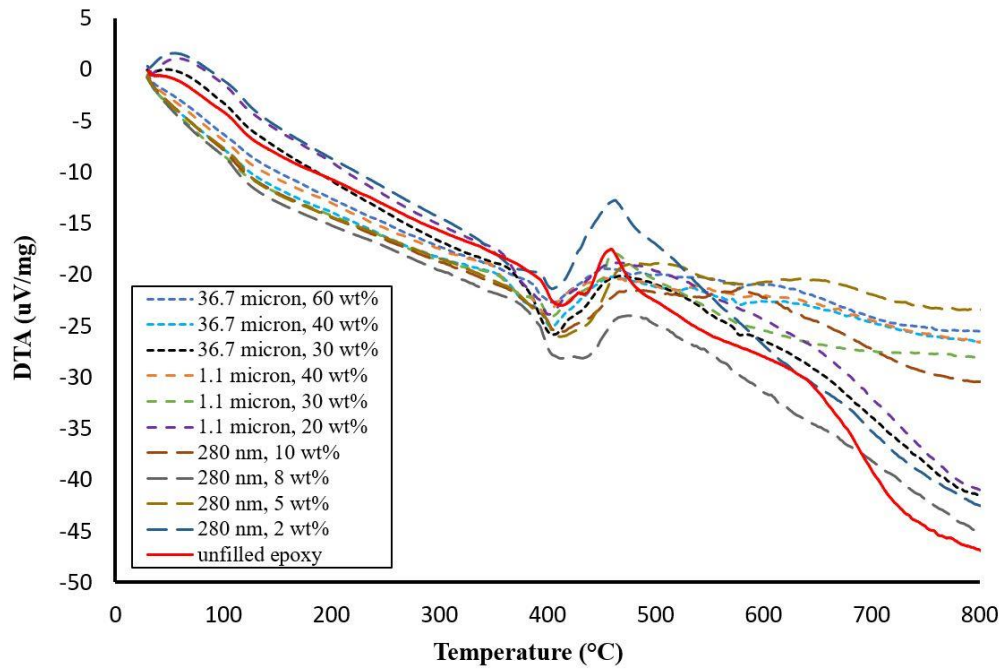


Figure 4.27 DTA thermograms of silica filled and unfilled epoxy composites

4.6 Coefficient of Thermal Expansion (CTE)

CTE results as a function of silica filler content are given with Figure 4.28. CTE apparently decreases with increasing silica particles content for all filled epoxy systems. CTE of unfilled epoxy was measured $57 \mu\text{m}/\text{m}^\circ\text{C}$ while composite with 36.7 μm and 60 wt% filler content was $21 \mu\text{m}/\text{m}^\circ\text{C}$, which is 63% decrease compared to unfilled epoxy. The decrease in CTE at higher filler content is due to a relatively lower CTE of the raw silica particle, which is $0.55 \mu\text{m}/\text{m}^\circ\text{C}$ (Mauro, & Varshneya, 2019). Nano-silica filled epoxy shows much drastic decrease of CTE compared to 1.1 and 36.7 μm due to high volumetric silica content.

It is clearly seen that as the silica particle size decreases from micron-size to nano-size, the CTE also decreases drastically. Qu and Wong (2002) and Dittanet (2012) also reported similar results in their separate works. They observed a strong particle content and size dependence on the CTE values. This can be explained by the total surface area of the silica filler particles. They claimed that the particle surfaces restrict the distortion of the matrix by creating a mechanical restraint, which prevents the

expansion of the epoxy matrix during heating. The total surface area of the particles increases with decreasing silica particle size, depending on the diameter. Depending on the decreased particle size, the interfacial area between the silica filler and epoxy also increases. This increased interfacial area leads to a decrease in the expansion of the matrix.

The reason for the CTE of the composite with 1.1 μm particle size slightly greater than the composite with 36.7 μm particle size for the 30 wt% and 40 wt% filler contents, may arise from the particle distribution of 36.7 μm silica has very large span comparing to 1.1 μm silica. Dittanet and Pearson (2012) also reported similar results in their study involving bimodal particle size effect on CTE of epoxy composite. When examined at the same volume fraction, they discovered that all of the bimodal silica particle combinations had CTEs that were equivalent and somewhat lower than those of the unimodal systems (Dittanet, 2012).

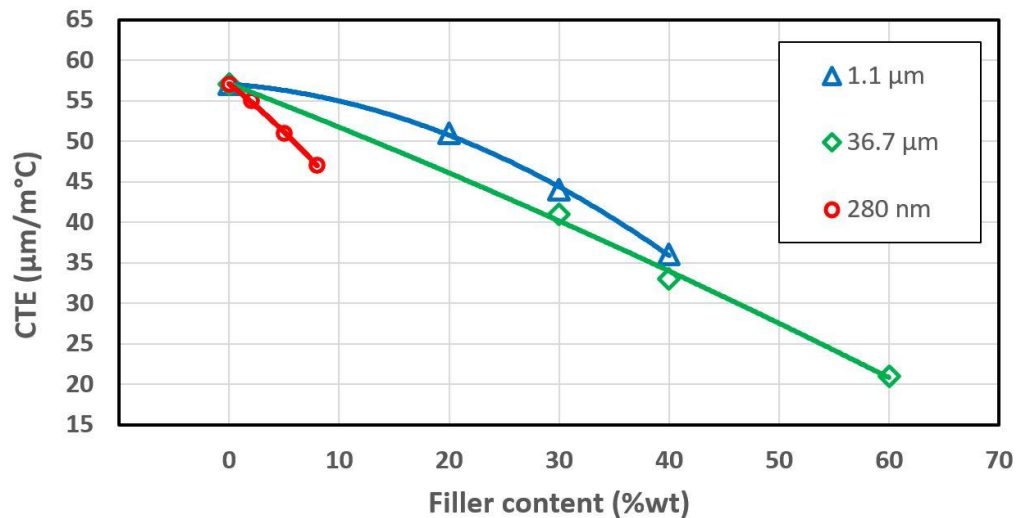


Figure 4.28 Change of coefficient of thermal expansion depending on the filler content

4.7 Fracture Surface Analysis

The primary toughness improvement mechanism for 36.7 μm size and 60 wt% configuration is trans-particle fracture. K_{Ic} increases proportionally with particle loading, which might be related to the progressive increase in the incidence of trans-particle fracture. When the adhesion strength between particles and matrix is greater

than the intrinsic strength of the particle itself, larger particles with the size of greater than $80\text{ }\mu\text{m}$ tend to fracture while the crack is propagating in its route. High fracture resistance of the silica particles in the structure increases the fracture toughness of the composite structure. SEM image given in Figure 4.29 shows pure brittle fracture of silica particles. Clear flat surfaces and straight boundaries of the fractured particle surfaces support the brittle manner fracture notion. It is concluded that there is a strong adhesion between the filler and the matrix since no particle debonding is seen from the SEM images, Figure 4.30, and 4.31. The crack that progresses in the matrix structure during deformation prefers to proceed by breaking the large silica particles thoroughly since the energy of deflection or separating the particle from the matrix structure will be higher than the particle breaking energy due to the high interface adhesion. A minor decrease in K_{Ic} , G_{Ic} , and even tensile strength can be explained by the sedimentation of the large silica particles during the curing reaction for the composites, with 40 wt% filler content and $36.7\text{ }\mu\text{m}$ particle size.

