

**CYCLODEXTRIN FUNCTIONALIZED NANOFIBERS VIA
ELECTROSPINNING**

**A DISSERTATION SUBMITTED TO
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FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY**

By

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August, 2014

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ABSTRACT

CYCLODEXTRIN FUNCTIONALIZED NANOFIBERS via ELECTROSPINNING

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Electrospinning is a commonly studied and widely applied technique for generating nanofibers, with a diameter ranging from several tens of nanometers to a few micrometers. The low-cost, simple set-up, relatively high production rate and reproducibility increase the interests on this method in both academia and industry. Electrospun nanofibers are produced from a broad range of materials with extremely high surface area, very light-weight, nano-porous features and distinct physical/mechanical properties. The general talk in this technique focuses on the production of nanofibers from polymer base materials. However, very recent studies demonstrated that, it is also possible to obtain nanofibers from non-polymeric systems. For this novel development in electrospinning researches, we have achieved to generate nanofibers from cyclodextrins (CD) without using a polymeric template. CD are cyclic oligosaccharides consisting of α -(1,4)-linked glucopyranose units. The truncated cone shape structure of CD provides a favorable place for various kinds of organic molecules to form non-covalent host-guest inclusion complexes (IC). The enhancements and progressing at the guest molecules property and situation, creating with the inclusion complexation, make CD applicable in variety of areas including filtration, pharmaceuticals, cosmetics, functional foods, textiles, analytic chemistry etc.

In this thesis, we report on the electrospinning of CD nanofibers, represent their functionalization and potential applications. Firstly, we produced CD nanofibers from three different chemically modified CD types (hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD)). Afterwards, the electrospinning of native CD (α -CD, β -CD and γ -CD) nanofibers was achieved. The molecular entrapment capability of CD nanofibers was shown by capturing toxic volatile organic compounds (VOCs) from the surrounding. As the next step, the polymer-free nanofibers were obtained from the cyclodextrin inclusion complexes (CD-IC) with antibacterial agent, vanillin and essential oils. Here, we have also indicated applicability of CD-IC nanofibers as a result of antibacterial test. The functionalization of the CD nanofibers was continued with the green and one-step synthesis of metal nanoparticles (Ag-NP, Au-NP and Pd-NP)

incorporated nanofibers, in which CD were used as reducing, stabilizing agent and fiber template. Even, the antibacterial, SERS and catalyst potential of these CD based nanofibers were demonstrated for the related nanoparticles. Our research is expanded to a new stage by the production of insoluble poly-CD nanofibers. We have worked on different crosslinking agents to attain insoluble poly-CD nanofibers with uniform morphology. After the optimization of poly-CD nanofibers, the most durable poly-CD nanowebs were selected for further analysis and evaluation of the filtration performance in liquid environment. Within poly-CD nanofibers, we have eliminated the solubility challenge of CD nanofibers that restrict their usage. So, we assume that, poly-CD nanofibers will lead-up to generation of new advances for practices of CD nanofibers. All studies showed that, the self-assembly and self-aggregation property of CD are the prior requirements for the electrospinnability of these small molecules. To conclude, very intriguing materials were obtained by integrating large surface area of nanofibers with specific host-guest inclusion complexation capability and non-toxic, biocompatible nature of the CD. Moreover, CD molecules, which are generally used in the powder form, were rendered into more applicable nanofibers form that will represent ease during their usage.

Keywords: electrospinning, cyclodextrin, nanofibers, inclusion complex, antibacterial agent, vanillin, essential oils, nanoparticles, silver, gold, palladium, molecular encapsulation, antibacterial activity, SERS, catalyst, crosslinking.

ÖZET

ELEKTROEĞİRME YÖNTEMİ İLE SIKLODEKSTRİN FONKSİYONLU NANOLİFLER

Aslı Çelebioğlu

Malzeme Bilimi ve Nanoteknoloji, Doktora

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Elektroeğirme, nanometre düzeyinden birkaç mikrometreye kadar değişen aralıkta çapa sahip nanoliflerin üretilmesi için, yaygın olarak çalışılan ve uygulanan bir tekniktir. Düşük maliyeti, basit düzeneği, göreceli olarak yüksek üretim hızı ve tekrarlanabilirliği, bu yöntemin hem akademide hem de endüstride ilgi çekmesini sağlamaktadır. Elektroeğirilmiş nanolifler, oldukça yüksek yüzey alanları, çok düşük ağırlıkları, nano-boyuttaki gözeneklilikleri ve belirgin fiziksel/mechanik özellikleri ile çok geniş malzeme aralığında üretilebilmektedirler. Bu yöntemde nanolif üretimi, genel olarak polimerik tabanlı malzemelere odaklanmıştır. Fakat, yeni çalışmalar göstermiştir ki, polimerik olmayan sistemlerden de nanolif elde etmek mümkündür. Elektroeğirme araştırmalarındaki bu yeni gelişmeye bizim katkımız ise, polimerik malzeme kullanmayarak ürettiğimiz siklodekstrin (CD) nanolifleri ile olmuştur. CD'ler α -(1,4)-glikozidik bağlarıyla birbirine bağlanmış glukopiranoz yapılarından oluşan siklik oligosakkaridlerdir. Kesik koni şeklindeki yapıları, CD'lere, çok farklı organik moleküller ile kovalent olmayan ev sahibi-misafir tipi inklüzyon kompleks (IC) yapacağı ortamı sunmaktadır. IC oluşumu ile, misafir moleküllerin özelliklerinde ve konumunda meydana gelen iyileşme ve gelişmeler, CD'lerin, filtrasyon, tıbbi ilaçlar, kozmetik, fonksiyonel gıda, tekstil ve analitik kimya gibi birçok farklı alanda kullanımını sağlamaktadır.

Bu tezde, CD nanoliflerinin elektroeğirilmesi rapor etmekte ve fonksiyonlaştırılmaları ile uygulama potansiyellerini sunmaktayız. Öncelikle, üç farklı modifiye CD (hidroksipropil- β -siklodekstrin (HP β CD), hidroksipropil- γ -siklodekstrin (HP γ CD) and metil- β -siklodekstrin (M β CD)) çeşidinden nanolifler elde edilmiştir. Daha sonra, doğal CD (α -CD, β -CD and γ -CD) nanoliflerinin elektroeğirilmesi başarılmıştır. Bu nanoliflerin, moleküler tutuklama kapasiteleri, hava ortamındaki toksik uçucu organik bileşiklerin (VOCs) enkapsülasyonu ile gösterilmiştir. Bir sonraki aşama olarak, polimersiz nanolifler, CD'lerin antibakteriyel ajanlar (triklosan) ve esansiyel yağlar ile yaptığı IC'lerden elde edilmiştir. Burada, IC nanoliflerinin uygulanabilirliği de yapılan antibakteriyel test sonuçları ile gösterilmiştir. CD nanoliflerinin fonksiyonlaştırılmaları, yeşil ve tek adımda metal nanoparçacıkların (Ag-NP, Au-NP ve Pd-NP) sentezinin ve nanoliflerin katkılandırılmasını içeren; CD'lerin indirgeyici, stabilize edici ve lif

kalıbı olarak kullanıldığı, çalışmalar ile devam etmiştir. Hatta, ilgili nanoparçacığı içeren CD nanolifler için, antibakteriyel, SERS ve kataliz olarak kullanım potansiyelleri gösterilmiştir. Çalışmalarımız, çözünmeyen poli-CD nanoliflerinin üretimi ile genişletilmiş ve yeni bir boyut kazanmıştır. Çözünmeyen ve homojen lif yapısına sahip olan nanoliflerin üretimi için birçok farklı çapraz bağlayıcı ajanlar denemiştir, bütün ajanlar için şartlar optimize edildikten sonra, en dayanıklı olan nanoağ yapısı, ilerleyen analizler ve sulu ortamdaki filtrasyon performansını değerlendirmek için seçilmiştir. Poli-CD nanoliflerinin üretimi ile, CD nanoliflerinin kullanımını kısıtlayan suda çözünme problemi ortadan kaldırılmıştır. Bu nedenle, poli-CD nanoliflerinin, CD nanoliflerinin kullanımında yeni gelişmeler sağlayacağını ummaktayız. Bütün bu çalışmalar göstermiştir ki, CD'lerin kendiliğinden topaklanma ve kümelenme özellikleri, bu moleküllerin elektroğrılması için öncelikli gerekliliklerdendir. Sonuç olarak, nanoliflerin yüksek yüzey alanı; toksik olmayan ve biyoyumlu CD'lerin ev sahibi-misafir tipi kompleks yapabilme özellikleri ile entegre edilerek çok ilginç yapıda malzemeler elde edilmiştir. Ayrıca, genellikle toz halinde kullanılan CD'ler, uygulamaları sırasında kolaylık sağlayacak olan nanolif formuna getirilmiştir.

Anahtar kelimeler: elektroğirme, siklodekstrin, nanolifler, inklüzyon kompleks, antibakteriyel ajan, vanilya, esansiyel yağlar, nanoparçacık, gümüş, altın, paladyum, moleküler enkapsülasyon, antibakteriyel aktivite, SERS, kataliz, çapraz bağlama.

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LIST OF ABBREVIATIONS

AFD	:	Average fiber diameter
AFM	:	Atomic force microscope
APS	:	The average particle sizes
BET	:	Brunauer–Emmett–Teller surface area analyzer
BTCA	:	1,2,3,4-Butaneteracarboxylic acid
CA	:	Citric acid
CD	:	Cyclodextrin
α-CD	:	α -cyclodextrin
β-CD	:	β -cyclodextrin
γ-CD	:	γ -cyclodextrin
DSC	:	Differential scanning calorimeter
DMAc	:	Dimethylacetamide
DMF	:	N,N Dimethylformamide
DLS	:	Dynamic light scattering
ECH	:	Epichlorohydrin
<i>E. coli</i>	:	<i>Escherichia coli</i>
EOs	:	Essential oils
FTIR	:	Fourier transform infrared spectrometer
HMDI	:	Hexamethylene diisocyanate
HPLC	:	High performance liquid chromatography
HR-TEM	:	High resolution transmission electron microscope
HPβCD	:	Hydroxypropyl- β -cyclodextrin
HPγCD	:	Hydroxypropyl- γ -cyclodextrin
IC	:	Inclusion complex
ITC	:	Isothermal titration calorimeter
MβCD	:	Methyl- β -cyclodextrin
NF	:	Nanofibers
NP	:	Nanoparticle
PDI	:	Polydispersity index

PEGDE	: Poly(ethylene glycol) diglycidyl ether
PVA	: Polyvinyl alcohol
¹H NMR	: Proton magnetic resonance
SEM	: Scanning electron microscope
SAED	: Selected area electron diffraction
<i>S. aureus</i>	: <i>Staphylococcus aureus</i>
SERS	: Surface enhanced Raman scattering
SPR	: Surface plasmonic resonance
TEM	: Transmission electron microscope
TGA	: Thermogravimetric analyzer
XRD	: X-ray diffraction
XPS	: X-ray photoelectron spectrometer

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INTRODUCTION

1.1. Electrospinning

Electrospinning is the most prominent nanofiber fabrication technique, which left one's mark in the last two decades. Although, there are several methods for the production of nanofibers (melt drawing, melt fibrillation, phase separation, self-assembly, island-in-sea, gas jet etc.), electrospinning is distinguished among other methods with its comparative low-cost, simplicity of set-up, relatively high production rate and reproducibility [1, 2]. Electrospinning has also another exceptional advantage over conventional fiber production techniques since nanofibers can be readily produced from a variety of polymers, polymer blends, sol-gels, suspensions, emulsions and composite structures [1-9]. Electrospun nanofibers can be obtained by having diameters ranging from tens of nanometers to few microns with uniform morphology that leads up to numerous remarkable and unique characteristics including, extremely high surface area, very light-weight, nano-porous features and distinct physical/mechanical properties along with design flexibility for specific physical and chemical functionalization [1, 4, 10, 11].

The basic set-up of electrospinning consists of three main components; high voltage power supply, syringe pump (spinneret) and grounded collector (Figure 1). The electrospinning apparatus that we use in our laboratory at UNAM is depicted in Figure 2. In this technique, the polymer solution or melt, which are loaded into syringe, are pumped through the spinneret with the use of a syringe pump at a controllable rate. In the meanwhile, high voltage (in the range of 1 to 30 kV) is applied to spinneret; the drop at the tip of the nozzle is highly electrified; finally the formed charges on the surface create electrostatic forces and interactions which cause cone-shaped deformation at the drop, by the name of Taylor cone. When the electrical field is high enough, the electrostatic forces are able to overcome the surface tension of the electrospinning solution and thereby a liquid jet forms that goes towards the grounded collector. While this consisted jet is moving through the collector, it is exposed to stretching and whipping process which provides thin and

long fiber formation in company with the solvent evaporation. Finally, the ultimate nanofibers are deposited randomly (or aligned) on the collector as a non-woven mat [1, 4, 12].

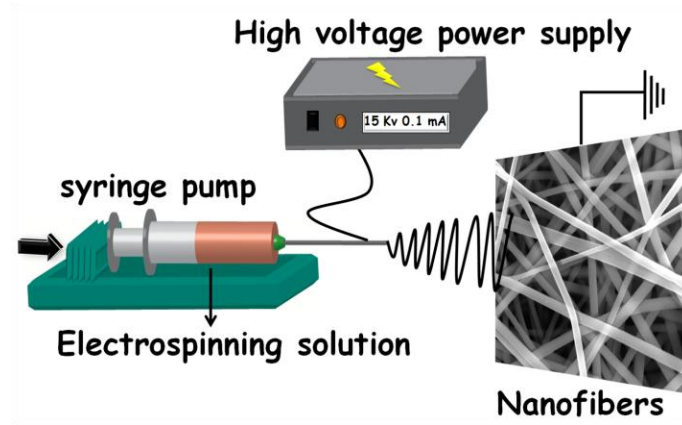


Figure 1. Schematic view of the electrospinning set-up.

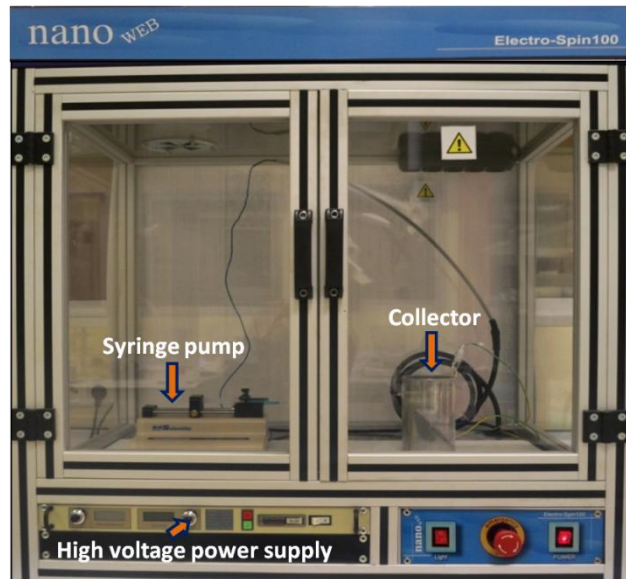


Figure 2. Electrospinning set-up at UNAM.

The morphology and the thickness of the electrospun nanofibers are highly depend on the various parameters which are summarized under three main titles; i) polymer solution parameters; polymer type, molecular weight of polymer, concentration, viscosity, surface tension, conductivity, fluid elasticity, dielectric constant and volatility of solutions; ii) operational conditions; applied voltage, distance between spinneret and collector, feed rate, type of the collector and diameter

of the needle; iii) ambient conditions; temperature, humidity and pressure/vacuum [1, 13-23]. To obtain uniform nanofibers, all these factors should be taken into consideration and applied or fixed at the optimum level. Among all mentioned parameters, the intrinsic properties of the electrospinning solutions are the most crucial and influential ones for the determination of nanofiber morphology. The molecular weight of polymer and concentration can be considered as the most important factors which affect the viscosity of the electrospinning solutions [1]. The sufficient viscosity of the system is provided by the sufficient molecular weight and concentration of the polymer that determine the amount of chain entanglement within the solution. The required level of entanglement and overlapping are essential to sustain the continuity of the jet during the electrospinning, otherwise the driven jets break up and electrospraying occurs which yields beads instead of fibers [1]. Figure 3 indicates the effect of increasing concentration on the morphology of polycarbonate (PC) nanofibers. From SEM images, the morphology alteration from beaded to bead-free uniform nanofibers can be easily detected by the increasing of PC concentration from 16% (w/v) to 25% (w/v). Since, the viscosity of solution reached to adequate level by the 25% (w/v) that stabilize the electrospinning jet during the process. The conductivity of solution is another effective factor for the electrospinning. The higher conductivity of the electrospinning system, increase the charges potential in the solution and jet is being exposed higher stretching during process thus, nanofibers having smaller diameters are yielded [1, 19].

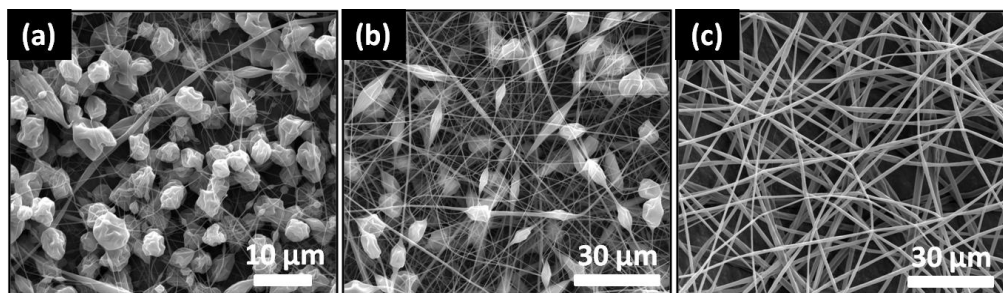


Figure 3. The representative SEM images of PC nanofibers obtained at (a) 16% (w/v), (b) 20% (w/v) and (c) 25% (w/v) polymers concentrations.

By varying the electrospinning parameters or set-up, it is easy to obtain nanofibers having different morphology or arrangements. Beside the basic and

smooth nanofiber structure, it is also possible to produce porous, hollow, core-shell or aligned fibers by applying some modifications to electrospinning systems [1, 4, 12]. As it is mentioned, electrospun nanowebs already have high porosity, however porous structures can be also created on the fiber exterior, and the surface area of the nanofibers can be extremely increased [24]. Porous nanofibers are being obtained by using different approaches and one of them involves the use of solvent blend system which composes of solvent types having different volatility [25]. Figure 4 indicates the SEM images of porous cellulose acetate (CA) ultrathin fibers which were produced in dichloromethane (DCM)/acetone blend system by electrospinning. Here, the fast evaporation of solvent gives rise to local phase separation, and the solvent-rich regions transform into pores during the electrospinning process [25]. In the case of basic electrospinning settling, nanofibers are generally obtained in random arrangements on the fixed collector type. On the other hand, ordered and aligned nanofibers can be also produced through the manipulation of the collector as a cylindrical rotating drum or split plate [26]. The nozzle system can be also modified so as to obtain different featured nanofibers. For instance, it is possible to produce core-shell systems in which two concentrically aligned nozzles are used for electrospinning and same voltage is applied to both nozzles [27]. This configuration generally carried out when one of the components is too low to be spun into fibers (drugs, biomolecules, enzyme, bacteria, viruses etc.) and so get involved as core of the system [28]. Hollow nanofibers are another structure which can be easily obtained by the selectively removing of the inner part of the core-shell system [29, 30].