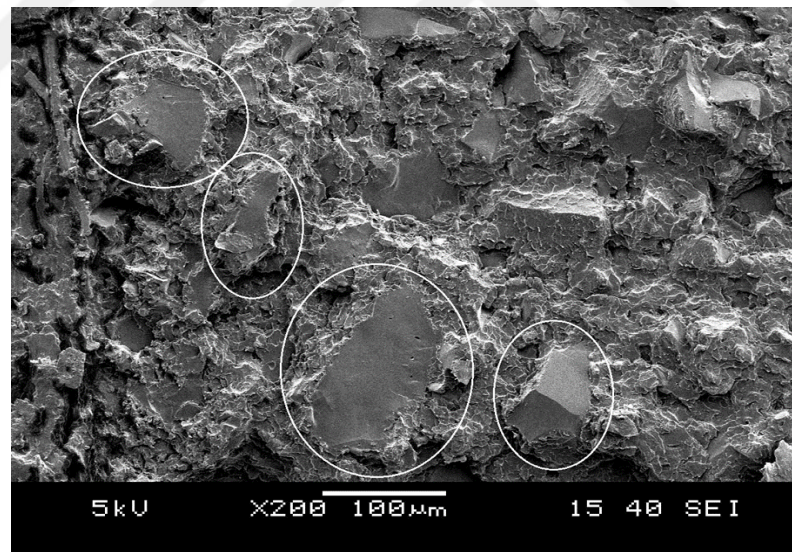


Figure 4.29 SEM image of fracture surface of the composite with the particle size of $36.7\text{ }\mu\text{m}$ and 60 wt% filler content. Clear view of trans-particle fractured silica particles

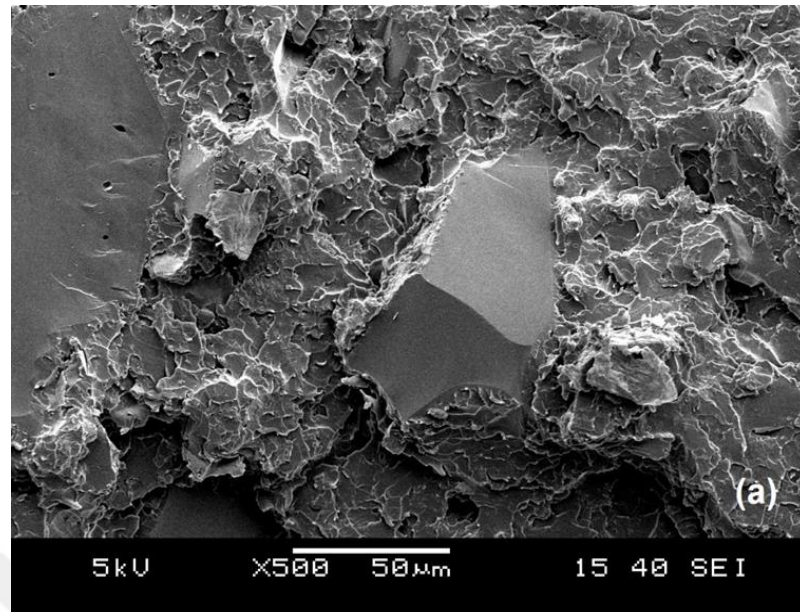


Figure 4.30 SEM images of fracture surface of the composite with the particle size of 36.7 μm and 60 wt% filler content and detailed views of the brittle fractured silica particles

The sedimentation rate was measured by burning tests, and it was %3 for the composite with 30 wt% and 40% filler contents and 36.7 μm particle size. It is considered that any sedimentation of the larger particles is blocked by the interaction of other smaller particles in the structure with 60 wt% filler content. Then, the trans-particle fracture mechanism is more dominant for a higher silica filler content compared to the lower ones. Dittanet (2013) found in her study that bimodal type filler of the resin, which is the mixing of nano and micro silica particles, shows better fracture toughness, which supports present findings (Dittanet, 2013).

Crack front deflection is a secondary mechanism for the specimens with the higher filler content. In the crack path deflection mechanism, the mechanical interaction between the propagating crack front and silica particles may cause a perturbation of the crack route. Consequently, the crack front tilts and warps when it meets the particles and then propagates surrounding the particles, which creates a non-planar crack propagation. The direction change of the crack dissipates crack propagating energy, which increases the total fracture surface and roughness, and improves the fracture toughness (Qin, & Ye, 2015). SEM images of strongly bonded coarse fracture surfaces of the specimens, with 36.7 μm particle size and 60 wt% filler content, affirm the crack path deflection mechanism, Figure 4.29. Excessively rough appearances of

the specimen fracture surfaces testify that the fracture toughness is a function of filler content and particle size (Wetzel, 2006). Increasing particle size and filler content improves the fracture properties of the composite due to the synergetic effect of two mechanisms, which are trans-particle fracture and crack path deflection.

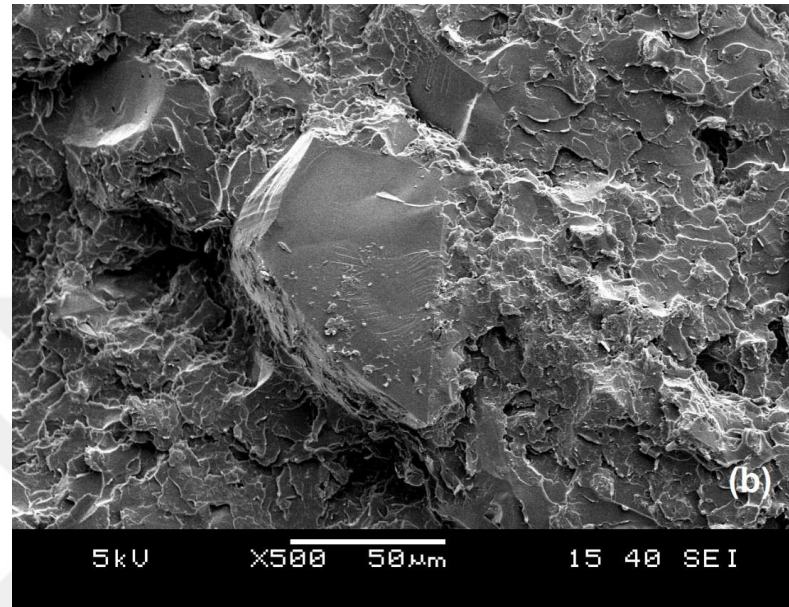


Figure 4.31 SEM images of fracture surface of the composite with the particle size of $36.7\ \mu\text{m}$ and 60 wt% filler content and detailed views of the brittle fractured silica particles

Crack pinning is the dominant mechanism in improving fracture toughness properties for the specimens with $1.1\ \mu\text{m}$ particle size and lower filler content. In the crack pinning mechanism, when a crack propagates, hard particles can serve as pinning points to keep the crack from advancing into the matrix by dissipating its energy. In the propagating phase of the crack, rigid particles anchor the crack bending front between them, which increases line energy. Pinning fracture mechanism is only suitable for low volume fractions (Lange, 1971). There may be a significant breakdown of the particle-matrix interface when the volume percentage rises, which attenuates the governing effect of the pinning mechanism. Pinning mechanism substitutes for the crack deflection mechanism with the decrease of filler content as can be seen in Figure 4.32, and Figure 4.33.

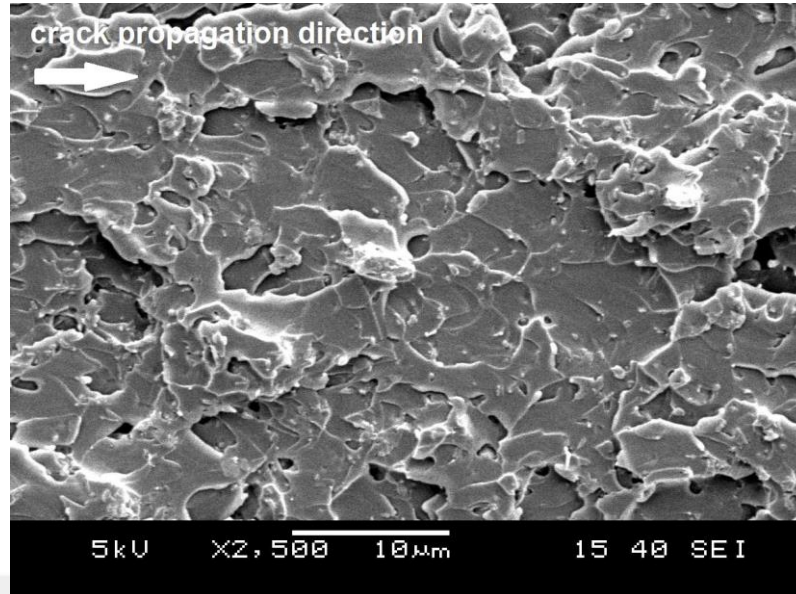


Figure 4.32 SEM image of fracture surface of the composite with the particle size of 1.1 μm and 20 wt% filler content

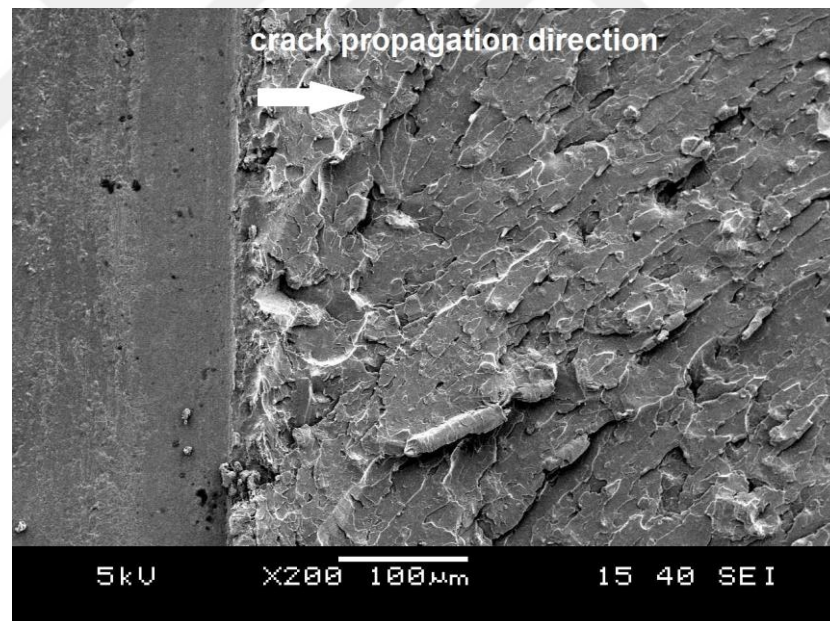


Figure 4.33 SEM image of fracture surface of the composite with the particle size of 36.7 μm and 30% filler content. Smooth surface zone is the crack initiation area

The simultaneous interaction of the propagating crack front with two particles can be seen in Figure 4.34. Crack front changes its curvature as it moves between two particles, while it remains pinned at the particles. When the crack front interacts with silica particles, the crack front length increases due to the change in curvature between

each couple of silica particles. Bowing lines can be seen clearly in the figure, which is indicated by ellipses.

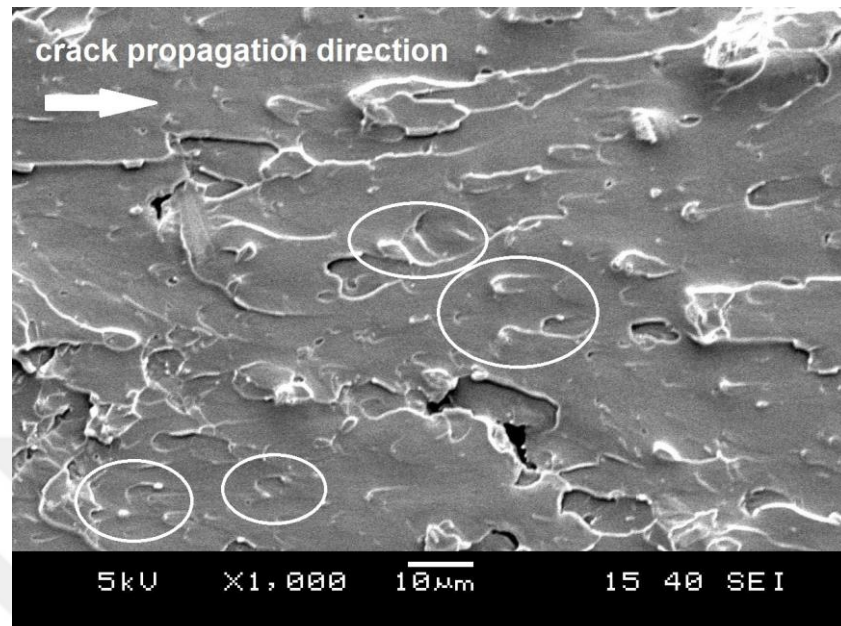


Figure 4.34 SEM image of fracture surface of the composite with the particle size of 36.7 μm and 30 wt% filler content. The pinning mechanism is responsible for the bowing lines on the fracture surface

When the fracture surface of the SEM micrographs was examined, any debonding was observed at the particle-epoxy interface in 1.1 μm particle structure, which is similar to 36.7 μm silica filled composite. Dittanet et al., (2012) reported debonding and consequently plastic void formation at the silica/epoxy interface in their study conducted with nano- and micro-sized spherical silica particles. They explain the improvement in fracture toughness caused by the particle filler with plastic void growth around the particles (Dittanet, 2012). When we compare these results with our study, we can conclude that particle shape also an effect in improving the fracture toughness of the composite structure besides particle size and the content of the filler. Consequently, spherical particles improve the fracture properties by the plastic void growth mechanism, while angular particles provide an improvement according to the trans-particle fracture mechanism for large sizes and the pinning mechanism for small sizes.

The crack initiation that causes failure in the composite filled with 280 nm silica particles is crazing and can be easily distinguished by the mid-rib whitened region. In

Figure 4.35, and Figure 4.36 the whitened mid-rib region just in front of the crack can be seen easily. The polymeric chains of an epoxy polymer are connected by covalent bonds. On the other hand, covalent bonded chains can interact with each other through weak van der Waals forces. When a local strain is applied to resist these forces, a tiny gap develops. This gap is called craze, and can not to grow further, due to the covalent bonds among the chains.

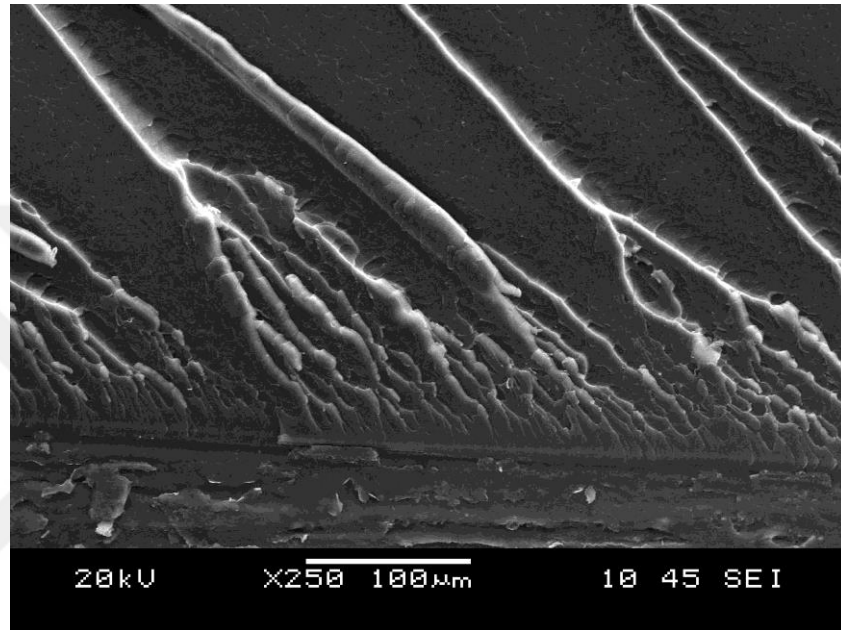


Figure 4.35 Composite with 280 nm particle size, and 2 wt% filler content. Stress whitening line can be seen easily in front of crack line

In glassy polymers such as epoxy crazes are usually initiated at the surface imperfections. Internal defects such as inorganic particles are also sources of craze initiation. The stress concentrations needed for the first micro-void creation are provided by these imperfections.