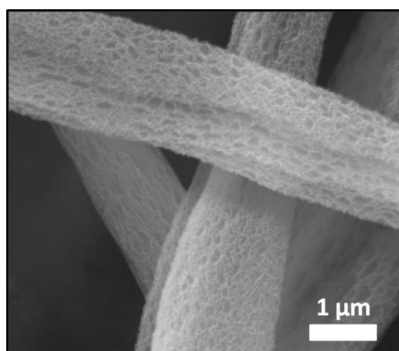


Figure 4. The SEM image of electrosun porous CA ultrathin fibers.
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In addition to above mentioned manipulations, it is also possible to enhance the functionalities of electrospun nanofibers by integrating them with metal nanoparticles, nanowires, inorganic precursors, drugs, dyes, bioactive agents (cell, enzyme, DNA, peptide, bacteria etc.), food additives (flavor/fragrance, essential oils) etc. [31-43]. Furthermore, their surface can be easily modified by applying various kinds of chemical reactions [10, 44, 45]. Due to all these functionalization, electrospun nanofibers are being gained intriguing electronic, magnetic, optical and biological features. In summary, the unique properties and the multi-functional nature of electrospun nanofibers make them applicable in numerous are [4, 11, 12, 46] including; textile [4], filter/membrane (separation and affinity membrane, molecular filtration, liquid and gas filtration) [47-57], biotechnology (delivery of drug and bioactive agents, tissue engineering, wound healing dress) [32, 58-66], catalyst/enzyme (chemical reactions and biological process) [37, 67-73], sensors (thermal, piezoelectric, biochemical) [74-79], energy/electronics (solar cells, fuel cells, hydrogen storage, batteries, transistor, supercapacitors) [80-84] and food/agriculture (Figure 5) [31, 40-42, 85-88].

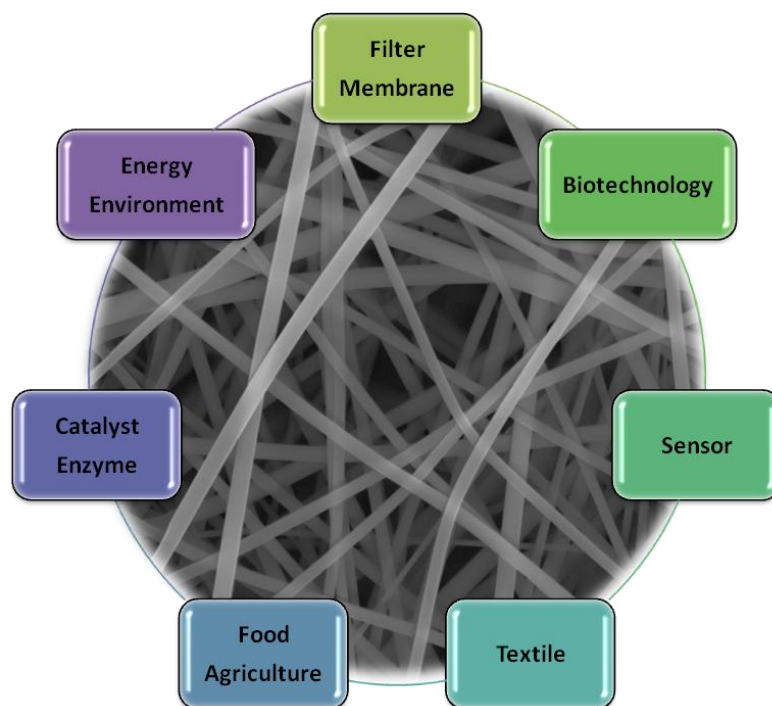


Figure 5. Application areas of electrospun nanofibers.

1.2. Cyclodextrins

Cyclodextrins (CD) are cyclic oligosaccharides consisting of α -(1,4)-linked glucopyranose sub-units. CD are produced as a result of starch degradation by the help of glucosyl transferase enzyme (CGTase) which are obtained from various microorganisms [89-91]. The most abundant and common CD types are α -CD, β -CD and γ -CD having six, seven and eight glucopyranose units in their cyclic system, respectively (Figure 6). These three CD are commonly considered as first generation or parent CD and they are generally names as “native” CD [90-92]. The characteristic physical and chemical properties of native CD are summarized in Table 1. In the ring structure of CD, the C-2-OH group of one glucopyranose unit can form a H-bond with the C-3-OH group of the neighboring glucopyranose unit. This intramolecular H-bonding determines the solubility of native CD in water [90, 91, 93]. In the case of β -CD, a complete secondary belt is formed by these H-bonds, so β -CD has quite rigid structure and lowest water solubility among other native CD. For α -CD, the H-bond belt is not complete, because one of the glucopyranose units is in a disordered position and it is able form four H-bonds instead of six H-bonds. On the other hand, γ -CD is more flexible with its non-coplanar structure; therefore, it has the highest aqueous solubility in three CD types (Table 1) [90].

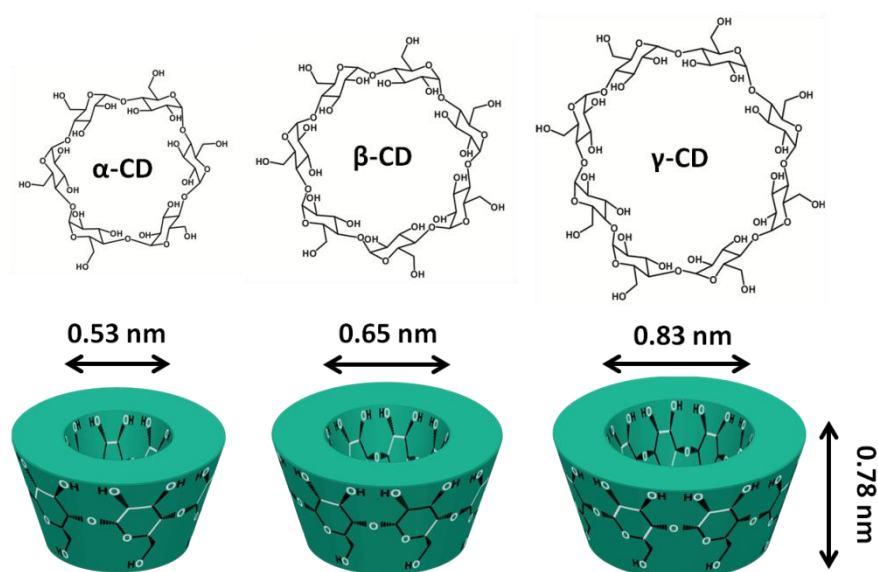


Figure 6. Chemical structure and schematic view of α -CD, β -CD and γ -CD.

Table 1. General properties of native CD.

Properties	α -CD	β -CD	γ -CD
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7-5.3	6.0-6.5	7.5-8.3
Height of torus (Å)	7.8	7.8	7.8
Approximate cavity volume (Å ³)	174	262	472
Solubility in water at 25 °C (g/100 mL)	14.5	1.85	23.2

Apart from these three natural CD types, there are also many different CD derivatives which are obtained by chemical or enzymatic modifications. For this reason, the OH (or H) of CD molecules are generally modified by the substitution of different groups such as; alkyl, hydroxylalkyl, carboxyalkyl, amino, thio, tosyl, ether, ester etc.[90, 91, 94, 95]. As it is known, β -CD is the most widely consumed native CD for numerous reasons (price, availability, approval status, etc.) [95]. However it has very limited solubility, so the main aim of these modifications is generally based on the solubility enhancement of native CD (especially β -CD) which is rather restricted in aqueous medium. In addition, different cavity volume and stability against light and oxygen can be provided with CD derivatization [95]. On the other hand, availability is an important issue in the case of modified CD, since after multistep reactions and purifications, the acquired CD amount and the prices should be at acceptable level for the practical usage. From this point, when we look through the market, the highly water soluble hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD) come into prominence with their industrially production scale, standardization and superior availability (Figure 7(a)) [90, 94, 95].

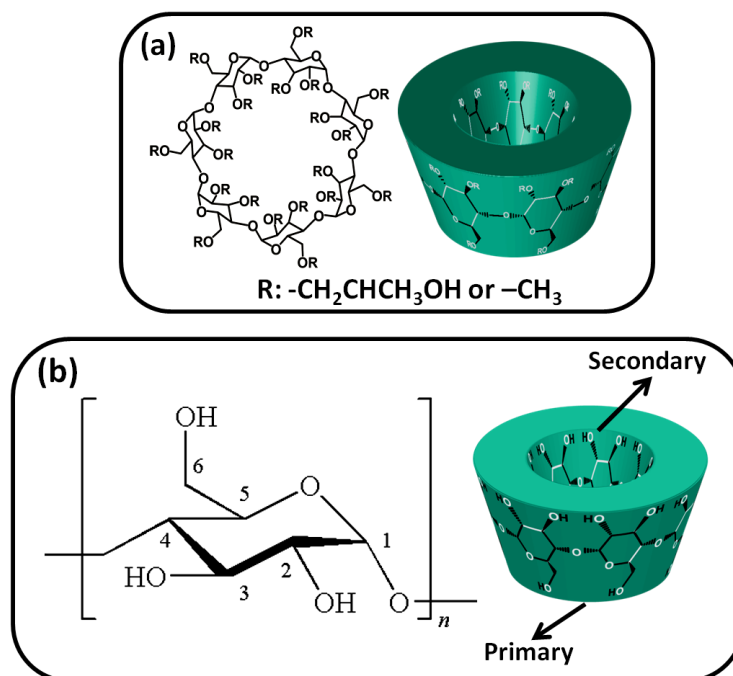


Figure 7. (a) Chemical structure and the schematic view of the modified HPβCD or MβCD. (b) Chemical structure of glucopyranose unit and schematic representation of the primary, secondary side of CD molecules.

CD molecules are composed of ${}^4C_1$ conformation of the glucopyranose units, so all secondary hydroxyl groups (C2 and C3) are located on one edge of the ring, while all the primary hydroxyl groups (C6) are situated on the other edge. The primary hydroxyl groups have free rotation ability whereas the secondary ones are more strict and stable. Hence, the diameters of two edges are different from each other with narrower (primary hydroxyl) and wider (secondary hydroxyl) rims and so CD have truncated cone shape structure (Figure 7(b)) [90-92]. Additionally, the apolar C3 and C5 hydrogen and glycosidic oxygen bridges are placed at the inside of the CD molecule which provides a relatively hydrophobic (apolar) cavity and hydrophilic outside [90]. Due to their unique molecular structure, CD can form intriguing supramolecular assemblies by forming non-covalent host-guest inclusion complexes (IC) with a variety of small molecules as well as macromolecules (drugs, antibacterial, food additives, textile auxiliaries, and so forth) (Figure 8) [89-91, 94, 96, 97].

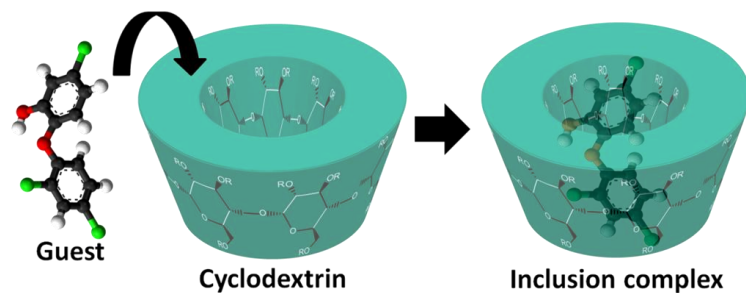


Figure 8. Schematic view of IC formation between CD and guest molecule.

The inclusion complexation of CD (host) with different compounds (guest) mainly depends on two factors; dimensional fit and specific local interaction between host and guest molecules [90, 91, 96]. On the other hand, the energetic factors, that encourage and contribute to the inclusion complexation, can be generalized under three main issue; (1) the apolar CD cavity is occupied slightly by the polar water molecules so, the displacement of water molecules with the more proper apolar compound is favorable, (2) depending on this, the repulsive interaction between guest molecules and aqueous environment is decreased and the H-bond in the pool is increased by release of water molecules from CD cavity, (3) finally the apolar-apolar association is provided by insertion of guest molecules into CD which results in conformational change and strain release of the CD rings [90, 91]. In other respects, inclusion complexation is a dynamic process in which van der Waals and hydrophobic interactions largely occur between host and guest molecules, besides, H-bonding can also take place [92, 96]. There are several ways to form CD IC including; co-precipitation, slurry, paste, dry mixing etc., and they are differentiated from each other according to employed water amount. For laboratory scale, co-precipitation is the most suitable method in which required level of water is used for the dissolution of CD and dispersion/emulsion of guest molecules, hence more favorable conditions are provided for the IC formation compared to other methods.

The inclusion complexation phenomena reach significance by providing beneficial modifications to physicochemical properties of guest molecules. By the inclusion complexation, the solubility of insoluble compound is enhanced, the stability against oxidation, visible/UV-light and heat are improved, volatility and sublimation of the molecules are controlled, the unpleasant odors and flavors are

masked off, chromatographic separations are achieved and drugs/flavors are released in a controlled manner [89-91, 94].

Due to non-covalent host-guest complexation ability and non-toxic nature, CD are particularly applicable in many areas including; filtration/separation/purification systems, pharmaceuticals, cosmetics, home/personal care, functional foods, textiles, analytic chemistry, adhesive and coatings system, as well as advanced functional systems such as smart materials, sustained/controlled delivery systems, sensors, molecular switches, diagnostic system and devices [96, 98-111]. To enhance the application potential of CD molecules, especially in liquid environment, insoluble CD polymers are also being produced by using various kinds of crosslinking agents and by applying different polymerization techniques [112-117].

1.3. Electrospinning of non-polymeric systems

In principle, electrospinning of nanofibers involves high molecular weight polymers and high solution concentrations since entanglements and overlapping between the polymers chains play an important role for the continuous stretching of electrified jet for uniform fiber formation otherwise, electrospraying occurs which yields beads instead of fibers [1, 17, 18, 118-121]. For the electrospinnability of solutions, the importance of elasticity and relaxation time rather than molecular entanglements has also been reported [20, 122]. So, the electrospinning of non-polymeric systems (low molecular weight molecules) is much more challenging than the polymeric systems. However, very recent studies have indicated that high molecular weight polymers are not vital for the uniform fiber formation. Correspondingly, there are notable reports in the literature regarding to electrospinning of non-polymeric systems.

The preliminary study about this subject was firstly reported by Long and his group members. They achieved to obtain polymer-free ultrathin fibers (1 to 5 micrometers) from lecithin, which is a natural mixture of phospholipids and neutral lipids, by using electrospinning. It was shown that, the cylindrical micelles are formed in the high concentrated solution of lecithin and they are able to overlap and entangle

in a similar way to polymer chains in solutions [123]. In another study of the same group, the electrospinning of ammonium gemini surfactant (*N,N'*-didodecyl-*N,N,N',N'*-tetramethyl-*N,N'*-ethanedioldiammonium di-bromide (12-2-12)) was reported without using polymeric matrix. Here, it was demonstrated that, supramolecular assemblies were formed in the gemini surfactant solutions, which provide stabilization of electrospinning jet for continuous fiber formation [124]. In the study of Kern et al. polymer-free nanofibers were obtained from diphenylalanine (Phe-Phe) which is a well-known amino-acid type. The self-assembly property of this amino-acid enabled the production of both micron and nanosized fibers [125].

In another related study, Huang et al. benefitted from the non-covalent interaction between benzo-21-crown-7 (B21C7) and dialkylammonium salt for the production of nanofibers. Here, B21C7 bind to secondary ammonium salt and form linear supramolecular polymers which are based on low-molecular-weight monomers. Then, by the self-organization of these supramolecular structures, the nanofibers production became possible via electrospinning [126]. The similar concept was also adapted in the study of Yang et al. This time, pillar[5]arene based receptors were used to form stimuli-responsive supramolecular polymers in the high concentrated solutions and finally nanofibers from their assemblies [127]. One of the associated study, Schmidt et al. reported the production of polymer-free nanofibers from supramolecular structures of self-assembling 1,3,5-cyclo-hexane- and 1,3,5-benzenetrisamides by melt-electrospinning process, since the liquid phases of mentioned compounds are so viscous to be electrospun [128].

We have contributed this novel research area, related to electrospinning of non-polymeric systems, by producing nanofibers from cyclodextrins (CD) molecules. It is worth mentioning that at the time we started these studies, there were only few publications reporting on polymer-free nanofibers formation and we have also firstly reported the electrospinning of nanofibers from very small molecules [123-125]. Initially, we obtained CD nanofibers from three different chemically modified CD types ((hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD)) [129, 130]. Then we

have achieved the electrospinning of native CD (α -CD, β -CD and γ -CD) [131, 132]. We have also obtained multifunctional CD nanofibers from their inclusion complexes (IC) with specific compounds [133-135]. In addition, the green and one-step synthesis of metal nanoparticles (Ag-NP, Au-NP and Pd-NP) incorporated CD nanofiber were succeeded in which CD was used as reducing and stabilizing agent as well as fiber template [136]. Even, we have produced insoluble poly-CD nanofibers by using various kinds of crosslinking agents. Likewise other studies, the CD nanofiber formation also rely on the self-assembly and aggregation property of CD molecules that effectively act as chain entanglements and overlapping in their highly concentrated solutions [93, 137-140]. Following our reports, a few studies, which are about the electrospinning of CD molecules, were also published by other research groups [141-143]. In general, CD molecules are used in the powder form which is a distinctive limitation during their practices, so these functional molecules are rendered into more applicable form by electrospinning. The obtained CD nanofibers are easily handled and can be readily used for the required purposes. Here, intriguing materials were produced by integrating very large surface area of nanofibers/nanowebs with specific host-guest inclusion complexation capability of CD. Within the scope of this thesis, we will explain all the details of above mentioned studies that are regarding to electrospinning of CD nanofiber performed in our laboratory. The four chapters in the next sections respectively focus on; the optimization of the electrospinning of modified CD and native CD without using polymeric matrix as well as investigation of their potential for the molecular filtration purposes (Chapter 1); production of polymer free IC nanofibers from antibacterial agent (triclosan), vanillin and essential oils, beside antibacterial activity determination of the triclosan/CD-IC nanofibers (Chapter 2); metal nanoparticles including CD functionalized nanofibers production by one-step and green approach (Chapter 3); generation of the insoluble poly-CD nanofibers by using different crosslinking agent and evaluation of their molecular entrapment performance in liquid environment (Chapter 4).

All these studies showed that the primary criterion for the electrospinnability of low molecular weight molecules is the self-assembly and self-aggregation of them

in their concentrated solutions or in their melt state. In short, electrospinning of nanofibers from supramolecular structures is quite interesting and needs further investigation since electrospun supramolecular nanofibers can be used for designing and constructing new advanced functional nanofibrous materials. Electrospinning of nanofibers from polymers, which usually require organic solvents, is very common; however, electrospinning of nanofibers from renewable resources is always attractive and on demand.

EXPERIMENTAL DETAILS

2.1. Materials

Hydroxypropyl- β -cyclodextrin ((HP β CD), molar substitution:~0.6), hydroxypropyl- γ -cyclodextrin ((HP γ CD), molar substitution:~0.6), methyl- β -cyclodextrin ((M β CD), molar substitution:1.6-1.9), α -CD, β -CD and γ -CD were purchased from Wacker Chemie AG, Germany. N,N-dimethylformamide (DMF) (Riedel, Pestenal), dimethylacetamide (DMAc) (Sigma-Aldrich, 99%), acetonitrile (Chromasolv, HPLC $\geq$ 99.9%), dimethyl sulfoxide (DMSO) (Sigma-Aldrich, 99.9%), ethanol (Sigma-Aldrich $\geq$ 99.8% (GC)), methanol (Sigma-Aldrich $\geq$ 99.7% (GC)), chloroform (Sigma-Aldrich 99-99.4% (GC)), acetone (Sigma-Aldrich, $\geq$ 99% (GC)), aniline (Sigma-Aldrich, 99%), benzene (Sigma-Aldrich, 99.8%), toluene (Sigma-Aldrich, $\geq$ 99.5%), deuterated dimethylsulfoxide (*d*6-DMSO, deuteration degree min. 99.8% for NMR spectroscopy, Merck), deuteriumoxid (Merck, D₂O, deuteration degree min. 99.9% for NMR spectroscopy), sodium hydroxide (NaOH) (Fluka, P98%, small beads), potassium bromide (KBr, 99%, FTIR grade, Sigma-Aldrich), polyvinyl alcohol (PVA, Scientific Polymer, 88% hydrolyzed, Mw 125,000), urea (Merk, $>$ 99.5%), triclosan ($>$ 97% (HPLC), Sigma, Germany), vanillin (99% purity, Sigma-Aldrich), thymol ($\geq$ 98, Alfa Aesar), eugenol (99% Sigma Aldrich), citral (95%, Sigma Aldrich), camphor ($\geq$ 95, Fluka), cineole ($\geq$ 85 (GC), Sigma Aldrich), cymene (97%, Alfa Aesar), silver nitrate (AgNO₃, Sigma Aldrich, $\geq$ 99.5%), hydraulic acid salt (HAuCl₄, Sigma Aldrich, ACS reagent, $\geq$ 49%), palladium (II) acetate trimer (C₁₂H₁₈O₁₂Pd₃, Alfa Aesar, Pd 45.9-48.4%), epichlorohydrin (ECH) (Fluka, $\geq$ 99% (GC)), citric acid (CA) (Sigma Aldrich, 99.5-100.5%, grit), 1,2,3,4-butanetetracarboxylic acid (BTCA) (Sigma Aldrich, 99%), hexamethylene diisocyanate (HMDI) (Fluka, $\geq$ 98.0% (GC)), poly(ethylene glycol) diglycidyl ether (PEGDE) (Sigma Aldrich, average Mn 500), sodium hypophosphite hydrate (Sigma Aldrich), phenolphthalein (Sigma Aldrich, indicator, 98-102%) and phenanthrene (Sigma Aldrich, 98%) were obtained commercially. The water used was from a Millipore Milli-Q Ultrapure Water System. All the materials were used without any purification.