Crazes support loads because several tiny fibril bundles connect their two surfaces. (Beahan, Bevis, & Hull, 1975). The initiation of numerous minor crazes constitutes a significant degenerative media for the release of strain energy, despite the fact that craze creation is inherently undesirable because it is the prelude to crack formation. These small crazes assist in distributing the stress concentration at the principal crack front. The silica particles also help to prevent moving cracks. When the crack forms, disintegration of the fibril structure reveals a resistance to the propagation of cracks.

Therefore, depending on the situation, crazing may be advantageous to retard crack propagation. Crazing is a plastic deformation process, and it is the most important way of increasing fracture toughness in glassy polymers which deform by crazing rather than shear. The plastic deformation to create crazes very ahead of the growing crack is the main contribution to improved fracture toughness. Consequently, prior to the formation of fractures, very high densities of crazes may nucleate and develop from nano-silica particles. In this way substantial macroscopic plastic strains because of the crazing might be achieved to improve fracture properties of the composite material. In summary, the nano-silica particles in the structure are a source for the formation of craze that resists the crack propagation. Morgan (1977) investigated in detail crazing process by straining BPA epoxy film in the electron microscope (Morgan, 1977).

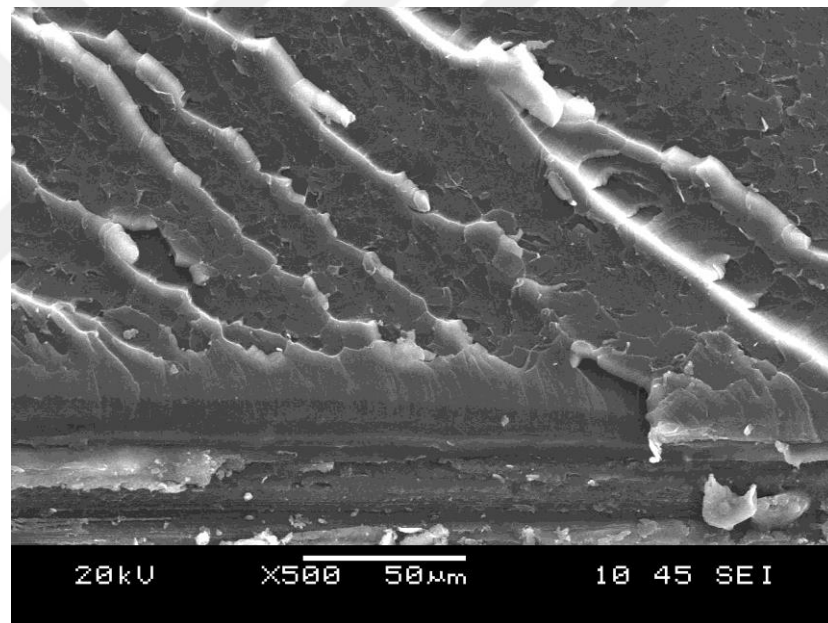


Figure 4.36 Composite with 280 nm particle size, and 2 wt% filler content. Enlarged view of Figure 4.35. Stress whitening is visible in front of the crack line

Crazing is the main mechanism of crack initiation for the composite with 280 nm particle size and 2, 5, 8, and 10 wt% filler content. Silica particles are major sources of craze initiation that take place ahead of the sharp crack line. Stress whitening, crack arrest zone and plastic deformation zone can be seen clearly from the Figure 4.37. Since the refractive index of the craze is lower than that of the parent polymer due to

fibril formation, the presence of the craze is readily observed as a stress-whitened line. It appears that crack arrest zone starts to form after craze initiation during the loading.

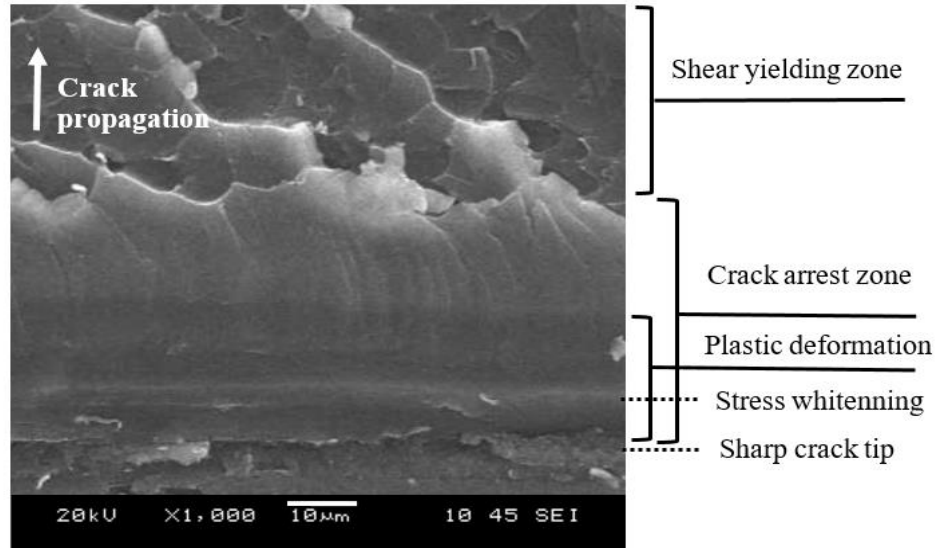


Figure 4.37 Composite with 280 nm particle size, and 2 wt% filler content. Enlarged view of Figure 4.36. Stress whitening due to crazing, plastic deformation zone, and crack arrest zone are clear in enlarged view. Shear bands after the crack arrest zone orient 45° with the crack propagation direction.

The propagation then continues by slow growth through the plastic zone followed by fast growth through the virgin epoxy matrix. The slow advancing zone thus defines the plastic field in front of the crack tip. Dark coloured zone ahead of the craze whitened line represents the plastic deformation zone at the tip of the crack. The appearance of surface discolouration on the fracture surface of amorphous polymers can be considered to be a sign of plastic deformation process during the fracture (Broutman, & McGarry, 1965; Pritchard, & Rhoades, 1976).

The plastic zone widths of 2 wt% and 10 wt% nano-silica content composites were measured from SEM photos as $40\text{ }\mu\text{m}$ and $10\text{ }\mu\text{m}$, respectively. The excessive decrease in the width of the plastic deformation zone due to the increased amount of silica can easily explain the decrease of the K_{Ic} value of composite with % wt10 nano-silica content. Increasing silica content reduces the plastic deformation area in front of the crack, reducing the resistance of the composite structure to crack propagation. Increased nano-silica content has a blocking effect on the plastic deformation of the

interfacial area between the nano-silica filler and epoxy structure ahead of the crack tip.

Shear yielding, which can be clearly distinguished with 45° orientation to crack propagation direction given with the Figure 4.38 and Figure 4.39, which is the second fracture mechanism for the crack propagation for the composite with 2% and 5% nano-silica content. It can be clearly seen from the Figure 4.39 that the very rough, torn like surfaces containing many river markings are clear evidence of severe shear failure combining the surrounding crack fronts on several planes.

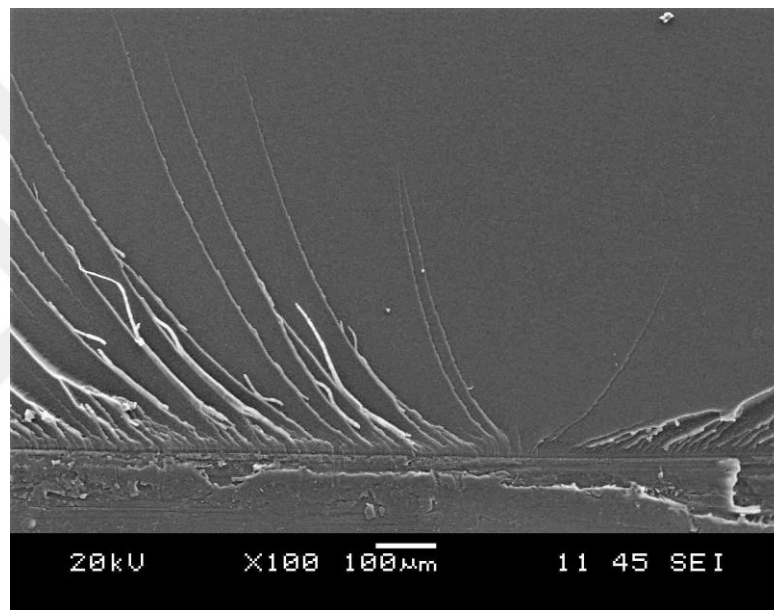


Figure 4.38 Composite with 280 nm particle size, and 5 wt% filler content

Shear bands emerge at the tip of the expanding craze, preventing it from propagating farther. Craze/shear band interaction of this kind has been discussed in detail by Donald (1982), Kinloch (1983), and Bucknall (1977). It was suggested that, in addition to crazing, the plastic flow in the epoxy matrix may result from shear deformations and these deformations may create a significant contribution to the toughening mechanism (Gould, 1976).

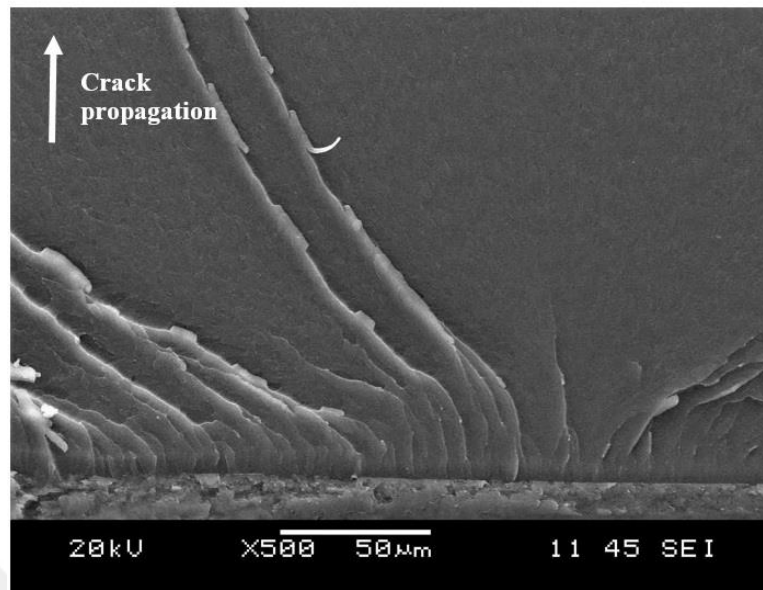


Figure 4.39 Composite with 280 nm particle size, and 5 wt% filler content

During the propagation of the crack in the matrix structure, bowing marks that start to appear at the end of the shear bands are an indication that the crack pinning mechanism has been activated. Figure 4.40 and Figure 4.41 depicts bowing marks for the nano-silica composites of 5 wt% and 2 wt% contents, respectively.

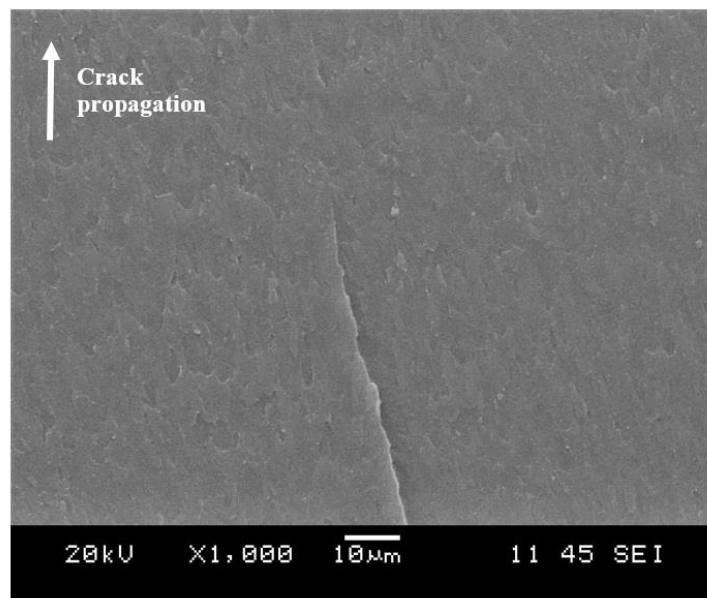


Figure 4.40 Composite with 280 nm particle size, and 5 wt% filler content

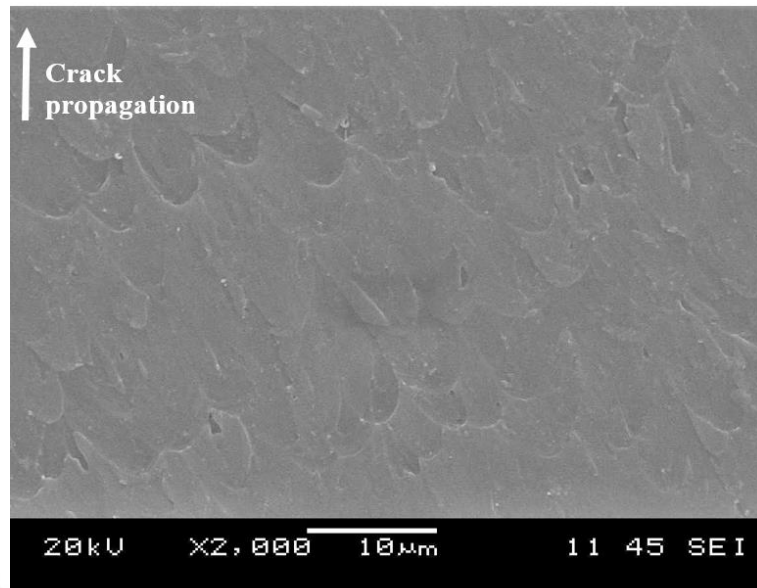


Figure 4.41 Composite with 280 nm particle size, and 2 wt% filler content

The crack initiation mechanism in 8 wt% and 10 wt% nanosilica added epoxy composites can be explained by crazing due to the stress whitening line in front of the crack tip as shown in Figure 4.42.