2.2. Preparation of Solutions and Electrospinning of Nanofibers

2.2.1. Preparation of modified CD solutions

The solutions of HP β CD, HP γ CD and M β CD were prepared in various concentrations (100% (w/v) to 160% (w/v)) by using water, DMF and DMAc as solvent systems. The clear and homogeneous CD solutions were obtained after stirring for 1 hour at 50 °C and additional stirring for 30 minutes at room temperature. To see the effect of urea on the fiber formation, 20% (w/w, with respect to CD) urea was added into the CD solutions of water and DMF at the optimized CD concentrations. Since urea has a very limited solubility in DMAc, we were unable to study the effect of urea on the electrospinning of CD from DMAc solutions.

2.2.2. Preparation of native CD solutions

The electrospinning of CD (α -CD, β -CD and γ -CD) solutions was determined according to their solubility limits by trying different solvent types. Electrospinning requires highly concentrated CD solutions; therefore, in order to obtain highly concentrated homogeneous CD solutions, various solvent types including water, DMF, DMAc, and DMSO as well as their mixtures were tested, and finally, we were able to get highly concentrated homogeneous α -CD and β -CD solutions by using 10% NaOH aqueous solution. Therefore, α -CD and β -CD nanofibers were electrospun from their 10% NaOH aqueous solution. On the other hand, highly concentrated solutions of γ -CD were prepared by using DMSO/water (50/50, v/v) solvent mixture system, since the γ -CD were precipitated in the 10% NaOH aqueous solution. The solutions were started to be prepared from 120% (w/v) CD concentration, and they were increased to the optimized level until the bead-free uniform nanofibers were produced. The homogenous nanofibers of α -CD, β -CD and γ -CD were obtained at 160%, 150% and 140% (w/v) concentrations, respectively. The effect of urea on the fiber formation was investigated by adding 20% urea (w/w, with respect to CD) into the optimized concentration of CD solutions.

2.2.3. Preparation of triclosan/CD-IC suspension

The formation of inclusion complex (IC) between triclosan and CD was achieved in aqueous solution in order to have 1:1 molar ratio of triclosan/CD. For triclosan/CD-IC, first triclosan was put in water and stirred at 40 °C for 0.5 h. Because triclosan is not water soluble, we obtained dispersion. Then, CD (160%, w/v) was added to the triclosan solution, and the solution became clear after stirring for 0.5 h at 40 °C because of the dissolution of triclosan by forming an IC with CD. As the solution was cooled down and stirred overnight at room temperature, a white, highly turbid triclosan/CD-IC solution was obtained. The turbid triclosan/CD-IC suspensions were electrosun. Beside, a physical mixture of triclosan/HP β CD was prepared in the solid state by grinding HP β CD nanofibers and triclosan in an agar mortar for 15 min by using an identical molar ratio (1:1).

2.2.4. Preparation of vanillin/CD-IC solutions

IC of vanillin with HP β CD, HP γ CD and M β CD were prepared by using 1:1 molar ratio of vanillin/CD in water, DMF and DMAc. First of all, vanillin was dispersed in water, DMF and DMAc then HP β CD (160% (w/v)-water, 120% (w/v)-DMF, 120% (w/v)-DMAc) HP γ CD (160% (w/v)-water, 125% (w/v)-DMF, 125% (w/v)-DMAc) and M β CD (160% (w/v)-water, 160% (w/v)-DMF, 160% (w/v)-DMAc) were separately added to the vanillin dispersion. The dispersions were stirred overnight and the solutions became clear and homogeneous due to the dissolution of vanillin by IC formation.

2.2.5. Preparation of essential oils/CD-IC solutions

IC formation between CD and essential oils (EOs) (thymol, eugenol, citral, camphor, cineole and cymene) were carried out in their aqueous solution. First of all, EOs were dispersed in water, then HP β CD (160%, w/v), HP γ CD (160%, w/v) and M β CD (160%, w/v) were separately added to the EOs dispersion. The amount of CD and EOs were adjusted accordingly in order to have 1:1 molar ratio of EOs/CD-IC. After the addition of CD to EOs dispersion, they were stirred overnight and the solutions became clear and homogeneous due to the dissolution of EOs by IC formation. We

obtained IC nanofibers of thymol, eugenol and citral for three types of CD (HP β CD, HP γ CD and M β CD), however, we produced IC nanofibers of camphor, cineole and cymene for two types of CD; HP β CD and HP γ CD, because the IC solutions of M β CD precipitated during the process for camphor, cineole and cymene, so we could not perform the electrospinning process for these systems.

2.2.6. Preparation of PVA, PVA/HP β CD and PVA/HP β CD/Ag-NP systems

First, the aqueous PVA solution was prepared by using 7.5% (w/v, with respect to solvent) concentration. On the other hand, HP β CD was added to the aqueous PVA solution (7.5%, w/v) at three different concentrations (7.5%, 15% and 25%, w/v, with respect to solvent). After obtaining a clear and homogeneous aqueous solutions of PVA and PVA/HP β CD, AgNO₃ was added to each of these solutions and the concentration of AgNO₃ was adjusted accordingly to have 1% (w/w, with respect to total PVA or PVA/HP β CD concentration) elemental Ag in the electrospun nanofibers. After the AgNO₃ was dissolved completely, pH of the systems were adjusted to ~8.5 by adding 1M NaOH to the solutions. The pH of PVA solution without HP β CD was also adjusted to the same pH level to keep the medium similar to each other. As the solutions were stirred overnight, the dark brown solutions were obtained indicating the formation of Ag-NP in the electrospinning solutions. For comparison, PVA (7.5%, w/v) and PVA (7.5%, w/v)/HP β CD (25%, w/v) solutions without containing AgNO₃ were also prepared for electrospinning.

2.2.7. Preparation of HP β CD/metal nanoparticles solutions

The electrospinning solutions were prepared by using two solvent systems; DMF and water. First, the homogenous HP β CD solutions were obtained at 120% (w/v) and at 160% (w/v) HP β CD concentrations in DMF and water, respectively. Then, certain amount of metal salt were added to the HP β CD solutions to adjust the weight load to be 1 wt% and 2 wt% elemental metal (Ag, Au, Pd) in the electrospinning solutions. As mentioned previously, there are reports in the literature about the production of metal NP by using carbohydrates (glucose, starch, etc.) [107, 144, 145], however, because of the limited reduction capacity in the ambient circumstances, alkaline

(NaOH) conditions are provided to enhance and accelerate the reduction of ionic salt [107, 144, 145]. From this point, after the salt was dissolved homogenously, the pH of the systems were adjusted to ~8.5-9 by adding 1M NaOH to the solutions to utilize from the HP β CD molecules reducing potential that have very similar chemical structure with other types of carbohydrates. As the solutions were stirred overnight, the dark brown, dark purple and almost black solutions were obtained indicating the formation of Ag-NP, Au-NP and Pd-NP in the HP β CD solutions, respectively.

2.2.8. Preparation of crosslinked poly-CD solutions

The insoluble electrospun webs from CD were obtained in different parameters and for all crosslinking agents. For ECH, a known concentration of HP β CD (120% (w/v)) was dissolved in 25% NaOH aqueous solution at room temperature. As the HP β CD dissolved, ECH was added slowly to the clear CD solution as crosslinking agent in the 1:10 molar ratio (HP β CD/ECH). The temperature of solution was kept at 50 °C and stirring was continued for 45 minutes before the fully solidification (gellation) of HP β CD polymer solution. Once the system was cooled down to room temperature, the electrospinning was carried out as the second step. Finally, the crosslinked, insoluble and ultrathin poly-CD fibers were obtained with curing treatment that executed in oven at 150 °C for 5 hours. For the comparison of adsorption performance of dye, the poly-CD granules were also produced. The 120% HP β CD was dissolved in 25% NaOH solvent thereafter the ECH (1:10 molar ratio (CD/ECH)) was added slowly to the solution. The solution was stirred at 50 °C for about 1.5 hour thru the formation of stable gel. The curing step was also applied for the granule form at 150 °C for 5 hours. The solvent durability of electrospun webs were investigated by soaking samples in water, ethanol, methanol, chloroform, acetone, DMF and DMSO for 24 hours. The ultimate nanowebs obtained with ECH were washed in appropriate solvents (water and ethanol) to remove excess amount of un-react CD and ECH. In the case of CA and BTCA, HP β CD was dissolved in water at 170% (w/v) and 140% (w/v) concentration, respectively. After the clear solutions were obtained crosslinking agents; CA and BTCA were added into the HP β CD systems at 30% (w/w) and 20% (w/w) concentrations, respectively at room

temperature. Then, 2% (w/w) of initiator (SHP) was loaded to both of the CA and BTCA solutions. When the viscosity of solutions reached to critical points, the electrospinning was performed. Afterwards, the ultimate nanowebs were put into oven for the post-thermal treatment. While CA based nanowebs were crosslinked at 175 °C for 30 min, the BTCA ones were treated at 175 °C for 1 hour. For HMDI and PEGDE, HP β CD were dissolved at 120% (w/v) concentration in DMF and water, respectively. Then HMDI and PEGDE were added to the HP β CD solutions having the molar ratio (crosslinking agent:HP β CD) of 2:1 for HMDI and 1:1 for PEGDE. Unlike, NaOH was added to the PEGDE solution as an initiator at 7.5% (w/v) concentration. After solutions were stirred for a while at room temperature and come to required level of viscosity, they were loaded to electrospinning system to form nanofibers. The post-thermal treatment of HMDI was performed at 150 °C for 1 hour; on the other hand, the crosslinking of PEGDE was optimized in two steps, 125 °C-1 hour and 150 °C-1 hour. The durability of electrospun webs were investigated by soaking samples in water for 24 hour.

2.2.9. Electrospinning

For the electrospinning, solutions were loaded in syringes (1 mL-10mL) (metallic needle with different inner diameter (0.45 or 0.60), thereafter, positioned horizontally on the syringe pump (Model: SP 101IZ, WPI). The electrode of the high voltage power supply (Matsusada Precision, AU Series) was clamped to the metal needle tip and the aluminum collector was grounded. The electrospinning of the solutions was performed at the given ranges of parameters: applied voltage=10-15 kV, tip-to-collector distance=8-15 cm and the solution flow rate=0.5-1.0 mL/h. Electrospun CD fibers were deposited on a grounded stationary metal collector covered by a piece of aluminum foil. The electrospinning apparatus was enclosed in a Plexiglas box and the electrospinning was carried out at 22-26 °C at 25-30% relative humidity. The nanofibers/nanowebs, which were used for the different applications, were dried in the vacuum oven overnight in order to remove the residual solvent if present.

2.3. Characterizations and Measurements

2.3.1. Instrumentation

The viscosity measurements of the solutions were performed with a rheometer (Physica MCR 301, Anton Paar) equipped with a cone/plate accessory (CP40-2). While the shear rate sweep tests were carried out at the range of 0-100 1/s, the shear sweep tests were performed in the range of 0.1 to 100 Pa at 22 °C. The frequency sweep oscillatory tests were done at the 0-10 Hz frequency range. For viscoelastic property measurements, the linear viscoelastic region was determined as 0.01% strain value. For poly-CD solutions, the time sweep viscosity test and the oscillatory tests were carried out between the, pre-heated plates (50 °C) to supply the experiment conditions. In the viscoelastic property measurements of poly-CD solutions, the linear viscoelastic region was determined as 0.01 % strain value and it was recorded in the frequency of 1 Hz against time.

The particle size of the aggregates in solutions was measured by a Nano-ZS Zetasizer dynamic light scattering (DLS) system (Malvern Instruments). The equilibrium at 25 °C for 2 minutes was applied prior to DLS measurements of the solutions. The conductivity of the solutions was measured with a Multiparameter meter InoLabMulti 720 (WTW) at room temperature.

The morphology and the diameter of the nanofibers were investigated by a scanning electron microscope (SEM) (Quanta 200 FEG, FEI). The average fiber diameters (AFDs) were calculated by analyzing around 100 fibers from the SEM images. Prior to SEM imaging, samples were coated with 5 nm Au/Pd (PECS-682).

X-ray diffractometer (XRD) (X'Pert powder diffractometer, PANalytical) was used to determine the X-ray diffraction pattern of samples with Cu K α radiation in the $2\theta=5-30^\circ$ range for pure CD based samples and in the $2\theta=10^\circ-80^\circ$ range for metal nanoparticles incorporating nanofibers.

A thermogravimetric analyzer (TGA) (Q500, TA Instruments) was used for the investigation of the thermal properties of the nanofibers and pure agents. TGA of

the samples was carried out from 25 °C to 500 °C at 20 °C/min heating rate and nitrogen was used as a purge gas. Differential scanning calorimetry (DSC) (TA Q2000) analyses were carried out under nitrogen; initially, samples were equilibrated at 0 °C and then heated to 200 °C at a heating rate of 10 °C/min.

The atomic force microscope (AFM) imaging of fibers collected on a microscope slide was performed in intermittent contact mode in air with a scan rate of 0.1 Hz. TAP 300 (Budget Sensors) type of cantilever which has resonant frequency=200-400 kHz and force constant=20-75 N/m was used. The 3D representation and the roughness graph of the fibers were prepared from AFM images by using XEI software.

Brunauer-Emmett-Teller (BET) surface area analyzer (Quantachrome, IQ-C model) was used to calculate the surface area of powder and nanofibers. Nitrogen adsorption isotherm data were collected at 77 K in the range of 0.00-1.00 relative pressure. Prior to analysis, powder and nanofibers were located into 9 mm cell and degassed for 12 h at 373K.

The isothermal titration experiment was performed by using isothermal titration calorimetry (ITC) (ITC200 Microcalorimeter), and the data were analyzed with Origin software. Water was used as the solvent system for both HP β CD and triclosan. A 0.025 mM triclosan dispersion was prepared and sonicated for 15 min. While the reaction cell was filled with 200 μ L of triclosan solution, the syringe was filled with 40 μ L of the HP β CD solution (0.25 mM). The experiment was carried out at 25 °C by titrating (1 μ L/injection, 40 injections total) the HP β CD solution into the triclosan solution. The reference cell was charged with 150 μ L of deionized water, and the system was stirred at 500 rpm during the titration. To attain thermal equilibrium between each titration, 200 s time intervals were applied.

Transmission electron microscope (TEM) and high resolution transmission electron microscope (HR-TEM) (FEI-Tecna G2F30) were also used for the detailed structural characterization of native CD nanofibers and detection of metal nanoparticles (NP) in the nanofiber structure. In the case of metal NP, scanning

transmission electron microscope (STEM) was also performed. For TEM imaging, HC200 grids were attached on the aluminum foil and the nanofiber samples were directly electrospun onto the grids. The average particle sizes (APS) and particle size distributions (PSD) of NP were determined from GATAN digital micrograph program. For HR-TEM imaging, the HP β CD/NP solutions were diluted and drop-cast onto carbon coated TEM grids. Selected area electron diffraction (SAED) patterns of the Pd-NP included nanofiber was also obtained from TEM.

The UV-vis-NIR spectrophotometer (Varian Cary 5000, USA) was used in the wavelength range of 400-800 nm. For PVA/HP β CD/Ag-NP study, UV-vis spectra were obtained by dissolving the nanofibers in water. The background was corrected with the aqueous solution of pure PVA and PVA/HP β CD nanofibers without Ag-NP. In the case of HP β CD/NP study, the UV-vis spectra of nanofibrous mat were obtained from the solid-state condition of nanofibers and the background was corrected with the pure HP β CD nanofibers.

The infrared spectra of the samples were obtained by using a Fourier transform infrared spectrometer (FTIR) (Bruker-VERTEX70). The samples were mixed with potassium bromide (KBr) and pressed as pellets. The scans (64 scans) were recorded between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} . Raman measurements are performed using a WITTEC Alpha 300S system. A diode-pumped solid-state 532 nm wavelength laser is used for excitation in the Raman measurements. Laser power has been calibrated using a silicon photodiode at sample plane.

The X-ray photoelectron spectra of the nanofibers were recorded by using X-ray photoelectron spectrometer (XPS) (Thermo Scientific). XPS was used by means of a flood gun charge neutralizer system equipped with a monochromated Al $K\alpha$ X-ray source ($h\nu=1486.6$ eV). In order to obtain detailed information, the high resolution spectra were recorded for the spectral regions relating to metal NP at pass energy of 50 eV.

The molar ratio between guest molecules/CD was determined by using proton nuclear magnetic resonance (^1H NMR, Bruker D PX-400) system. The electrospun nanofibers were dissolved in *d*6-DMSO at the 20g/L concentration. The spectra were recorded at 400 MHz and at 16 total scan. Integration of the chemical shifts (δ) given in parts per million (ppm) of the samples was calculated by using NMR software.

2.3.2. Molecular entrapment of volatile organic compounds (VOCs) by modified CD nanofibrous web

The molecular filtration performance of modified CD nanofibers was evaluated by trapping VOCs (aniline and benzene) vapors. For this experiment, 10 mL of aniline or benzene were put into glass Petri dishes and located at the bottom of the desiccators (30 cm (diameter) and 30 cm (height)). As well, the 100 mg CD nanofibers produced from HP β CD and HP γ CD in water and DMF, beside their as-received powder were placed into the sealed desiccators. Samples were exposed aniline and benzene atmosphere for 12 h, afterwards, they were taken out of the desiccators and kept into suction hood for 1 h to remove the solvent molecules that were just adsorbed and could not form inclusion complex (IC) with CD molecules. The examination of the encapsulated amount was carried out by proton magnetic resonance (^1H NMR) and high performance liquid chromatography (HPLC). Thermogravimetric analyzer (TGA) was used to demonstrate the thermal shifts of aniline and benzene degradation/evaporation due to the IC formation during the filtration.

The entrapped amount of VOCs was firstly analyzed by using ^1H NMR (Bruker D PX-400) system. The samples were dissolved in *d*6-DMSO for both aniline and benzene experiments at the 20g/L concentration. The spectra were recorded at 400 MHz and at 16 total scan. The molar ratios between organic molecules to CD (VOCs:CD) were determined by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to CD, aniline and benzene by using NMR software. The particular peaks belong to aniline and benzene were observed at the aromatic region of NMR spectrum (6.7 and 7.1 ppm for aniline, 7.3 ppm for benzene). The molar ratios were calculated by taking account the integration of

aniline, benzene aromatic peaks and the CD's characteristic peak at about 1.0 ppm (CH_3 of -hydroxypropyl group) for d_6 -DMSO system. The measurements were repeated three times for each sample.

The filtration capability of samples was also investigated by using HPLC system (Agilent 1200 Series). Before the measurements, aniline and benzene exposed CD nanofibers and powder were dissolved in an appropriate solvent system for the detection of VOCs encapsulated in the CD molecules. While the aniline treated nanofibers and powder (5 mg) were dissolved in water (1 mL), the benzene treated nanofibers and powder were prepared in water/acetonitrile (ACN) (7/3) (1 mL) blend system. The measurements were repeated three times for aniline and benzene exposed samples. The separation of both aniline and benzene were achieved by using Zorbax Eclipse XDB-C18 column (150 mm $\times$ 4.6 mm, 5 μm particle sizes) and they were detected at 254 nm and 200 nm wavelengths, respectively. For aniline experiment, water/ACN (50/50) (v/v) was used as mobile phase at a flow rate of 0.75 mL/min. and the injection volume was kept at 5 μL . The calibration curve of aniline was prepared from 600 ppm to 10 ppm concentrations by diluting each aniline solution and it showed linearity and acceptability with $R^2 \geq 0.99$. For benzene experiment, water/ACN (25/75) (v/v) was used as mobile phase at a flow rate of 0.75 mL/min. and the injection volume was kept at 20 μL . The calibration curve of benzene was prepared from 200 ppm to 0.002 ppm concentrations by diluting each benzene solution and it showed linearity and acceptability with $R^2 \geq 0.99$. All measurement results were adapted to their calibration curves in terms of peak area under curves.

2.3.3. Molecular entrapment of VOCs by γ -CD nanofibrous web

The molecular entrapment capability of γ -CD nanofibers was investigated by exposing them to the aniline and toluene vapors. For this experiment, 10 mL of aniline or toluene were put into glass Petri dishes and placed at the bottom of the desiccators (30 cm (diameter) and 30 cm (height)). Then, about 10 mg of γ -CD nanofiber mat and as-received γ -CD powder were placed into the sealed desiccators. The γ -CD nanofiber mat and γ -CD powder were kept in aniline or toluene vapor for

12 h, afterwards, they were taken out of the desiccators and placed in suction hood for 2 h in order to remove the uncomplexed aniline or toluene which were only adsorbed onto the surface of the samples. The amount of entrapped aniline and toluene were examined by using proton nuclear magnetic resonance (^1H NMR, Bruker D PX-400) system. The samples were dissolved in *d*6-DMSO for toluene and in D_2O for aniline experiments at the 20g/L concentration. The spectra were recorded at 400 MHz and at 16 total scan. The stoichiometry between γ -CD to toluene and aniline were determined by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to γ -CD, aniline and toluene by using NMR software. The particular peaks belong to aniline and toluene were observed at the aromatic region of NMR spectrum (6.7 and 7.1 ppm for aniline, 7.1 and 7.2 ppm for toluene). The stoichiometries were calculated by taking account the integration of aniline, toluene aromatic peaks and the γ -CD's characteristic peak at about 5.0 ppm for D_2O and 4.8 ppm for *d*6-DMSO system.

2.3.4. Antibacterial tests of triclosan/CD-IC nanofibers

The antibacterial activities of triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers were tested against *Escherichia coli* (*E. coli*) RSHM 888 (RSHM, National Type Culture Collection Laboratory, Ankara, Turkey) and *Staphylococcus aureus* (*S. aureus*) RSHM 96090/07035 (ATCC 25923) representing Gram-negative and Gram-positive bacteria, respectively. The tests of activities were performed using disc agar diffusion method. *E. coli* and *S. aureus* were grown overnight and 150 μL of cultures were spread on Luria-Bertani (LB) agar. For antibacterial tests, the triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibrous webs were cut into 1.2 cm sized circular pieces and the weight of the nanofibers samples were adjusted accordingly in order to have same amount of triclosan. Then, they were placed on *E. coli* and *S. aureus* spreaded agar plates and visualized after 24 h incubation. For comparison, the antibacterial activity of pure triclosan was also investigated. Hence, triclosan powder was weighed so as to be at the identical amount in the CD-IC nanofibers and their dispersions were prepared with very few water. Then this dispersion was dropped on the agar plate in order to provide same diameter with the

nanofiber samples. The tests were repeated three times for each sample. Diameters of zones in which there is no bacterial growth were measured after 24 h and the inhibition zones were compared.

2.3.5. Water solubility of vanillin/CD-IC nanofibers

For the water solubility test, the vanillin/CD-IC nanofibers, which were obtained in water, were selected due to their more proper features for food applications compared to other solvent types; DMF and DMAc. The water solubility limit of vanillin is known as 10mg/mL. Here, we have prepared pure vanillin solution at 20mg/mL concentration and dissolved the water based vanillin/CD-IC nanofibers of three CD types (HP β CD, HP γ CD and M β CD) including the same concentration of vanillin. We have observed that, while vanillin/CD-IC nanofibers were dissolved immediately, there are still insoluble parts of vanillin in its pure solution even after stirring over-night. The solubility determination of solutions was performed by using high performance liquid chromatography (HPLC) technique. Before the HPLC measurement, all vanillin/CD-IC solutions and vanillin dispersion were filtered to remove the un-dissolved parts of the vanillin. The filtered solutions were loaded to the HPLC system and the separation of vanillin was performed with Zorbax Eclipse XDB-C18 column (150 mm $\times$ 4.6 mm, 5 μ m particle size) and it was detected at 254 nm wavelength. The water:methanol (40:60) was used as mobile phase at a flow rate of 0.3 mL/min. and the injection volume was kept at 1 μ l. The calibration curve of vanillin was prepared from by using stock solutions in 10 different concentrations from 10 mg/mL to 20 μ g/mL. It showed linearity and acceptability with $R^2 \geq 0.99$. The experiments were performed in triplicate.

2.3.6. Antibacterial tests of PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibers

The antibacterial activities of the nanofibers were performed against *Escherichia coli* RSHM 888 (RSHM, National Type Culture Collection Laboratory, Ankara, Turkey) as a Gram-negative bacteria and *Staphylococcus aureus* RSHM 96090/07035 (ATCC 25923) as a Gram-positive bacteria. The nanofibrous mats were cut into circular discs having diameter of 0.8 cm. The disc agar diffusion method was conducted. 150 μ L of

the overnight grown cultures ($\sim 10^{12}$ cfu/mL of *E. coli* and $\sim 10^9$ cfu/mL of *S. aureus*) were spreaded on Luria-Bertani (LB) agar. The nanofibrous mats were placed on top of the agar plate. The petri dishes were incubated at 37 °C for 24 h. The tests were repeated three times for each of bacteria. The zones where the bacterial growth was not observed were recorded as inhibition zones and diameters were measured.

2.3.7. Catalytic activity of HP β CD/Pd-NP nanofibers

The catalytic property of Pd-NP including CD nanofibers was investigated by performing a model catalytic reaction consisting of the reduction of p-nitrophenol (PNP) into p-aminophenol (PAP) with borohydride. Firstly, the freshly prepared 1.0 mL of 7 mM sodium borohydride (NaBH_4) was mixed with 1.7 mL of 0.1 mM PNP in 3 mL standard quartz cell. By the addition of NaBH_4 solution into the PNP solution, the color of the system turned from light yellow to yellow green showing the formation of PAP. Meanwhile, the 1 mg nanowebs were dissolved in 1 mL water then, 0.3 mL of these solutions were added into prepared systems and UV-vis absorption spectra were recorded instantly in the 15 second. Other measurements were carried out with 60 s time intervals at 200-600 nm range.

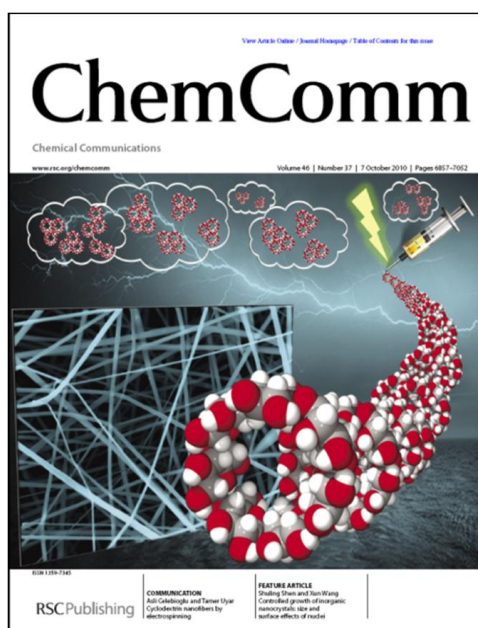
2.3.8. Molecular entrapment of organic molecules from liquid environment by poly-CD nanofibers

The UV-vis NIR spectrophotometer (Varian Cary 5000) was used in the wavelength range of 400-800 nm to follow the absorbance decreasing of the phenolphthalein solution over time as a results molecular filtration of CD molecules. For this, 0.1 g weighted poly-CD nanofibers and granules were located at the bottom of quartz vials which contain phenolphthalein solution prepared from pH 11 adjusted buffer solution. The absorbance data were collected for both samples in a regular time intervals. The phenanthrene filtration performance of nanofiber was investigated by using HPLC system (Agilent 1200 Series). The separation of phenanthrene was performed with Zorbax Eclipse XDB-C18 column (150 mm $\times$ 4.6 mm, 5 μm particle size) and it was detected at 254 nm wavelength. Acetonitrile (100%) was used as mobile phase at a flow rate of 0.3 mL/min. and the injection volume was kept at 10 μl . The

phenanthrene was dissolved in acetonitrile and then diluted in water to carry out the filtration measurements. (The 0.1 g weighted samples were immersed and waited in 1.8 ppm phenanthrene included aqueous solutions.) The calibration curve of phenanthrene was prepared from by using stock solutions in 4 different concentrations; 1.8 $\mu\text{g/mL}$, 0.9 $\mu\text{g/mL}$ 0.45 $\mu\text{g/mL}$, and 0.23 $\mu\text{g/mL}$. It showed linearity and acceptability with $R^2 \geq 0.99$. The measurement results were adapted to this calibration curve in terms of peak area under curves. Moreover, the re-usability of poly-CD nanofibers was investigated. First, they were washed with acetonitrile and 80% of phenanthrene was removed from the nanowebs. Then, its measurement was performed at the same concentration of phenanthrene aqueous solution.

RESULTS AND DISCUSSION

CHAPTER-1: ELECTROSPINNING OF CYCLODEXTRIN NANOFIBERS



Inside Front Cover of ChemComm (**A. Celebioglu** and T. Uyar, Cyclodextrin nanofibers by electrospinning, *Chemical Communications*, 2010, 46, 6903-6905.) (Copyright © 2010, Royal Society of Chemistry. Reprinted with permission from Ref.[129])

3. Electrospinning of Polymer-free Nanofibers from Cyclodextrin Derivatives

According to general aspect, the electrospinnability of systems highly depend on high molecular weight polymer and high polymer concentration existences for ensuring the chain entanglement and overlapping which are important issues for uniform fiber formation. So, the electrospinning of non-polymeric systems was considered as a challenge until a couple of studies were reported about the electrospinning of polymer-free nanofibers. Within this study, we have demonstrated the possibility of the production of polymer-free nanofibers from small cyclic oligosaccharides; Cyclodextrins (CD). Here, we have successfully achieved to obtain nanofibers from chemically modified CD without using a carrier polymer matrix [130]. Polymer-free nanofibers were electrospun from three different CD derivatives, hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD) in three different solvent systems, water, dimethylformamide (DMF) and dimethylacetamide (DMAc) (Figure 9). Viscosity and dynamic light scattering (DLS) measurements were performed to understand the driving conditions for the nanofiber formation from small CD molecules. The morphological characterizations were performed by scanning electron microscope (SEM) in addition; structural, thermal and mechanical characteristics of the CD nanofibers were investigated. This is the pioneer study that combined electrospinning with CD molecules, and comprises the base of our further studies regarding to CD functionalized nanofibers. Here, we have surmounted to understand the common concept and properties of the CD nanofibers, so we have firstly managed the detailed characterizations that provided us general knowledge about this novel topic.

In electrospinning of polymers, the morphology of the electrospun nanofibers is affected by the polymer solution properties such as polymer type, solvent type, solution concentration and/or viscosity, solution conductivity etc.[1, 14-20, 22, 23]. Here, we have investigated the effect of solvent type, concentration/viscosity and solution conductivity on the final morphology of electrospun nanofibers obtained from HP β CD, HP γ CD and M β CD. Interestingly, we have observed that these CDs

behave very similar to polymeric systems during the electrospinning process where the solvent type, solution viscosity and conductivity played a major role in the formation of bead-free uniform CD nanofibers.

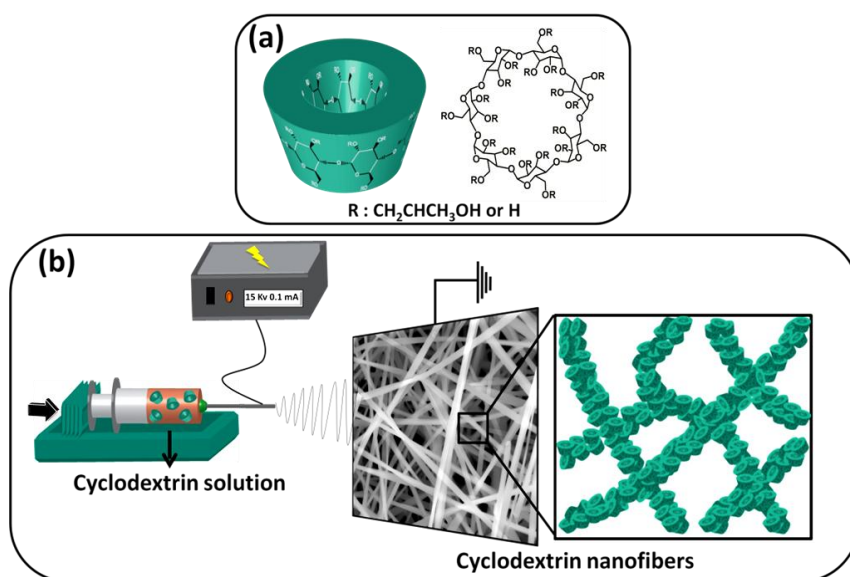


Figure 9. (a) Schematic view and chemical structure of modified CD. (b) Schematic representation of the electrospinning of the modified CD nanofibers.

3.1. Electrospinning of HP β CD nanofibers

The electrospun HP β CD nanofibers were produced from water, DMF and DMAc solvent systems. The characteristics of HP β CD solutions and the morphological properties of the resulting electrospun nanofibers are summarized in Table 2. For each solvent type, the initial HP β CD concentration was 100% (w/v) and increased up to the optimal concentration that nanofibers without beaded structure were produced. Bead-free HP β CD nanofibers were obtained at 160% (w/v) for water (Figure 10(d)) and at 120% (w/v) for DMF (Figure 10(f)) and DMAc (Figure 10(h)). HP β CD nanofibers having fiber diameter in the range of 250-1780 nm (AFD=745 $\pm$ 370 nm), 400-1800 nm (AFD=1125 $\pm$ 360 nm) and 310-1860 nm (AFD=1360 $\pm$ 295 nm) were obtained from water, DMF and DMAc solvent systems, respectively (Table 2).

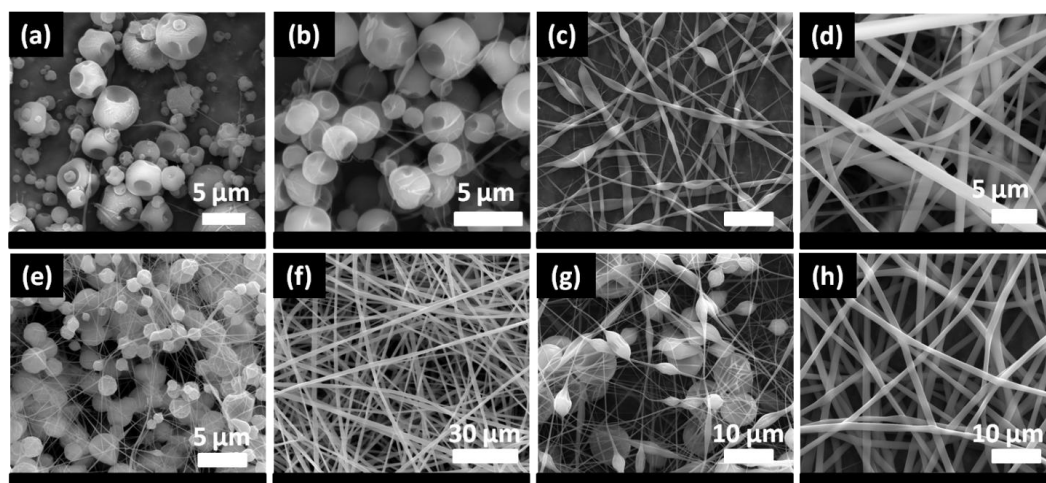


Figure 10. The representative SEM images of the electrospun HP β CD nanofibers obtained from water, DMF and DMAc solutions having different HP β CD concentrations. (a) 100% (w/v), (b) 120% (w/v), (c) 140% (w/v) and (d) 160% (w/v) HP β CD in water; (e) 100% (w/v) and (f) 120% (w/v) HP β CD in DMF; and (g) 100% (w/v) and (h) 120% (w/v) HP β CD in DMAc. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

The dynamic light scattering (DLS) and viscosity measurements were performed for concentrated HP β CD solutions in order to understand the electrospinnability of HP β CD by itself. Substantial viscosity increase was observed as the concentration of the HP β CD increased from 100% to 160% (w/v) in water, and from 100% to 120% (w/v) in DMF and DMAc (Table 2). The DLS measurements revealed the presence of self-aggregated HP β CD molecules in their concentrated solutions (Figure 11 and Table 2); in addition, it was evident that the sizes of the HP β CD aggregates were increased and the particle size distribution became broader as the concentration of the HP β CD solution increased from 100% to 160% (w/v) in water. Similar trends were observed for DMF and DMAc solvent systems, that is, larger HP β CD aggregates were formed as the concentration of the HP β CD solution increased from 100% to 120% (w/v). Moreover, the size of the HP β CD aggregates was larger in DMF when compared to water. In the case of the DMAc solvent system, HP β CD aggregates were significantly bigger than the ones formed in water and DMF. Hence, the viscosity of the same HP β CD concentrations (100% and 120% (w/v)) was highest in DMAc and lowest in water because of the differences in aggregate sizes.