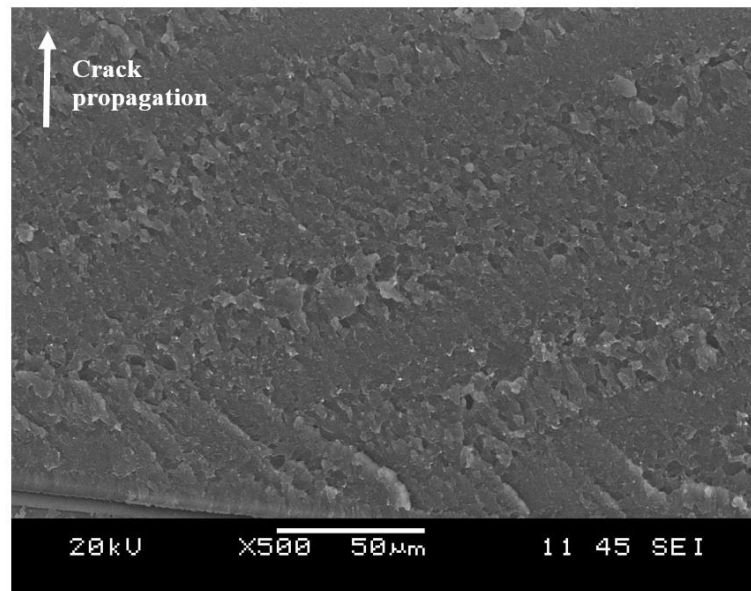


Figure 4.42 Composite with 280 nm particle size, and 10 wt% filler content

However, crack propagation following this relatively confined plastic deformation zone can be explained by the very special case of "mackerel" band formations locally, which were originated on the shearing bands for this fracture situation. For the low nano-silica filled composites, while the crack continues to propagate as shear yielding in the slip bands after crazing, it prefers to propagate partially as Mackerel band waves in the form of crazing mechanism over the slip bands for the composite with high nano-silica content as can be seen in Figure 4.43.

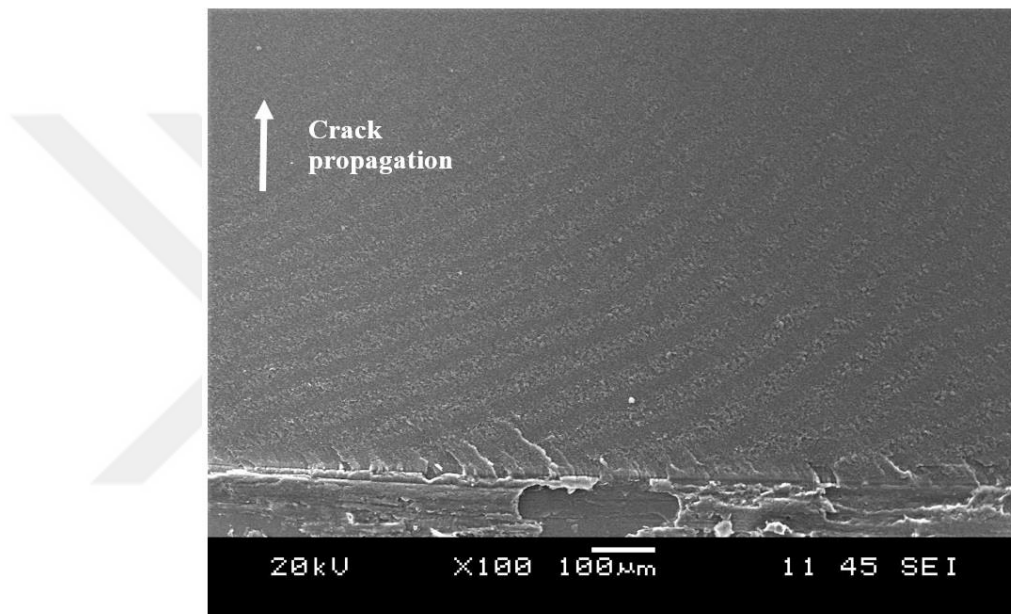


Figure 4.43 Composite with 280 nm particle size, and 8 wt% filler content

Crack propagation characteristics can be defined as related to the Mackerel pattern as follows, where a schematic presentation is provided in Figure 4.44. The main mode of separation takes place by splitting along the interface between the matrix and the craze. Propagating crack continues to oscillate between two matrix/crack interfaces. High speed crack propagation along the interface generates large tensile stress in front of the crack tip, which causes decohesion at both interfaces.

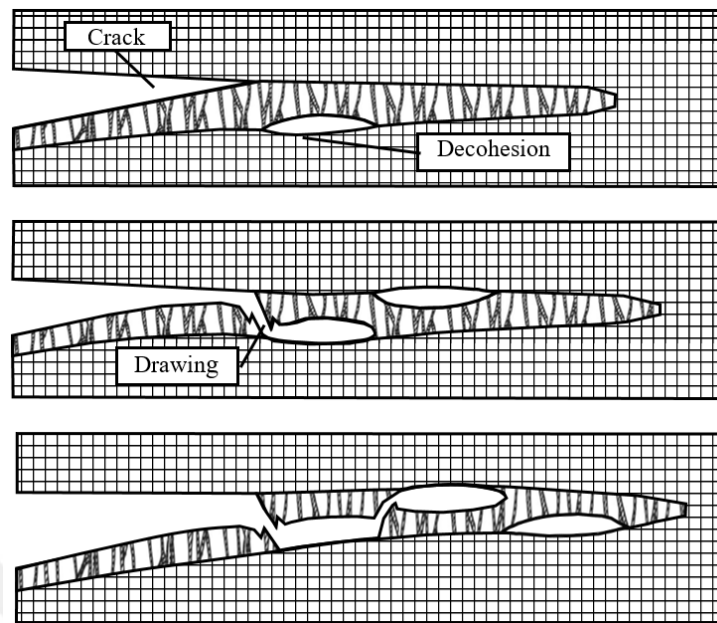


Figure 4.44 Diagram schematically illustrating how mackerel band patterns are created (Murray, 1970)

Decohesion of the only one interface might be formed at some critical instance. This one-sided decohesion creates an abrupt stress relaxation at the crack tip, which slows down the crack propagation. This slow crack growth rate creates relatively smooth fracture surfaces due to the increased reflection of the light, which can be seen as dark bright bands in Figure 4.45.

Simultaneously, increased heat due to the high strain rate at the crack tip make a change in the flow properties of the epoxy polymer. Then crack propagation continues along the same interface while creating secondary cracks on the opposite interface. Adiabatic heating arises from the changing direction of the crack from one interface to the other one during propagation, which might be confirmed by the high degree of drawing of the craze material. Finally, increased viscous flow of epoxy polymer leads to shearing of the craze bridge and causes the crack to jump to opposite interface. This decohesion of one interface and subsequent tearing of the craze bridge process are repeated during crack propagation resulting in the oscillating characteristics given in the Figure 4.46.

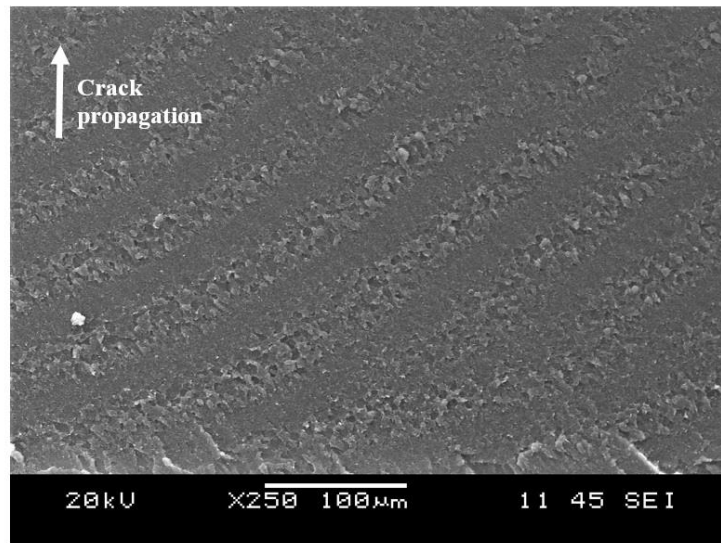


Figure 4.45 Composite with 280 nm particle size, and 8 wt% filler content. Dark bright and light rough stripe patterns as mackerel bands