Table 2. The characteristics of HP β CD solutions, fiber morphology, average fiber diameter and fiber diameter range of the electrospun HP β CD fibers. (DLS measurements of CD solutions at 25 °C (Equilibrium at 25 °C for 2 minutes prior to measurement) summarizing the average diameter (nm) and polydispersity index (PDI) of HP β CD aggregates). (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref. [130])

Solutions	Solvent	% CD (w/v)	Viscosity (Pa•s)	Conductivity (μ S/cm)	Intensity-average diameter (<i>d</i> , nm)	PDI	Fiber Morphology	Average Fiber Diameter (nm) (Fiber Diameter Range (nm))
100HP β CD	Water	100	0.0173	538	6.5	0.26	Bead structures	-
120HP β CD	Water	120	0.0357	429	7.0	0.32	Bead structures	-
140HP β CD	Water	140	0.0375	332	8.0	0.35	Beaded nanofibers	
160HP β CD	Water	160	0.117	222	9.2	0.40	Bead-free nanofibers	745 $\pm$ 370 (250-1780)
160HP β CD + 20% Urea	Water	160	0.0604	247	8.1	0.28	Bead structures	-
100HP β CD	DMF	100	0.106	11.94	11.9	0.18	Beaded nanofibers	-
120HP β CD	DMF	120	0.234	10.62	20.6	0.24	Bead-free nanofibers	1125 $\pm$ 360 (400-1800)
120HP β CD + 20% Urea	DMF	120	0.179	6.53	16.9	0.15	No fiber formation	-
100HP β CD	DMAc	100	0.107	3.92	21.0	0.25	Beaded nanofibers	-
120HP β CD	DMAc	120	0.329	1.92	65.5	0.42	Bead-free nanofibers	1360 $\pm$ 295(310-1860)

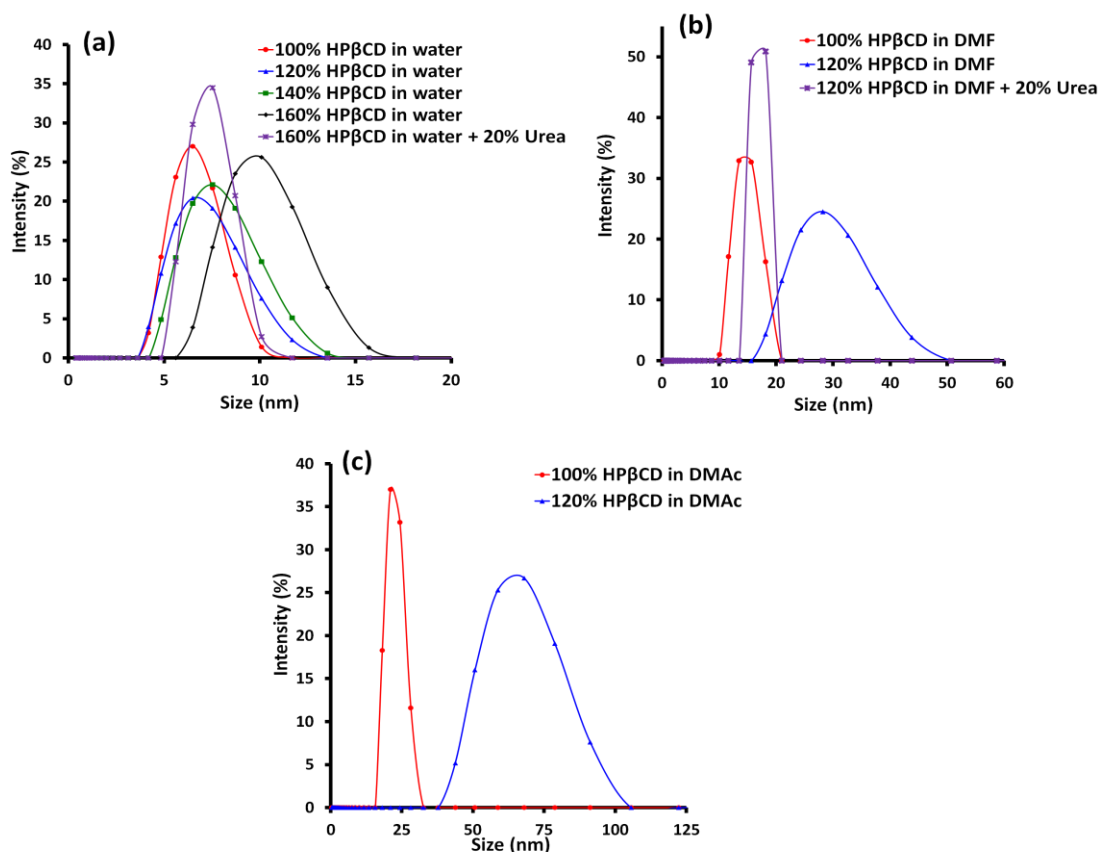


Figure 11. Size distribution of HPβCD aggregates for (a) 100%, 120%, 140%, 160% (w/v) HPβCD and 160% (w/v) HPβCD containing 20% (w/w) urea in water; (b) 100%, 120% (w/v) HPβCD and 120% (w/v) HPβCD containing 20% (w/w) urea in DMF; and (c) 100% and 120% (w/v) HPβCD in DMAc. (Copyright © 2012, Royal Society of Chemistry. Reproduced with permission from Ref.[130])

The DLS and viscosity data are in good agreement with each other and higher solution viscosity is owing to the higher amount of HPβCD aggregates and their growing sizes as the concentration of the HPβCD increased in water, DMF and DMAc solution systems. At lower HPβCD concentration (100%, w/v) in water, micron and nano-sized non-uniform beads were obtained (Figure 10(a)). This is due to the presence of insufficient amount of HPβCD aggregates at low concentration which resulted in destabilization of the electrified jet during the electrospinning and therefore yielded beads instead of continuous fibers. This behavior is typically observed for the electrospinning of polymer solutions having low concentration. When the concentration of the polymer solution is not at the optimal level, electrospinning occurs which yields only beads due to the lack of sufficient polymer

chain entanglements and overlapping [1, 18]. Likewise, HP β CD molecules at 100% (w/v) could not form sufficient aggregates to stabilize the electrospun jet for the formation of continuous fibers. When a 120% (w/v) aqueous HP β CD solution was electrospun, very fine fibers along with a substantial amount of beads were obtained (Figure 10(b)). In the case of the 140% (w/v) concentration, the aqueous HP β CD solution almost reached satisfactory viscosity value and aggregation sizes, so nanofibers along with some elongated beaded structures were obtained (Figure 10(c)). Apparently, the transition from beaded structure to bead-free nanofibers was observed when a 160% (w/v) HP β CD aqueous solution was electrospun. At this concentration, bead-free HP β CD nanofibers were produced with fiber diameters in the range of 250-1780 nm having an average fiber diameter of 745 ± 370 nm (Figure 10(d)). In the electrospinning of polymeric systems, bead-free fibers are usually obtained as the concentration of the polymer solution is increased, [1, 17-19] since polymer solutions with higher concentration have more chain entanglements which are very crucial to maintain the continuity of the jet during the electrospinning process. Here, we observed a very similar behavior for the electrospinning of HP β CD nanofibers from its aqueous solution. The DLS measurements indicated that at higher concentrations, HP β CD molecules form a considerable amount of aggregates which resulted in full stretching of the electrified solution jet and therefore yielded bead-free nanofibers. HP β CD nanofibers were also electrospun from its DMF solution. The beaded HP β CD nanofibers were obtained at 100% (w/v) HP β CD concentration in DMF (Figure 10(e)). When a 120% (w/v) HP β CD solution was electrospun, the bead-free nanofibers in the range of 400-1800 nm having an average fiber diameter of 1125 ± 360 nm were produced (Figure 10(f)). In DMF, the bead-free HP β CD nanofibers were attained at much lower concentration but at higher fiber diameter when compared to the water system. The reason can be attributed to the larger aggregate size, higher viscosity and lower conductivity of the HP β CD solution in DMF (Table 2) which yielded thicker fibers owing to less stretching of the jet during the electrospinning. At 120% (w/v) HP β CD in DMF, the aggregate size and viscosity were 20.6 nm and 0.234 Pa•s, respectively; whereas the aggregate size and viscosity were 9.2 nm and 0.117 Pa•s for the 160% (w/v) HP β CD in water, respectively. In addition, the conductivity of the HP β CD solution in DMF (10.62

$\mu\text{S/cm}$) was much less than in its water solution ($222 \mu\text{S/cm}$). This behavior of HP β CD solution is very typical for the electrospinning of polymeric systems in which solutions having high viscosity and low conductivity yield thicker fibers because of the decreased stretching of the jet [1, 19]. The bead-free fibers were also obtained from the electrospinning of HP β CD in DMAc solution. The results were very similar to the DMF solvent system, that is, at 100% (w/v) HP β CD in DMAc, beaded fibers were obtained (Figure 10(g)), but bead formation was less and more fiber structures were present when compared to 100% (w/v) HP β CD in DMF (Figure 10(e)). Bead-free HP β CD fibers were produced in the diameter range of 310-1860 nm with the average diameter of 1360 ± 295 nm at 120% (w/v) HP β CD solution in DMAc (Figure 10(h)). When electrospun HP β CD fibers obtained from DMAc were compared to the ones obtained from DMF, the diameter of the fibers produced from DMAc solution was thicker. The morphologic and fiber diameter differences between the water and DMF system were related to the differences in the viscosity and conductivity of the solutions. Similarly, the 120% (w/v) HP β CD solution in DMAc has bigger aggregate size (65.5 nm), higher viscosity ($0.329 \text{ Pa}\cdot\text{s}$) and much lower conductivity ($1.92 \mu\text{S/cm}$) when compared with 120% (w/v) HP β CD solution in DMF (aggregate size: 20.6 nm, viscosity: $0.234 \text{ Pa}\cdot\text{s}$ and conductivity: $10.62 \mu\text{S/cm}$); therefore, thicker HP β CD fibers were produced in the case of the DMAc solvent system.

3.2. Electrospinning of HP γ CD fibers

HP γ CD is another type of chemically modified CD derivative that was electrospun from water, DMF and DMAc solution systems. Similar to HP β CD, electrospinning was carried out by varying the HP γ CD concentration from 100% to 160% (w/v) in water and from 100% to 125% (w/v) in DMF and DMAc. The bead-free fibers were obtained at 160% (w/v) concentration in water and at 125% (w/v) in DMF and DMAc (Figure 12).

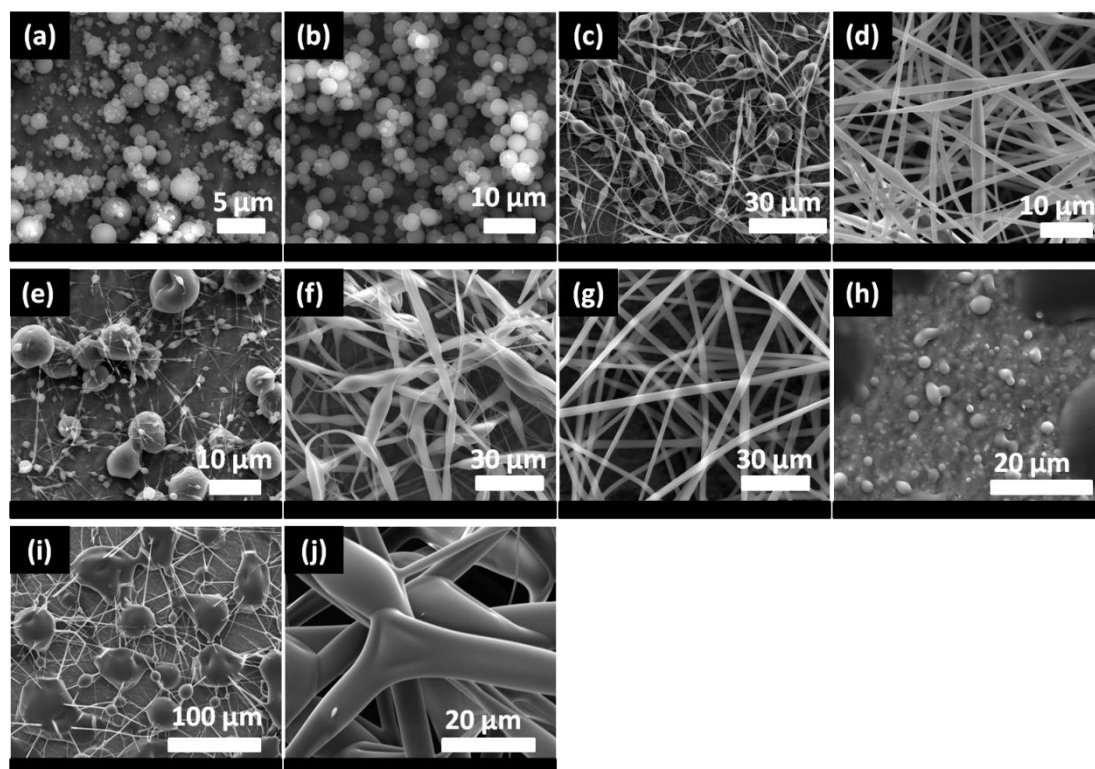


Figure 12. The representative SEM images of the electrospun HP γ CD nanofibers obtained from water, DMF and DMAc solutions having different HP γ CD concentrations. (a) 100% (w/v), (b) 120% (w/v), (c) 140% (w/v) and (d) 160% (w/v) HP γ CD in water; (e) 100% (w/v), (f) 120% (w/v) and (g) 125% (w/v) HP γ CD in DMF; (h) 100% (w/v), (i) 120% (w/v) and (j) 125% (w/v) HP γ CD in DMAc. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

The solution properties and the morphological findings of the fibers are summarized in Table 3. Unfortunately, the size of the HP γ CD aggregates cannot be measured accurately since these concentrated HP γ CD solutions in water, DMF and DMAc have a slightly yellowish color and therefore we were unable to acquire accurate data from DLS measurements. Yet, the viscosity of the HP γ CD solutions (Table 3) was much higher when compared to HP β CD and M β CD solutions (Table 3) suggesting that a substantial amount of aggregates was present in HP γ CD solutions.

Table 3. The characteristics of HP γ CD solutions, fiber morphology, average fiber diameter and fiber diameter range of the electrospun HP γ CD fibers. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

Solutions	Solvent	% CD (w/v)	Viscosity (Pa•s)	Conductivity (μ S/cm)	Fiber morphology	Average fiber diameter (nm) (Fiber diameter range (nm))
100HP γ CD	Water	100	0.0098	16.53	Bead structure	-
120HP γ CD	Water	120	0.0222	13.08	Bead structure	-
140HP γ CD	Water	140	0.0398	9.61	Beaded nanofibers	-
160HP γ CD	Water	160	0.0603	6.56	Bead-free nanofibers	1165 $\pm$ 455 (330-2100)
160HP γ CD + 20% Urea	Water	160	0.0547	8.58	No fiber formation	-
100HP γ CD	DMF	100	0.095	0.17	Beaded nanofibers	-
120HP γ CD	DMF	120	0.318	0.1	Beaded nanofibers	-
125HP γ CD	DMF	125	0.502	0.07	Bead-free nanofibers	2740 $\pm$ 725 (1030-5800)
125HP γ CD + 20% Urea	DMF	125	0.294	0.07	No fiber formation	-
100HP γ CD	DMAc	100	0.339	0.07	Bead structures	-
120HP γ CD	DMAc	120	1.6	0.00	Bead structures	-
125HP γ CD	DMAc	125	1.63	0.00	Beaded nanofibers	6385 $\pm$ 13565 (3600-9850)

When HP γ CD was electrospun from its aqueous solutions at low concentrations (100% and 120% (w/v)) only bead structures were formed (Figure 12(a-b)). Increasing the concentration to 140% (w/v) yielded elongated beaded fibers (Figure 12(c)) and finally bead-free fibers in the diameter range of 330-2100 nm having an average diameter of 1165 $\pm$ 455 nm were obtained at 160% (w/v) HP γ CD concentration (Figure 12(d)). The optimal concentration was 125% (w/v) for producing bead-free HP γ CD fibers (Figure 12(g)) in DMF and the diameter range of the fibers was 1030-5800 nm (AFD=2740 $\pm$ 725 nm). At 100% (w/v) and 120% (w/v), beaded fibers were obtained (Figure 12(e-f)). Although the 120% (w/v) HP γ CD

solution in DMF has a reasonable viscosity, the beaded structures were not eliminated possibly because of the very low conductivity of the solution, therefore, higher solution concentration (125%, w/v) was required for the formation of bead-free fibers. This behavior is commonly seen for the electrospinning of polymer solutions where higher polymer concentration is essential for solutions having low conductivity in order to eliminate the beads [1, 19]. The viscosity of the HP γ CD solution in DMAc was considerably higher than the ones in water and DMF and the conductivity of the solution was zero (Table 3). Beads and splashes were formed at 100%(w/v) (Figure 12(h)) and beaded fibers along with some splashes were obtained when 120%(w/v) HP γ CD solution was electrospun (Figure 12(i)). The electrospinning of 125% (w/v) HP γ CD solution in DMAc resulted in very thick non-uniform fibers (Figure 12(j)). Due to the very high viscosity and zero solution conductivity, the stretching of the jet was minimal and the HP γ CD micron-sized fibers in the diameter range of 3600-9850nm (AFD=6385 $\pm$ 1355 nm) were formed. In addition, some of the fibers were fused together indicating that the solvent evaporation was not completed during the electrospinning of the fibers. This is possibly because of the low volatility of DMAc and a very high viscosity of the HP γ CD solution (Table 3). DMAc (T_b=165 °C) has a higher boiling point than DMF (T_b=153 °C) and water (T_b=100 °C), hence, its evaporation at room temperature cannot be completed thus wet fibers having junctions within the touching points of the fibers were obtained. When the fiber diameters are compared, HP γ CD fibers are much thicker than the HP β CD fibers due to the much higher viscosity and very low conductivity of the HP γ CD solutions. The solution conductivity is one of the main parameters in the electrospinning process since the viscous solution is being stretched due to the repulsion of the charges present on its surface [1]. The charge density of the solution is higher in the case of higher solution conductivity, which causes a greater repulsion and a greater bending instability during electrospinning, and therefore the jet is subjected to more stretching under the high electrical field and resulted in thinner fibers [1]. Here, micron-sized fibers were obtained from HP γ CD because of the high viscosity and very low conductivity of the HP γ CD solutions.

3.3. Electrospinning of M β CD nanofibers

M β CD is the methylated derivative of β -CD and it has very high solubility like HP β CD and HP γ CD. The solution properties of M β CD in water, DMF and DMAc and the morphological findings of the resulting electrospun nanofibers are given in Table 4. The DLS measurements indicated that the size of M β CD aggregates became larger as the solution concentration increased from 100% to 160% (w/v) in water and DMF (Figure 13). The M β CD aggregates were larger in DMF solutions when compared to the water solutions in all concentrations. In the case of M β CD in DMAc solutions, we were unable to obtain reasonable data from DLS measurements since the solutions were slightly turbid, but the viscosity of the M β CD solutions was higher compared to the viscosities in water and DMF suggesting that a larger amount of M β CD aggregates were present in DMAc solutions.