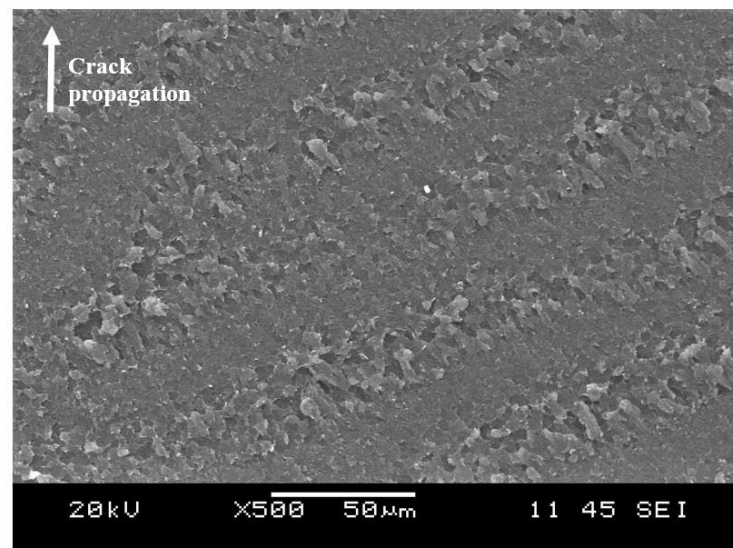


Figure 4.46 Composite with 280 nm particle size, and 8 wt% filler content. Clear view of fibril structure on the rough rib stripes

Oscillation of the propagating crack between the two matrix/craze interphases occurs in a stripe-like pattern, which can be described as a “mackerel” pattern (Murray, & Hull, 1970). Matrix-ligament bridging due to breaking of the craze ligaments can be observed in Figure 4.47 as the rough rib bands with light colour. Kusy and Turner (1976) and Döll (1975) have also reported similar results in their studies conducted with polymethylmethacrylate and shown that the spacing of these fracture bands

decreases with molecular weight and apparent fracture energy. Tips of the Mackerel bands diminish roughly 560 μm ahead of the crack tip line, and the final fracture surface represents pure brittle fracture characteristic due to a thoroughly featureless flat fracture surface.

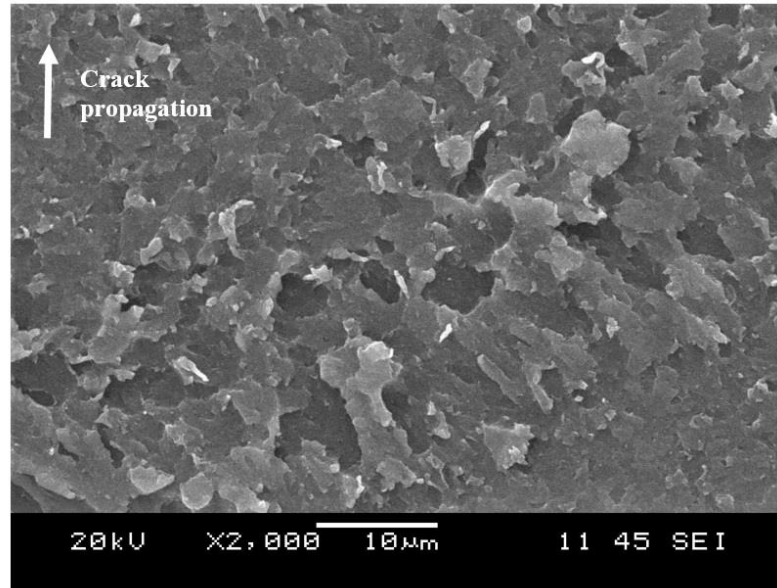


Figure 4.47 Composite with 280 nm particle size, and 8 wt% filler content. Fibril structure on the mackerel band

CHAPTER FIVE

CONCLUSIONS

5.1 TTT Diagram of Epoxy Polymer Composite

Time temperature transformation (TTT) diagram of MTHPA hardener cured DGEBA epoxy resin system reinforced with SiO₂ particles with 60 wt% filler content and 36.7 μm mean particle size was constructed by DSC method. Measurement interval for curing temperature was 30-170°C and curing time interval was 5-8640 minutes. Within these limits, measured glass transition temperatures (T_g) of the epoxy composite were used to establish specific zones such as sol liquid, sol glass, sol/gel rubber, sol/gel glass, gel rubber, and char region, which have different physical properties. The gelation line as the function of curing temperature, which determines the upper limit of the mold filling time, was created and at a nominal mold temperature of 150°C, the maximum mold filling time was determined as 5.3 minutes, since the fluidity would diminish due to the infinite viscosity beyond this time limit. While determining the mass production parameters, it was concluded that the char zone, in which decomposition begins, and the vitrification zones, where the curing reaction almost ceases, should be avoided. Char formation starts at the 170°C after 1000 minutes, or at 120°C after 1900 minutes. Isothermal T_g curves were constructed and maximum T_g value of 111°C for full cure was obtained at the curing temperature of 140°C for 360 minutes. Safe process zone (SPZ) was set at the zone limited by 140-160°C and 100-240 minutes, which meets the required quality requirements, allows optimum time consumption, and can be produced with optimum energy expenditure.

Conversion degree (α) which is the function of cross-link density of the curing epoxy was measured by DSC method using integrations of residual enthalpies as a function of T_g . A mathematic model was established by combining the experimental results with DiBenedetto equation, which provides relation between α and T_g . It was concluded that DiBenedetto equation can be used effectively to define conversion degree of the studied epoxy thermoset system depending on the glass transition temperature.

5.2 Effect of Silica Particles on Mechanical Properties

Effect of silica particle size and filler content on the mechanical and fracture properties of the same SiO₂ reinforced epoxy thermoset composite system were investigated. Mean particle sizes of the used silica filler were 36.7 μm , 1.1 μm , and 280 nm. Filler contents in weight were 2, 5, 8, 10, 20, 30, 40, and 60 wt% depending on the particle sizes. The tensile strength of the composite with the of 1.1 μm silica particle size and 30 wt% filler content shows the greatest value of 78 MPa among all configurations, including neat epoxy. Tensile strength shows a tendency to increase with increasing particle content for the composites of 36.7 μm , and 280 nm particle sizes, whereas the composite with 1.1 μm particles show a decrease after 30 wt% particle content, which is due to the dominant fracture mode depends on the particle size and content.

Modulus of elasticity of the silica filled epoxy composite increased with the increase of filler content for the composites with all sizes of the silica due to the high load-bearing capacity of hard silica particles. Modulus of the composite with 36.7 μm particle size and 60 wt% filler content was measured as 10.48 GPa, which is a 244% improvement compared to the 3.05 GPa value of unfilled epoxy.

The filling of the matrix with the silica deteriorates the elongation at break of the composite for all particle sizes. All composites show a very sharp decrease in elongation at break with the increasing filler content compared to unfilled epoxy. Composite with the smaller particle size exhibits better elongation characteristics since small particle size has less effect on the sharing of the matrix. Neat epoxy showed 4.7% elongation at break while the composite with 36.7 μm particle size and 60 wt% filler content was measured 0.9%, which was the lowest value among all composites.

The fracture toughness (K_{Ic}) and critical energy release rate (G_{Ic}) properties of silica filled epoxy composites were investigated by SENB three-point bending test method. The fracture toughness increased from 1.17 $\text{MPa}\cdot\text{m}^{1/2}$ for the unfilled epoxy to 2.32 $\text{MPa}\cdot\text{m}^{1/2}$ for the epoxy with 36.7 μm particle size and 60 wt% of silica content, which is an improvement of %98. Maximum K_{Ic} of 1.74 $\text{MPa}\cdot\text{m}^{1/2}$ was measured for 280 nm particle size with the 5 wt% silica content, which is also 49% improvement compared

to unfilled epoxy. Increasing silica content for the 280 nm particle size inversely affects fracture properties after 5 wt% filler content in contrary to 1.1 μm and 36.7 μm particle sizes. Decreasing fracture properties with increasing silica filler content in sub-micron dimension might be due to over filler content of silica in terms of volumetric base, which can cause agglomeration of sub-micron silica particles.