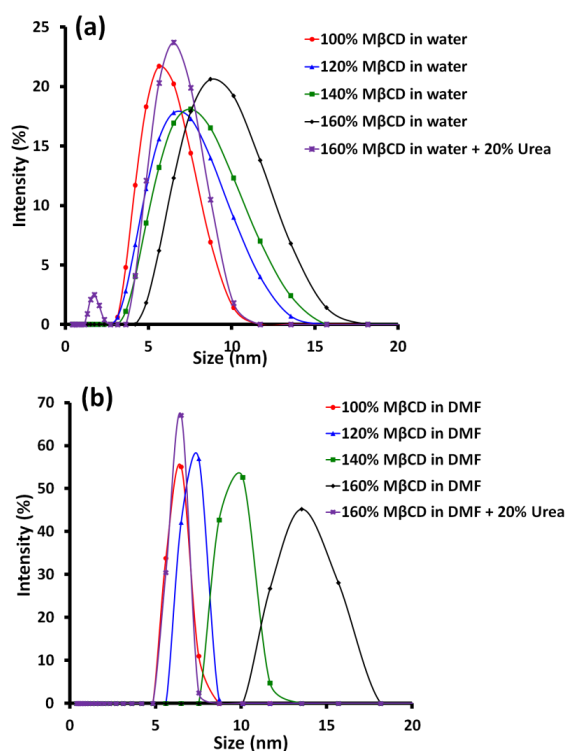


Figure 13. Size distributions of M β CD aggregates for (a) 100%, 120%, 140%, 160% (w/v) M β CD and 160% (w/v) M β CD containing 20% (w/w) urea in water; and (b) 100%, 120%, 140%, 160% (w/v) M β CD and 160% (w/v) M β CD containing 20% (w/w) urea in DMF. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

Table 4. The characteristics of M β CD solutions, fiber morphology, average fiber diameter and fiber diameter range of the electrospun M β CD fibers.(DLS measurements of CD solutions at 25 °C (Equilibrium at 25 °C for 2 minutes prior to measurement) summarizing the average diameter (nm) and polydispersity index (PDI) of HP β CD aggregates). (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

Solutions	Solvent	% CD (w/v)	Viscosity (Pa•s)	Conductivity (μ S/cm)	Intensity- average diameter (d , nm)	PDI	Fiber morphology	Average fiber diameter (nm) (Fiber diameter range (nm))
100M β CD	Water	100	0.0116	1842	5.9	0.32	Bead structures	-
120M β CD	Water	120	0.0217	1561	6.9	0.36	Beaded nanofibers	-
140M β CD	Water	140	0.0509	1177	7.6	0.41	Bead-free nanofibers	95 $\pm$ 90 (20-490)
160M β CD	Water	160	0.106	979	9.0	0.55	Bead-free nanofibers	100 $\pm$ 140 (20-650)
160M β CD + 20% Urea	Water	160	0.0061	780	6.5	0.30	No fiber formation	-
100M β CD	DMF	100	0.0176	46.2	6.3	0.25	Sphere structures	-
120M β CD	DMF	120	0.0755	28.2	7.1	0.28	Beaded nanofibers	-
140M β CD	DMF	140	0.275	15.58	10.2	0.31	Bead-free nanofibers	430 $\pm$ 170 (100-1000)
160M β CD	DMF	160	0.564	12.87	13.7	0.36	Bead-free naofibers	450 $\pm$ 200 (100-1200)
160M β CD + 20% Urea	DMF	160	0.442	12.96	6.2	0.22	No fiber formation	-
100M β CD	DMAc	100	0.0331	4.76	-	-	Sphere structure	-
120M β CD	DMAc	120	0.122	2.33	-	-	Bead structures	-
140M β CD	DMAc	140	0.255	1.54	-	-	Beaded nanofibers	-
160M β CD	DMAc	160	0.533	1.39	-	-	Bead-free nanofibers	1200 $\pm$ 555 (430-2450)

Electrospinning of 100% and 120% (w/v) M β CD aqueous solutions yielded elongated bead structures (Figure 14(a)) and beaded nanofibers (Figure 14(b)), respectively. These results suggested the presence of inadequate aggregations in the M β CD solution. On the other hand, uniform nanofibers having fiber diameters in the range of 20-490 nm (AFD=95 $\pm$ 90 nm) and 20-650 nm (AFD=100 $\pm$ 140 nm) were produced at 140% and 160% (w/v) concentrations, respectively, indicating that a sufficient aggregation level was achieved at these concentrations (Figure 14(c-d)). At lower M β CD concentration (100% (w/v)) in DMF, micron and nano-size droplets were formed (Figure 14(e)), but, once the 120% (w/v) M β CD solution was electrospun, ultrafine fibers with a considerable amount of beads were obtained (Figure 14(f)). The transition from beaded nanofibers to bead-free nanofibers was observed when 140% (w/v) and 160% (w/v) M β CD solutions were electrospun (Figure 14(g-h)). Bead-free nanofibers having fiber diameters in the range of 100-1000 nm (AFD=430 $\pm$ 170 nm) and 100-1200 nm (AFD=450 $\pm$ 200 nm) were obtained at 140% and 160% (w/v) concentrations, respectively. In the case of using DMAc as a solvent, 100% and 120% (w/v) M β CD solutions yielded nano and micron-size beads (Figure 14(i-j)). At 140% (w/v), nanofibers with vastly beaded structures were obtained (Figure 14(k)) and increasing the M β CD concentration to 160% (w/v) yielded bead-free nanofibers (Figure 14(l)). When the fiber diameters were compared with the ones obtained from water and DMF solution systems, it was found that thicker fibers in the range of 430-2450 nm (AFD=1200 $\pm$ 555 nm) were produced because of the higher viscosity and lower conductivity values of the M β CD solution in DMAc.

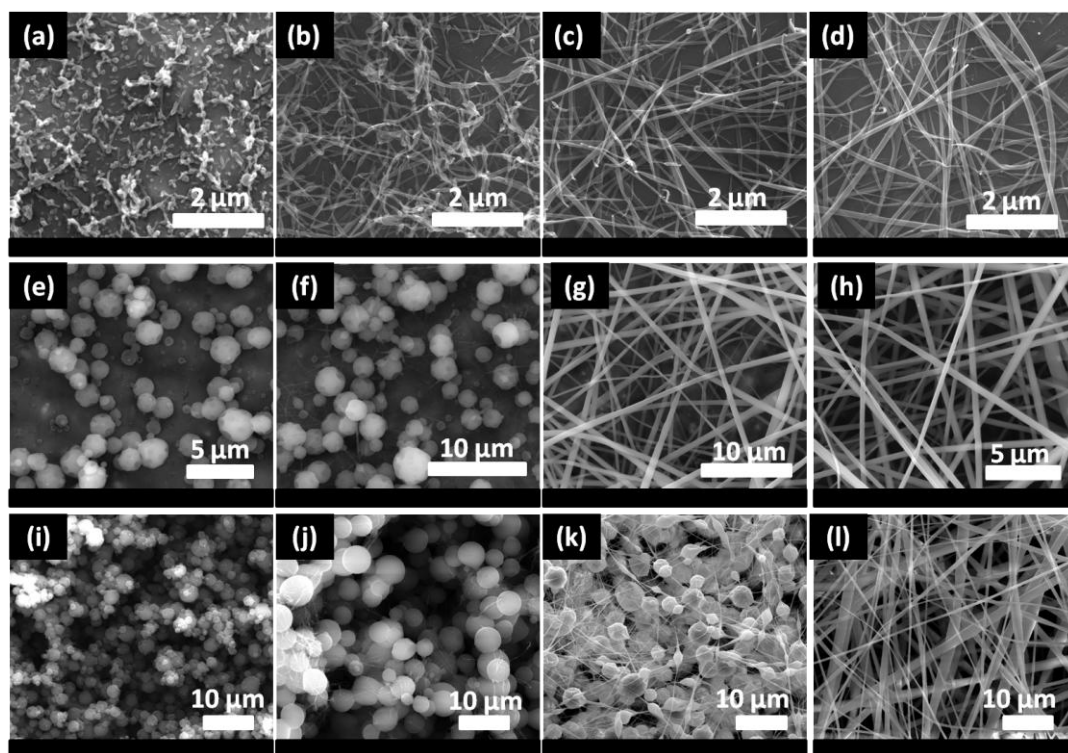


Figure 14. The representative SEM images of the electrospun M β CD nanofibers obtained from water, DMF and DMAc solutions having different M β CD concentrations. (a) 100% (w/v), (b) 120% (w/v), (c) 140% (w/v) and (d) 160% (w/v) M β CD in water; (e) 100% (w/v), (f) 120% (w/v), (g) 140% (w/v), and (h) 160% (w/v) M β CD in DMF; and (i) 100% (w/v), (j) 120% (w/v), (k) 140% (w/v) and (l) 160% (w/v) M β CD in DMAc. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

When compared with HP β CD and HP γ CD, M β CD nanofibers obtained from water noticeably have much smaller diameter. The possible reason is the smaller aggregate size, low viscosity and very high conductivity of the M β CD solutions in water (Table 4) which yielded much thinner fibers because of the increased stretching of the jet during the electrospinning. Similar results were also obtained from the electrospinning of M β CD solutions in DMF and DMAc which yielded thinner M β CD fibers when compared to HP β CD and HP γ CD fibers. This behavior is very similar to the electrospinning of polymer solutions in which solutions having low viscosity and high conductivity yield thinner fibers [1].

For M β CD nanofibers, we performed the AFM analyses to investigate the surface morphology of nanofibers. We have observed that, M β CD nanofibers produced from DMF solution are smoother compared to the ones obtained from aqueous solution of M β CD. Representative AFM images and cross-section profiles of M β CD nanofiber obtained from water and DMF solutions are given in Figure 15. DMF is a high boiling point (153 °C) solvent, thus, slow evaporation of the solvent during the electrospinning resulted in a much smoother fiber surface. This kind of morphological difference is also very common for electrospun polymeric nanofibers where smooth fibers are produced when high boiling point solvents (such as DMF, DMAc, etc.) are used whereas porous and rougher fiber surfaces are obtained in the case of using volatile solvents (chloroform, acetone, THF, water, etc.) [1, 4, 19].

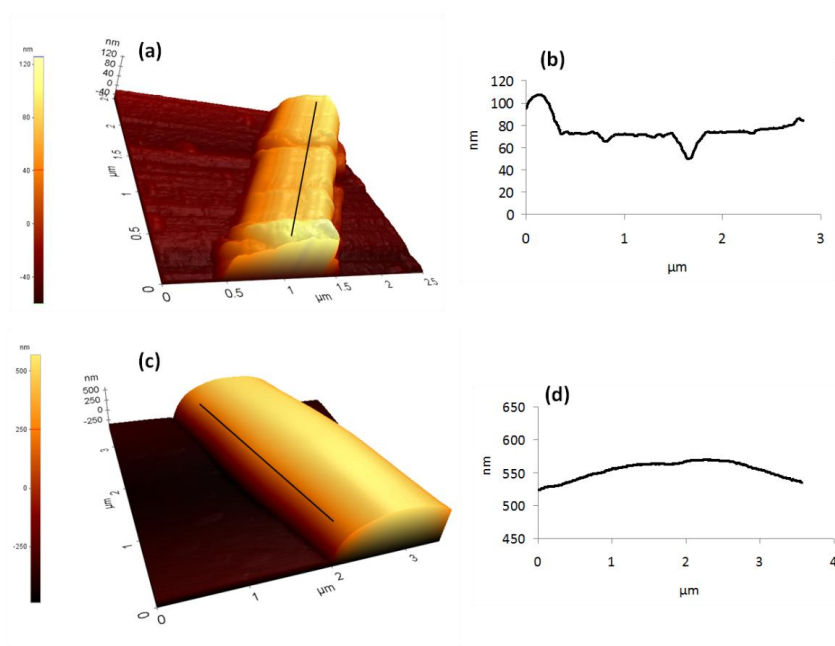


Figure 15. (a) AFM image and (b) fiber axis cross-section profile of the nanofiber obtained from 160% (w/v) M β CD in water. (c) AFM image and (d) fiber axis cross-section profile of the nanofiber obtained from 160% (w/v) M β CD in DMF. (Copyright © 2010, Royal Society of Chemistry. Reprinted with permission from Ref.[129])

3.4. The effect of urea on the electrospinning of CD nanofibers

It is known that the addition of urea to CD solutions causes notable depression of the self-association of the CD molecules since urea breaks up the H-bonds between the

CD molecules [138, 146]. Here, we added 20% urea (w/w, with respect to CD) to 160% (w/v) HP β CD, 160% (w/v) HP γ CD and 160% (w/v) M β CD in water solutions and to 120% (w/v) HP β CD, 125% (w/v) HP γ CD and 160% M β CD (w/v) in DMF solutions. The insolubility of urea in DMAc restricted the investigation of urea effect on the electrospinning of these CD in a DMAc solvent system. The DLS and viscosity measurements clearly showed that the size of the CD aggregates became smaller and the viscosity of the solutions was decreased after the addition of urea which was due to the destruction of the CD aggregates in their solutions (Figure 11 and 13, Tables 2, 3, 4) [146, 147]. The electrospinning of CD solutions containing urea yielded no fibers but only beads or splashes. Figure 16 shows the representative SEM images of splashed areas or beads which were obtained from the electrospinning of urea containing CD solutions. This is because of the breakup of the electrospinning jet due to the presence of inadequate CD aggregates in the solutions. This result further proved that the success of electrospinning of fibers from CD was due to the presence of intermolecular interactions (H-bonding) and sufficient aggregates in their highly concentrated solutions (Figure 17).

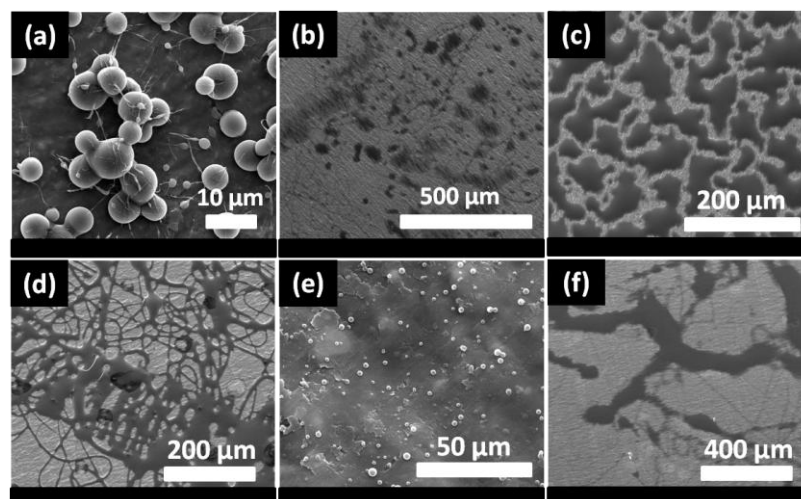


Figure 16. The representative SEM images of the splashed area that were obtained as a result of adding 20% (w/w) urea to CD solutions. (a) 160% (w/v) HP β CD containing 20% (w/w) urea in water, (b) 120% (w/v) HP β CD containing 20% (w/w) urea in DMF, (c) 160% (w/v) HP γ CD containing 20% (w/w) urea in water, (d) 125% (w/v) HP γ CD containing 20% (w/w) urea in DMF, (e) 160% (w/v) M β CD containing 20% (w/w) urea in water, and (f) 160% (w/v) M β CD containing 20% (w/w) urea in DMF. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

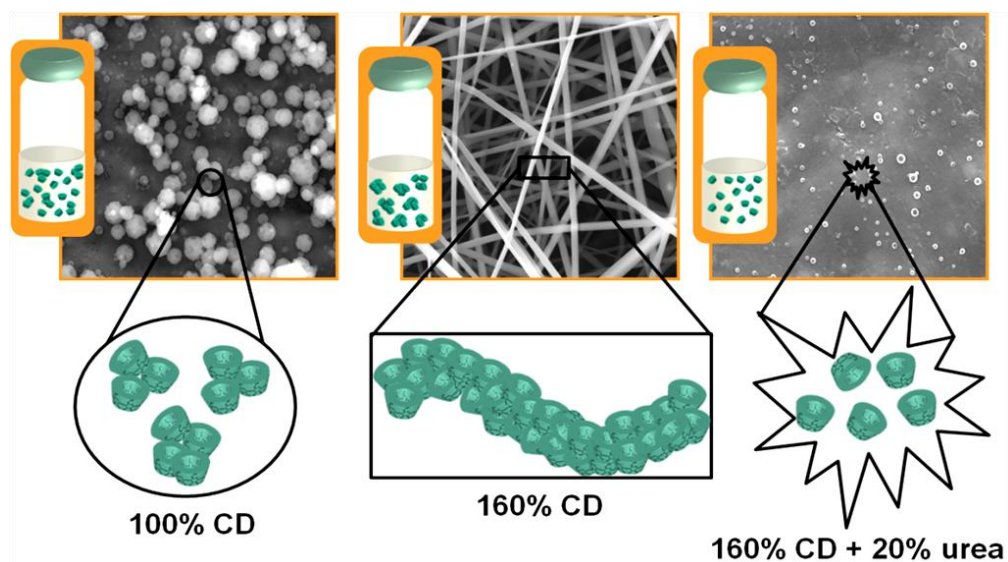


Figure 17. Schematic views of the aggregation situations of CD molecules in lowest and highest concentrated CD solution, as well in the urea added one.

3.5. Characterization of the electrospun CD nanowebs

The structural analyses of the electrospun CD nanowebs were performed by XRD. Native CD (α -CD, β -CD and γ -CD) are crystalline; however, random substitution of the hydroxyl groups of CD with methyl or hydroxypropyl groups resulted in amorphous materials. The XRD studies showed that the diffraction patterns of all the electrospun CD nanowebs are very similar to their powder form having amorphous structure (Figure 18). No additional diffraction peaks and/or sharpening of the present peaks were observed indicating the absence of any particular orientations of CD molecules during the fiber formation.

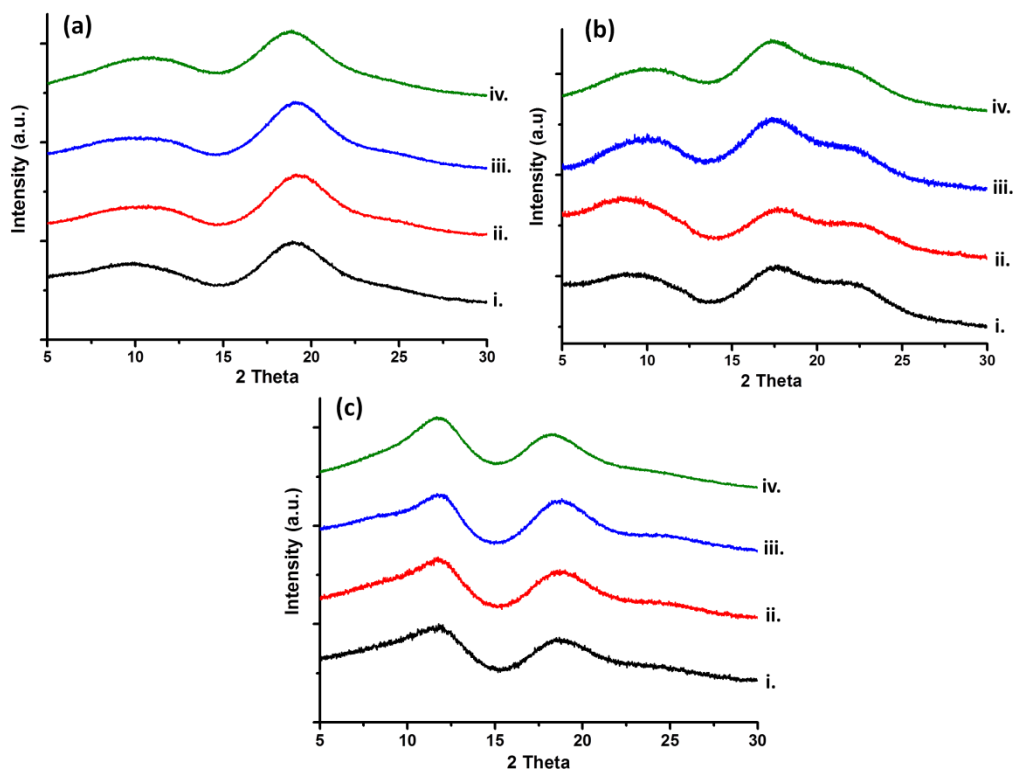


Figure 18. XRD patterns of (a) the HP β CD nanoweb produced from (i) water, (ii) DMF, (iii) DMAc solution and (iv) as-received HP β CD powder; (b) the HP γ CD web produced from (i) water, (ii) DMF, (iii) DMAc solution and (iv) as-received HP γ CD powder; and (c) the M β CD nanoweb produced from (i) water, (ii) DMF, (iii) DMAc solution and (iv) as-received M β CD powder. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

TGA showed minor weight losses between 25 and 100 °C which was due to the removal of water from the CD nanoweb (Figure 19). From the TGA data, it was calculated that the HP β CD and M β CD nanoweb contained 5% and 2 to 3% (w/w) of water, respectively. In the case of HP γ CD, the water content was about 5% and 2% (w/w) for the nanoweb produced from water, and from DMF and DMAc solvent systems, respectively. For all the CD nanoweb (HP β CD, HP γ CD, and M β CD), the main thermal degradation was between 300 and 350 °C. However, it was observed that the onset temperature of the main degradation was slightly different for CD nanoweb electrospun from different solvent systems. When compared to as-received CD powder, the main thermal degradation was observed at a slightly lower temperature for HP β CD nanoweb electrospun from water and DMF, HP γ CD nanoweb electrospun from water, and M β CD nanoweb electrospun from water and

DMF. This is possible due to the thinner fiber diameter of the CD nanowebbs which have higher surface area and higher contact points resulting in slightly earlier thermal degradation compared to powder CD. The TGA thermograms of HP β CD, HP γ CD, and M β CD nanowebbs electrospun from DMAc and HP γ CD nanowebbs electrospun from DMF were very similar to those of powder CD. These CD webs have much thicker fiber diameter and presumably the surface areas of these webs were not much different than the CD powder and therefore showed very similar thermal behavior.

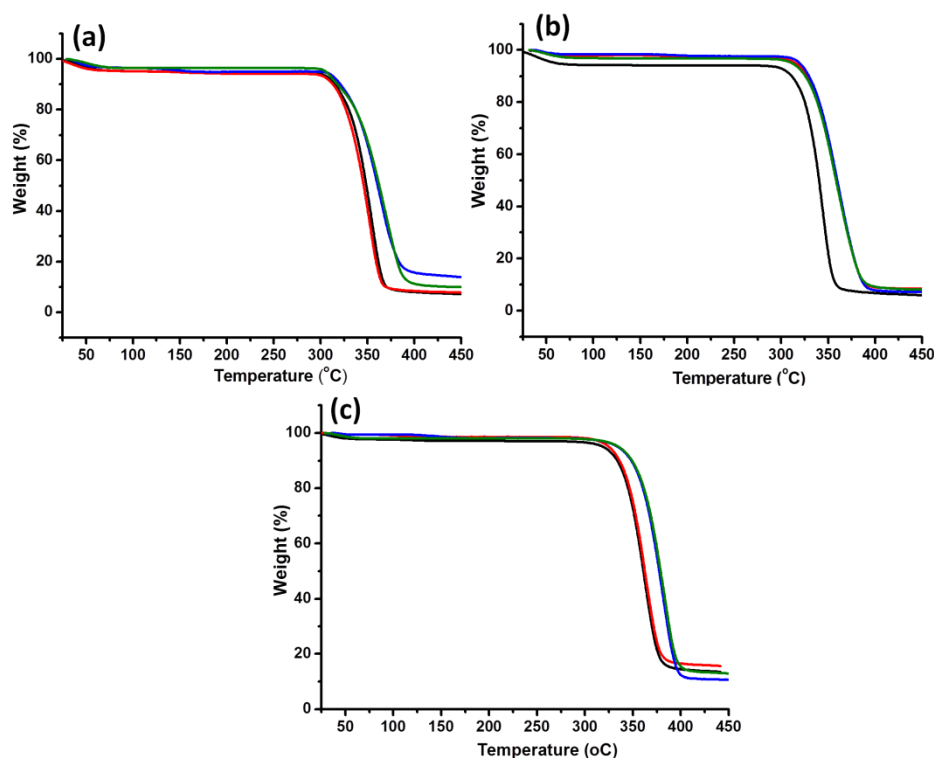


Figure 19. TGA thermograms of (a) the HP β CD nanoweb produced from water (black line), DMF (red line), DMAc (blue line) and the as-received powder form of HP β CD (green line); (b) the HP γ CD web produced from water (black line), DMF (red line), DMAc (blue line) and the as-received powder form of HP γ CD (green line); and (c) M β CD nanoweb produced from water (black line), DMF (red line), DMAc (blue line) and the as-received powder form of M β CD (green line). (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

The mechanical strength of the electrospun CD nanowebbs was also examined visually. These electrospun CD nanowebbs are consisting of small molecules having amorphous structure, and therefore, they are expected to be very weak and brittle when compared to polymeric systems. Nonetheless, the HP β CD and M β CD

electrospun nanowebs obtained from three different solvent systems (water, DMF and DMAc) have shown some mechanical strength and flexibility by which they can be easily handled and folded as free standing materials (Figure 20). In the case of HP γ CD, nanowebs electrospun from water were similar to HP β CD and M β CD, but, HP γ CD nanowebs obtained from DMF and DMAc solutions have more brittle nature and therefore it was difficult to handle them (Figure 20(e-f)). This suggested that the mechanical properties of HP γ CD nanowebs were significantly depending on the type of the solvent used for the electrospinning.

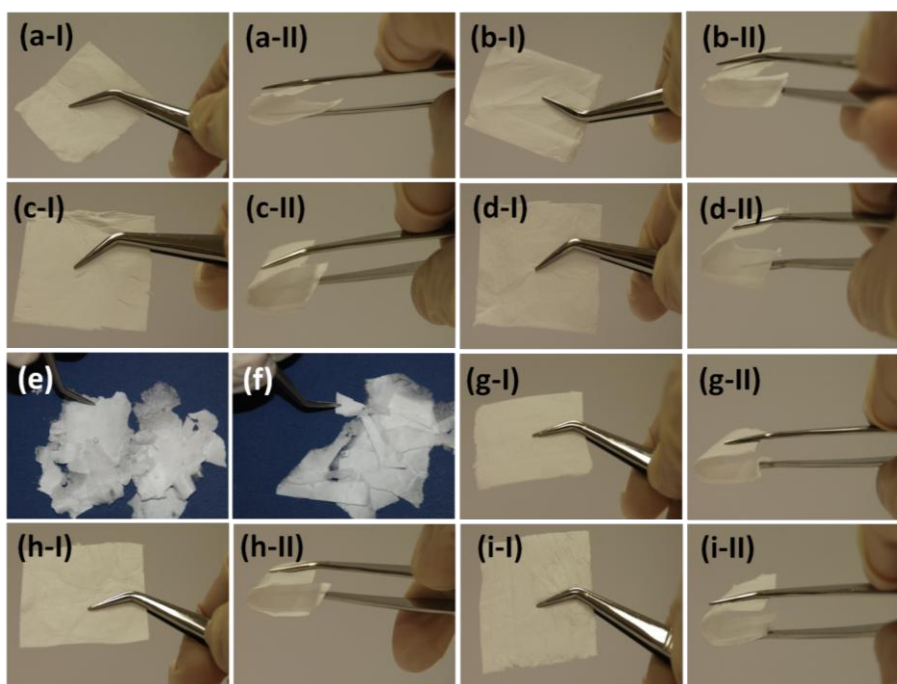


Figure 20. Nanowebs obtained from (a-I and II) 160% (w/v) HP β CD in water; (b-I and II) 120% (w/v) HP β CD in DMF; (c-I and II) 120% (w/v) HP β CD in DMAc; (d-I and II) 160% (w/v) HP γ CD in water; (e) 125% (w/v) HP γ CD in DMF; (f) 125% (w/v) HP γ CD in DMAc; (g-I and II) 160% (w/v) M β CD in water; (h-I and II) 160% (w/v) M β CD in DMF; and (i-I and II) 160% (w/v) M β CD in DMAc. (Copyright © 2012, Royal Society of Chemistry. Reprinted with permission from Ref.[130])

In this study, we were successful at producing polymer-free ultrafine fibers from three different CD derivatives; HP β CD, HP γ CD and M β CD in three different solvent systems, water, DMF and DMAc, via electrospinning. The success of the electrospinning of polymer-free fibers from these CD derivatives is due to the presence of considerable aggregates and intermolecular interactions between the CD

molecules in their concentrated solutions in which these aggregates and interactions can effectively stabilize the jet and therefore resulted in bead-free nanofibers when electrospun. The electrospinning of CD solutions containing urea yielded only beads or splashes instead of fibers since urea breaks the H-bonds between the CD molecules and therefore destroys the CD aggregates in their solutions. The optimization of the electrospinning of the bead-free nanofibers from HP β CD, HP γ CD and M β CD was carried out extensively in three different solvent systems (water, DMF and DMAc) by varying solution concentrations from 100% to 160% (w/v). We observed that the morphologies and the thickness of the electrospun fibers were highly dependent on the CD derivatives and the type of solvent system used. Only CD solutions having optimal concentration/viscosity and conductivity values were able to be electrospun into bead-free fibers. CD nanofibers electrospun from water solutions were much thinner when compared with the ones electrospun from DMF and DMAc solvent systems because of the low viscosity and high conductivity of the CD solutions in water. Micron-sized CD fibers were obtained in the case of the DMAc solvent system due to the high viscosity and very low conductivity of the solutions as well as the low evaporation rate of the solvent. Our results indicated that electrospinning of these CD is quite similar to polymeric systems where the high solution concentration/viscosity and high solution conductivity are very crucial for obtaining bead-free nanofibers from CD. The visual observations revealed that these CD nanowebs have some mechanical integrity and they can be easily handled and folded as a free standing web. Thus, these CD nanofibers/nanowebs would be particularly attractive due to the exclusive properties obtained by combining the very large surface area of nanofibers with specific functionality of the CD. As it is mentioned in the introduction part, CD already find application in a wide range of areas, so the electrospinning of these supramolecular structures into nanofibers can extend their use potential and enable the production of functional nanofibers with novelty.

4. Molecular Entrapment of Volatile Organic Compounds (VOCs) by Electrospun Modified Cyclodextrin Nanofibers

Volatile organic compounds (VOCs) are a wide group of organic molecules that are considered as one of the major sources of air pollution. VOCs are significantly emitted into air from industrial plants, vehicles, aircraft, perfumes, etc. [148, 149]. VOCs are well known with their highly toxic and carcinogenic features; therefore they can cause harmful impacts on human health and ecosystem. So it is essential to decrease the negative effect of VOCs by removing them from the environment [150]. As an efficient way, absorption\adsorption attract attention for the removal of VOCs from air. Active carbon is the commonly used material to reduce the VOCs degree in the surrounding due to its high surface area and porous structure [151-154]. However, the carbon based absorbents\adsorbents are generally applied in the powder or granular form and this creates challenges during their use [155]. For this reason, there are approaches in the literature including the formation of flexible nano-scaled matrix which were obtained with the incorporation of electrospinning technique [155-160].

Owing to their remarkable properties, electrospun nanofibers and their nanowebs are especially promising candidates to be used in membranes/filters and environmental applications [47, 48, 52, 53, 64, 161-163]. From this point of view, there are studies in the literature reporting that, the electrospun nanofibers were experienced as membrane system for VOCs filtration purposes. For instance, Scholten et al. firstly used the electrospun polyurethane fibers for the removal of VOCs [155]. In the study of Katepalli et al., VOC removing was achieved by using hierarchical fabric structures consisting of polyacrylonitrile (PAN) nanofibers electrospun on a mat of activated carbon microfibers [156]. In another study, Bai et al. prepared the activated carbon nanofibers (ACNFs) by electrospinning of PAN solutions, and subsequent steam activation process for VOCs filtration [157]. In another related study of the same group, reduced graphene oxide (RGO)/carbon composite ultrafine fibers were developed by using electrospinning and applying consequent carbonization to evaluate their VOCs adsorption performance [158]. One

of the associated studies, the fly ash particles were blended with polyurethane to produce composite electrospun membranes for the removal of VOCs [159]. In our very recent reports, electrospun poly (methyl methacrylate) (PMMA) nanofibers were functionalized with β -cyclodextrin (β -CD) molecules[56] and electrospun polyethylene terephthalate (PET) nanofibers were functionalized with three native CD types (α -CD, β -CD and γ -CD) to obtain promising nanofibrous webs for the entrapment of VOCs from environment [55].

Some molecules that CD form IC, can be hazardous and polluting chemicals, so CD are fairly useful for filtration/separation/purification areas [113, 164-167]. For this purpose, it can be considered that, CD have also potential for the elimination of VOCs from the environment [168, 169]. However, powder form and crosslinked polymeric granular form of CD cause some difficulties during their use. So, as an alternative approach we employed electrospun CD nanofibers for the removal of VOCs from the environment. As a matter of fact, CD nanofibers are definitely more applicable compared to powder form of CD.

For this reason, in the present study, we have chosen hydroxypropyl- β -cyclodextrin (HP β CD) and hydroxypropyl- γ -cyclodextrin (HP γ CD) nanofibers [130], to investigate the molecular filtration capability of electrospun CD nanofibers by entrapping VOCs (aniline and benzene) from the surrounding. Here, HP β CD and HP γ CD nanofibers were electrospun from two different solvent systems (water and DMF) in the large scale and these nanofibers were exposed to vapor of aniline and benzene. For comparison, the entrapment test was also performed for the powder form of HP β CD and HP γ CD. The morphological characteristics of the HP β CD nanofibers and HP γ CD nanofibers before and after the entrapment of VOCs and as-received powder were examined by scanning electron microscopy (SEM). Brunauer-Emmett-Teller (BET) surface area analyzer was used to measure the surface area of HP β CD and HP γ CD in powder form and nanofiber form. After exposing to VOCs vapor, the entrapped amount of VOCs by CD nanofibers and their powder were investigated by using proton nuclear magnetic resonance (^1H NMR) and high performance liquid chromatography (HPLC) techniques. Moreover,

thermogravimetric analyzer (TGA) was used to prove the inclusion complexation between CD and VOCs during the encapsulation.

4.1. Structural characterization of CD nanofibers

The electrospinning parameters for producing uniform nanofibers from HP β CD and HP γ CD by using water and DMF as solvent were reported in the experimental parts (see 2.2.1.) [130]. The representative SEM images of HP β CD and HP γ CD powder, HP β CD and HP γ CD nanofibers obtained from water and DMF at the required level of concentration for the production of bead-free electrospun nanofibers is illustrated in Figure 21. The SEM images of HP β CD/powder and HP γ CD/powder are given in Figure 21(a-i)-(b-i) and as it is observed, both of them have spherical morphology and the size of HP γ CD/powder beads indicate more homogenous distribution compared to HP β CD/powder beads. As it was determined from the previous study, the uniform HP β CD nanofibers were obtained at 160% (w/v) for water (Figure 21(a-ii)) and at 120% (w/v) for DMF (Figure 21(a-iii)). On the other hand, the bead-free HP γ CD nanofibers were produced at 160% (w/v) for water (Figure 21(b-ii)) and at 125% (w/v) for DMF (Figure 21(b-iii)) (Table 5). We have also observed that, the AFD values are not so different from the previous study determinations. While the AFDs of HP β CD/water-NF and HP β CD/DMF-NF were determined as 645 ± 350 nm and 1010 ± 410 nm respectively, they were calculated as 1320 ± 475 nm for HP γ CD/water-NF and 2755 ± 680 nm for HP γ CD/DMF-NF (Table 5). Both of HP β CD and HP γ CD nanofibers have thicker diameter when electrospun from DMF system as compared to water system. As explained in detail in our previous study (see 2.2.1.) [130], uniform CD nanofibers were obtained at lower concentration in DMF contrary to water system, in addition, HP γ CD nanofibers have thicker diameter compared to HP β CD nanofibers. HP γ CD solutions have higher viscosity and lower conductivity so its electrified jet is exposed to less stretching during electrospinning and yields thicker fibers compared to HP β CD solutions [1, 19, 130].

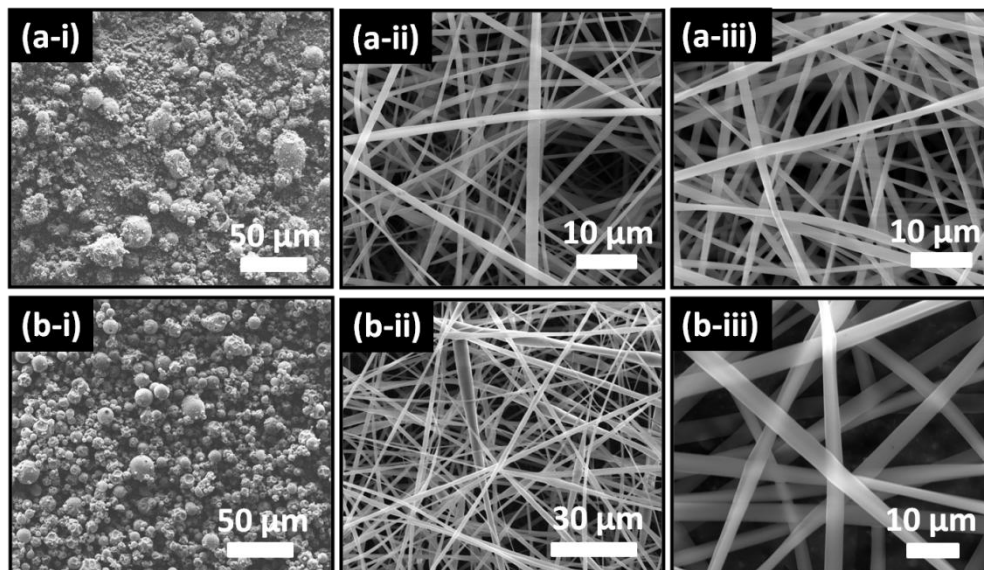


Figure 21. The representative SEM images of (a-i) HPβCD/powder, (a-ii) HPβCD/water-NF, (a-iii) HPβCD/DMF-NF, (b-i) HPγCD/powder, (b-ii) HPγCD/water-NF and (b-iii) HPγCD/DMF-NF.

Table 5. The characteristics of CD solutions, average fiber diameter, fiber diameter range and surface area of CD nanofibers and CD powder.

Sample	Solvent	%CD (w/v)	Average fiber diameter (nm) (Fiber diameter range(nm))	Surface area (m ² /g)
HPβCD/powder	-	-	-	1.88
HPβCD/water-NF	water	160	645±350 nm (230-1650)	3.16
HPβCD/DMF-NF	DMF	120	1010±410 nm (530-1925)	3.83
HPγCD/powder	-	-	-	2.21
HPγCD/water-NF	water	160	1320±475 nm (450-2050)	2.27
HPγCD/DMF-NF	DMF	125	2755±680 nm (1120-5900)	3.48

Here, we have investigated the surface area of CD nanofibers (HPβCD and HPγCD) and their as-received powder forms by BET analysis (Table 5). The multipoint BET surface area for powder form of HPβCD and HPγCD were calculated as 1.88 m²/g and 2.21 m²/g, respectively. The obtained values are compatible with these given in the literature [170, 171]. As a result of electrospinning process, the surface areas were determined as 3.16 m²/g for HPβCD/water-NF and 3.83 m²/g for HPβCD/DMF-NF. For HPγCD/water-NF and HPγCD/DMF-NF, the surface areas were calculated as 2.27 m²/g and 3.48 m²/g,

respectively. So, it is evident that, electrospinning of CD into fiber form resulted in higher surface area when compared to powder form of CD. As it is clear from the SEM images, the CD powder consist of spherical beads in the size of microns down to sub-micron which leads to high surface area as well. Hence, in the case of HP γ CD, only a slight difference was observed between the surface area of powder and nanofibers forms. In addition, there are slight changes at the surface areas of CD nanofibers depending on the CD types and the electrospinning solvent types.

4.2. VOCs entrapment capability of CD nanofibers and CD powder

Due to their relatively hydrophobic cavity, CD are capable of forming IC with variety of organic molecules and thus, CD can be effective for the removal of hazardous molecules from the surroundings [113, 164-167]. In our previous studies, we have demonstrated that CD functionalized polymeric nanofibers can be potentially used as molecular filters for the air and water filtration by removing organic molecules from the required environment [48, 54-57]. The integration of polymeric nanofibers with CD facilitates the enhanced entrapment property of nanofibrous webs owing to their complexation capability of CD molecules, located on the fiber surface [48, 54-57]. Here, the molecular filtration capability of polymer-free HP β CD and HP γ CD nanofibers was investigated by using aniline and benzene as model VOCs which are known to form IC with CD [172-174]. For this reason, HP β CD and HP γ CD nanofibers and their as-received powder form were placed in a desiccators which were saturated with aniline or benzene vapor (Figure 22). After exposure to VOCs vapor, the analyses of the CD nanofibers and CD powder were performed by using ^1H NMR, HPLC and TGA to confirm the existence of organic molecules in nanofibers and the inclusion complexation of these VOCs with CD. We have also investigated the morphological stability of these CD nanofibers by using SEM and the results confirmed that the CD nanofibers kept their fiber structure during the entrapment test (Figure 23).