The higher fracture toughness compared to the unfilled matrix for the 1.1 μm and 36.7 μm particle sizes is due to a combination of some mechanisms such as trans-particle fracturing of some large silica particles in the matrix, crack path deflection around particles which leads to energy dissipation in the damage zone, and crack pinning depending on the particle size and filler content. On the other hand, dominant fracture mechanisms for the composite with 280 nm particle size are crazing of the matrix ahead of the crack tip for the initiation phase, and shear yielding and crack pinning for the crack propagation phase.

When SEM images of fracture surfaces were investigated the primary toughness improvement mechanism for 36.7 μm size and 60 wt% configuration was found to be trans-particle fracture. K_{Ic} increases proportionally with particle loading, which might be related to the progressive increase in the incidence of trans-particle fracture. When the adhesion strength between particles and matrix is greater than the intrinsic strength of the particle itself, larger particles with the size of greater than 80 μm tend to fracture while the crack is propagating in its route. High fracture resistance of the silica particles in the structure increases the fracture toughness of the composite structure.

Crack front deflection was found as a secondary mechanism for the composites with the higher filler content. In the crack path deflection mechanism, the mechanical interaction between the propagating crack front and silica particles may cause a perturbation of the crack route, which creates a non-planar crack propagation. Increasing particle size and filler content improves the fracture properties of the composite due to the synergetic effect of two mechanisms, which are trans-particle fracture and crack path deflection.

Crack pinning is the dominant mechanism in improving fracture toughness properties for the composites with 1.1 μm particle size and lower filler content. In the

crack pinning mechanism, rigid particles can act as pinning points while the crack propagates through the matrix during the fracture and dissipates its energy.

The crack initiation that causes failure in the composite filled with 280 nm silica particles is crazing and can be easily distinguished by the mid-rib whitened region. Crazing is a plastic deformation process, and it is the most important way of increasing fracture toughness in glassy polymers. The plastic deformation to create crazes very ahead of the growing crack is the main contribution to improved fracture toughness. Before these crazes decompose to produce cracks, they may nucleate and develop to extremely high densities from nano-silica particles. Crazing is the main mechanism of crack initiation for the composite with 280 nm particle size and 2, 5, 8, and 10 wt% filler content. Silica particles are major sources of craze initiation that take place ahead of the sharp crack line.

The plastic zone widths of 2 wt% and 10 wt% nano-silica content composites were measured from SEM photos as 40 μm and 10 μm , respectively. The excessive decrease in the width of the plastic deformation zone due to the increased amount of silica can easily explain the decrease of the K_{Ic} value of composite with 10 wt% nano-silica content. Shear yielding is the second fracture mechanism for the crack propagation for the composite with 2 wt% and 5 wt% nano-silica content. During the propagation of the crack in the matrix structure, bowing marks that start to appear at the end of the shear bands are an indication that the crack pinning mechanism has been activated for the nano-silica composites of 2 wt% and 5 wt% contents.

The crack initiation mechanism in 8 wt% and 10 wt% nano-silica added epoxy composites can be explained by crazing due to the stress whitening line in front of the crack tip. However, crack propagation following this relatively confined plastic deformation zone can be explained by the very special case of "mackerel" band formations locally, which were originated on the shearing bands for this fracture situation.

Two important results were obtained from the SENB tests, depending on the particle size and the filler content: the behaviour of the fracture properties of the material depending on the grain size varies depending on whether the particle size is

at the micro- or nano- level. While K_{ic} and G_{ic} values increase with increasing particle size in micron dimension, they decrease with increasing particle size in nano dimension.

5.3 Effect of Silica Particles on Thermal Properties

Glass transient temperatures (T_g) of all silica reinforced composites were measured by DSC method. There was a slight decrease in T_g for both particle sizes, with 36.7 μm and 1.1 μm filled epoxies while the composite filled with 280 nm particle shows a drastic decrease after 5 wt% silica content compared to the unfilled one. Maximum T_g decreases depending on the particle sizes with the maximum filler content are 4.7°C, 4.8°C, and 6.6°C for the composite with 36.7 μm , 1.1 μm , and 280 nm particle size respectively compared to unfilled epoxy. This decrease in T_g is thought to be due to the blockage of covalent bond formation in the final stages of the reaction due to the excessive number of particles in the structure. The structure that cannot complete the covalent bond formation in the final stages of the curing reaction due to the interaction with the smaller particles gives a lower T_g value. On the contrary, slightly higher T_g was measured for the composite with 280 nm particle size and 2 wt% particle content compared to unfilled epoxy. It is thought that the small amount of nano particles in the structure promotes the formation of more covalent bonds by creating nucleation sites in the initial stages of the curing reaction.

Thermogravimetric analysis was used to investigate the thermal stability of the silica reinforced epoxy polymer composites by TGA and DTA methods. Thermal resistance of the polymer composites was predicted by taking into consideration of the thermal stability of all TGA weight loss curves with three parameters, which are corrected integral procedure decomposition temperature (IPDT*), initial decomposition temperature (IDT), and activation energy (E_a) of decomposition process.

The highest IPDT* value was obtained with the composite of 280 nm particle size and 8 wt% filler composition, and its value was 483°C, which is slightly greater than the unfilled epoxy. On the other hand, lowest decomposition temperature was obtained for the composite with the epoxy 36.7 μm particle size and 60 wt% of silica content.

In general terms, increasing particle content decreases the thermal stability of the epoxy composite with increasing temperature. In nano-dimension, 280 nm silica has better effect on the IPDT* compared to unfilled epoxy while decreasing particle size decreases the decomposition temperature in micro-dimension. Particle size of 36.7 μm with 30 wt% and 40 wt% content shows better thermal stability compared to 1.1 μm particle size with the similar filler content.

The IDT value is slightly better for the 280 nm particle size compared to unfilled epoxy, and in the micro-dimension it is worsen with decreasing grain size and increasing silica content, which is also consistent with the IPDT* results.

Decomposition Activation energy (E_a) of the of the composites is also a good measure of thermal stability where higher E_a means better thermal stability due to resistance to thermal degradation. E_a change shows similar pattern with the IDP and IPDT*. Maximum E_a of 169 kJ/mol belongs to the composite with 280 nm particle size and 8 wt% filler content while the composite with 1.1 μm particle size and 30 wt% filler content has 134 kJ/mol which is the lowest one. In similar manner, decreased particle size and increased filler content lead to lower activation energy of decomposition in micron size dimension, which worsen the thermal stability of the composite.

Effect of silica particle size and content on the coefficient of thermal expansion (CTE) of the epoxy composites were investigated by using a thermomechanical analyser. CTE apparently decreases with increasing silica particles content for all filled epoxy systems. CTE of unfilled epoxy was measured 57 $\mu\text{m}/\text{m}^\circ\text{C}$ while composite with 36.7 μm and 60 wt% filler content was 21 $\mu\text{m}/\text{m}^\circ\text{C}$, which is 63% decrease compared to unfilled epoxy. The decrease in CTE at higher filler content is due to a relatively lower CTE of the raw silica particle, which is 0.55 $\mu\text{m}/\text{m}^\circ\text{C}$. Nano-silica filled epoxy shows much drastic decrease of CTE compared to 1.1 and 36.7 μm due to high volumetric silica content.

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