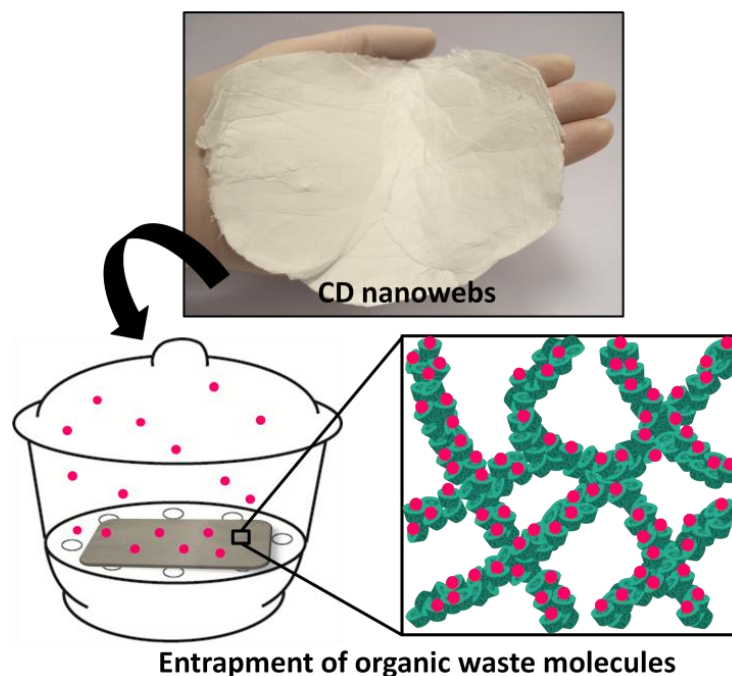


Figure 22. The photograph of HP β CD nanofibrous web and the schematic view of the molecular entrapment test.

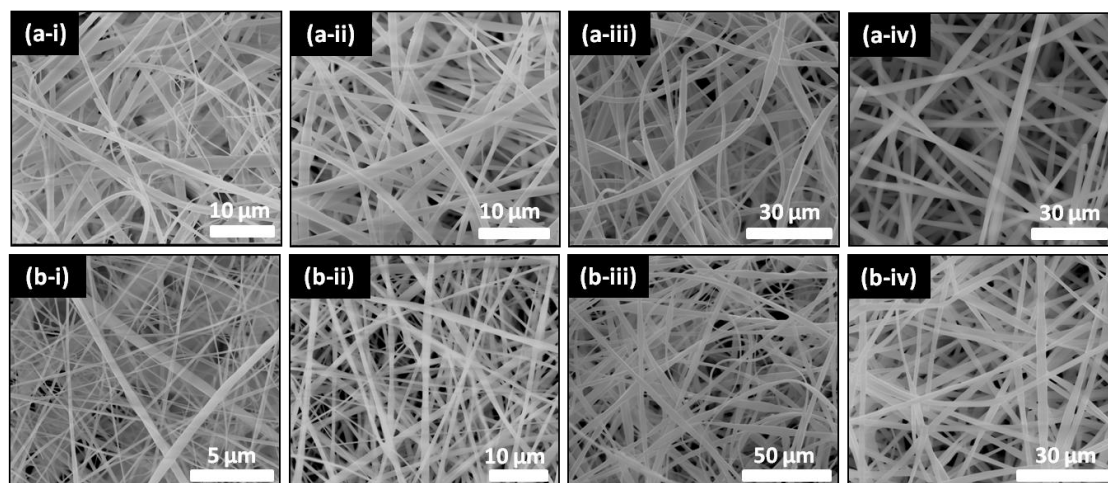


Figure 23. The representative SEM images of (a) aniline and (b) benzene exposed (i) HP β CD/water-NF, (ii) HP β CD/DMF-NF, (iii) HP γ CD/water-NF, (iv) HP γ CD/DMF-NF after entrapment test.

^1H NMR study was performed to determine the entrapped amount of VOCs by calculating the molar ratios of organic molecules (aniline and benzene) to CD (HP β CD and HP γ CD). Table 6 summarizes the average results which were obtained by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to VOCs and CD (Figure 24). The molar ratios were calculated by taking account the

integration of aniline and benzene aromatic peaks and the CD's characteristic peak at about 1 ppm. For CD molecules, the chemical shift (δ) (1 ppm) that was used for calculation corresponds to the CH_3 of hydroxypropyl- groups and the number of H belong this part was determined by using molar substitution of hydroxypropyl as 0.6 for both CD types. For aniline entrapment, it was observed that the molar ratio of aniline respect to $\text{HP}\beta\text{CD}$ (aniline:CD) is higher for $\text{HP}\beta\text{CD}/\text{DMF-NF}$ (1.38:1) compared to $\text{HP}\beta\text{CD}/\text{water-NF}$ (0.68:1) and it is lowest for $\text{HP}\beta\text{CD}/\text{powder}$ (0.32:1). The same trend was also obtained for $\text{HP}\gamma\text{CD}$ samples and the entrapped amount of aniline was calculated in the order of $\text{HP}\gamma\text{CD}/\text{DMF-NF}$ (0.25:1) > $\text{HP}\gamma\text{CD}/\text{water-NF}$ (0.15:1) > $\text{HP}\gamma\text{CD}/\text{powder}$ (0.09:1). As evident from our results, $\text{HP}\beta\text{CD}$ based samples encapsulated more amount of aniline compared to $\text{HP}\gamma\text{CD}$ based samples (Table 6). The possible reason would be bigger cavity size of $\text{HP}\gamma\text{CD}$ which leads to less stable interaction during the inclusion complexation, hence, less amount of aniline was possibly preserved in the $\text{HP}\gamma\text{CD}$ due to size mismatch between $\text{HP}\gamma\text{CD}$ cavity and aniline molecule. In the case of benzene entrapment, the molar ratios significantly decreased, that indicates the lower entrapping efficiency of samples compared to aniline exposed samples (Table 6). This situation can be originated from the weaker specific local interaction between benzene and CD molecules. For $\text{HP}\beta\text{CD}$ based samples, the entrapping efficiency is in the order of $\text{HP}\beta\text{CD}/\text{DMF-NF}$ (0.38:1) > $\text{HP}\beta\text{CD}/\text{water-NF}$ (0.18:1) > $\text{HP}\beta\text{CD}/\text{powder}$ (0.10:1), having a similar trend with aniline treatment. For $\text{HP}\gamma\text{CD}$ based samples, distinctive reduction was observed for the entrapped amount of benzene which was possibly originated from the improper size match between $\text{HP}\gamma\text{CD}$ cavity and benzene molecule. After all, similar to aniline test, $\text{HP}\gamma\text{CD}/\text{DMF-NF}$ (0.06:1) entrapped higher amount of benzene from the environment compared to $\text{HP}\gamma\text{CD}/\text{water-NF}$ (0.03:1), and $\text{HP}\gamma\text{CD}/\text{powder}$ (0.02:1) displayed the lowest entrapment efficiency among other samples. In short, CD nanofibers have shown higher amount of VOCs entrapment when compared to their powder form and this is possibly due to the higher surface area. Yet, high surface area may not be the only factor for the enhanced entrapment efficiency. For instance, CD nanofibers produced from DMF solvent system have shown higher amount of VOCs entrapment and this might be originated from the

higher accessibility and availability of CD cavity to entrap VOCs from the environment.

Table 6. The molar ratio values of VOC:CD calculated from ^1H NMR measurements. (n:3, std dev: ± 0.00).

VOC:CD	CD/powder	CD/water-NF	CD/DMF-NF
Aniline:HP β CD	0.32:1	0.68:1	1.38:1
Aniline:HP γ CD	0.09:1	0.15:1	0.25:1
Benzene:HP β CD	0.10:1	0.18:1	0.38:1
Benzene:HP γ CD	0.02:1	0.03:1	0.06:1

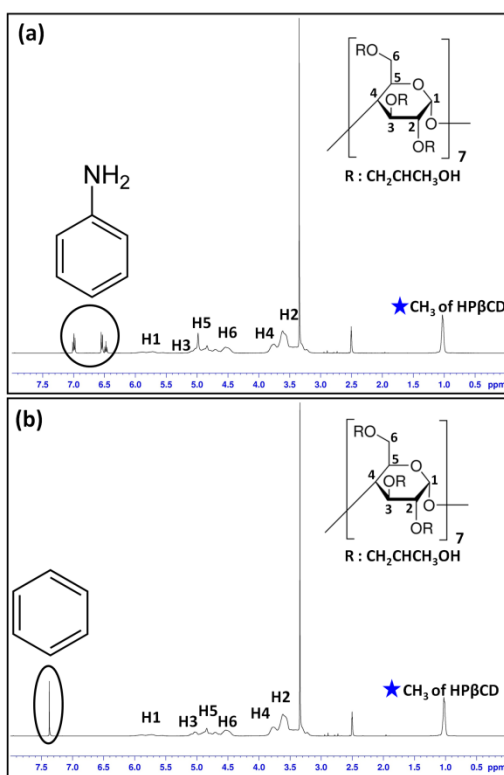


Figure 24. Representative ^1H NMR spectra of (a) aniline and (b) benzene exposed HP β CD/DMF-NF which were taken in d_6 -DMSO.

The entrapment performance of CD nanofibers was also tested by HPLC measurements. After exposure to aniline and benzene vapor, nanofibers were dissolved in water and water/ACN, respectively to perform chromatographic measurements. The HPLC analyses were performed three times for each of the sample. Figure 25 summarized the HPLC results which were taken for water and

DMF based samples of HP β CD and HP γ CD nanofibers, and as well their powder forms. The results were calculated in terms of ppm by adapting to calibration curve as a function of concentration of aniline and benzene. The HPLC results, given in terms of concentration (Figure 25), were also calculated as molar ratios (VOCs:CD). Table 7 depicts the molar ratio values which were converted from the HPLC results. When HPLC results were compared with ^1H NMR, it was found that, the molar ratios are not exactly same with each other, however, the values are close to each other and they follow a similar trend. We have noticed from the graph that, HP β CD nanofibers and powder can encapsulate higher amount of VOCs from the environment compared to HP γ CD nanofibers and powder. This was probably originated from the bigger cavity of HP γ CD, that is, size mismatch and weaker interaction between HP γ CD cavity and VOCs (aniline and benzene) for the encapsulation. When the HP β CD and HP γ CD based samples were compared, the entrapped amount of aniline and benzene were on the order of DMF > water > powder for both CD types which was also consistent with the ^1H NMR measurements. Moreover, aniline molecules can be more efficiently removed from the environment compared to benzene molecules by CD nanofibers and their powder.

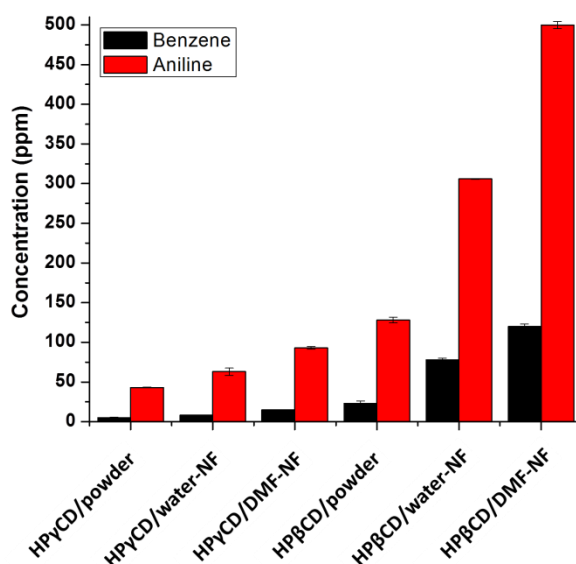


Figure 25. The summary of HPLC results showing the amount of aniline and benzene entrapped by HP β CD/powder, HP β CD/water-NF, HP β CD/DMF-NF, HP γ CD/powder, HP γ CD/water-NF and HP γ CD/DMF-NF.

Table 7. The molar ratio values of VOC:CD calculated from HPLC measurements. (n:3, std dev: ± 0.00).

VOC:CD	CD/powder	CD/water-NF	CD/DMF-NF
Aniline:HP β CD	0.40:1	0.97:1	1.67:1
Aniline:HP γ CD	0.14:1	0.21:1	0.32:1
Benzene:HP β CD	0.08:1	0.28:1	0.44:1
Benzene:HP γ CD	0.02:1	0.03:1	0.06:1

In order to confirm the complexation between CD molecules and VOCs, TGA was performed for CD nanofibers and their powder after exposed to aniline and benzene vapor. When the volatile organic molecules are encapsulated in CD cavities, the thermal decomposition/evaporation of the guest molecules shifts to higher temperature owing to the interaction between CD cavity. The TGA thermograms of all samples and pure aniline were shown in Figure 26. The major weight loss is observed at about 350 °C belongs to the thermal degradation of CD molecules and the initial weight loss for untreated samples correspond to water content in CD samples. In addition, it was observed that the pristine CD nanofibers produced from DMF have shown slight weight loss till 180 °C possible due to the remaining solvent residue after electrospinning process. For aniline, the inception point of thermal evaporation is interfered with water, so it was evaluated according to the temperature at which the evaporation came to an end (Figure 26(a-b)). While the evaporation of pure aniline occurs below 100 °C, it evolved close to 200 °C for the CD nanofibers and powder exposed to aniline vapor. In addition, for both HP β CD and HP γ CD samples, the % weight loss were increased in the order of powder < water < DMF which was consistent with quantitative results of ^1H NMR and HPLC measurements. In the case of pure benzene, we could not able to record the TGA data due to its extremely high volatility. The expected % weight loss was also observed for benzene exposed samples in the order of powder < water < DMF. However, in TGA thermograms of benzene exposed HP β CD and HP γ CD powder (Figure 26(c(i)-d(i))), the initial weight loss are observed at lower level compared to pristine samples. As it was mentioned above, the initial weight loss step of untreated CD samples is

originated due to water content present in the CD samples. Once the benzene was entrapped, the water molecules were replaced with benzene molecules, but the entrapped benzene amount was lower than the water content in powder CD samples. After all, we have determined that, the benzene exposed samples showed identical trend, and the evaporation of benzene was observed up to 150 °C (Figure 26(c-d)). It is clear that, the thermal decomposition/evaporation of aniline and benzene occurred at much higher temperature when compared to their pure form, suggesting that aniline and benzene molecules were encapsulated in CD cavity by inclusion complexation.

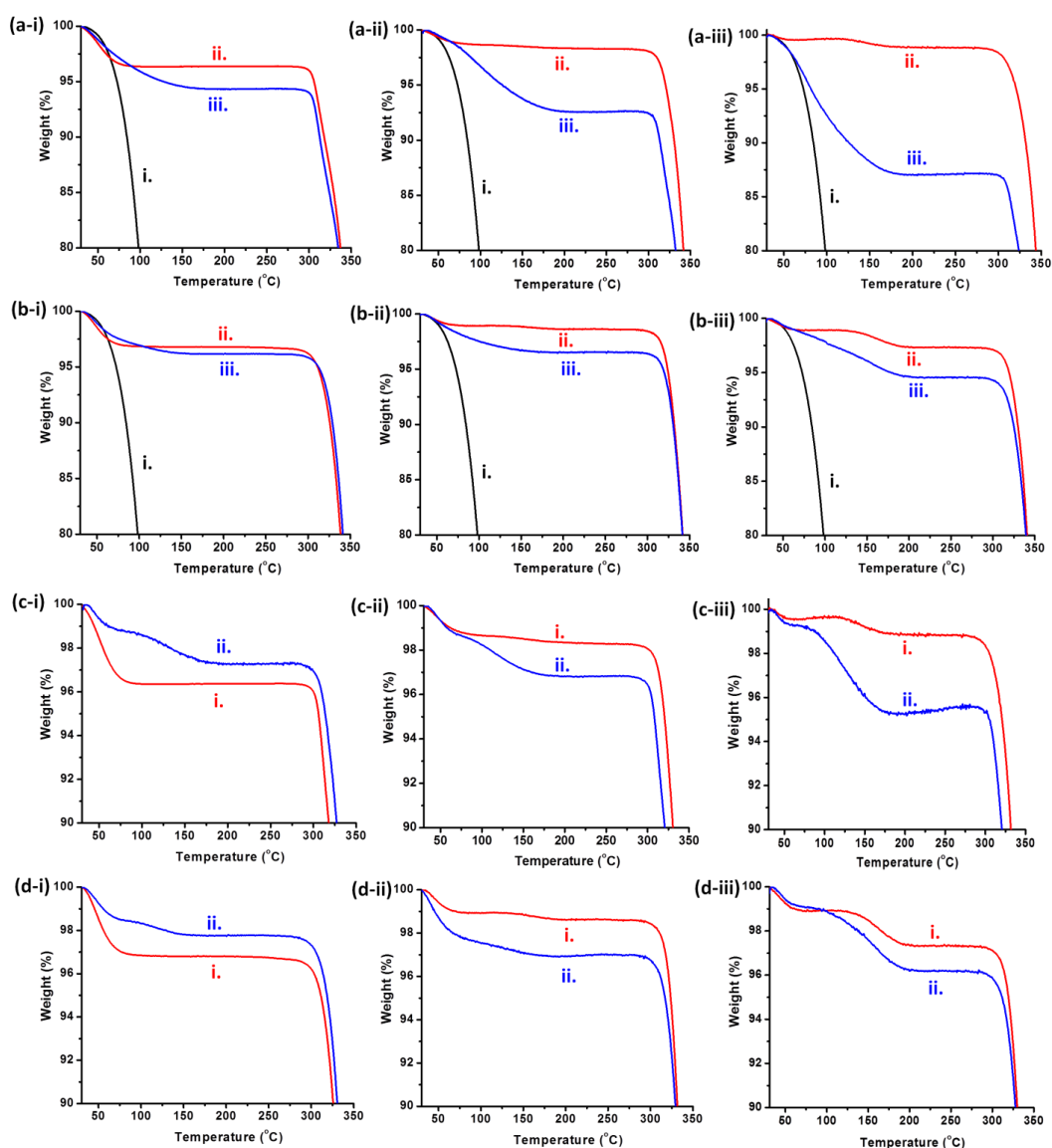


Figure 26. The TGA thermograms of (a-i) (i) pure aniline, (ii) HP β CD/powder, (iii) aniline exposed HP β CD/powder; (a-ii) (i) pure aniline, (ii) HP β CD/water-NF, (iii) aniline exposed HP β CD/water-NF; (a-iii) (i) pure aniline, (ii) HP β CD/DMF-NF, (iii) aniline exposed HP β CD/DMF-NF; (b-i) (i) pure aniline, (ii) HP γ CD/powder, (iii) aniline exposed HP γ CD/powder; (b-ii) (i) pure aniline, (ii) HP γ CD/water-NF, (iii) aniline exposed HP γ CD/water-NF; (b-iii) (i) pure aniline, (ii) HP γ CD/DMF-NF, (iii) aniline exposed HP γ CD/DMF-NF; (c-i) (i) HP β CD/powder, (ii) benzene exposed HP β CD/powder; (c-ii) (i) HP β CD/water-NF, (ii) benzene exposed HP β CD/water-NF; (c-iii) (i) HP β CD/DMF-NF, (ii) benzene exposed HP β CD/DMF-NF; (d-i) (i) HP γ CD/powder, (ii) benzene exposed HP γ CD/powder; (d-ii) (i) HP γ CD/water-NF, (ii) benzene exposed HP γ CD/water-NF; (d-iii) (i) HP γ CD/DMF-NF, (ii) benzene exposed HP γ CD/DMF-NF.

The HP β CD nanofibers and HP γ CD nanofibers which were successfully obtained from DMF and water solvent systems were selected for the determination of molecular filtration performance of CD nanofibers. The molecular entrapment performance of CD nanofibers and their powder forms were investigated by exposing them to VOCs; aniline and benzene vapor. We have observed that, CD nanofibers can entrap higher amount of VOCs from the surroundings compared to their powder forms, in addition, the entrapment efficiency was highly dependent on the CD type (HP β CD and HP γ CD) and VOCs type (aniline and benzene). The BET analysis showed that, the nanofibers have higher surface area compared to their powder forms. So the effective entrapment of VOCs by CD nanofibers may be originated from the higher surface area of nanofibers and the higher accessibility and availability of CD cavity to entrap VOCs. Here, we modified CD powder into more applicable nanofibrous form which can be readily used as filtering material for the entrapment of VOCs. In brief, electrospun CD nanofibers would be very attractive for air filtration applications due to their highly porous structure and high surface area as well as their molecular entrapment capability of VOCs by inclusion complexation.

5. Electrospinning of Polymer-free Nanofibers from Native Cyclodextrins (α -CD, β -CD and γ -CD)

As it is mentioned previously, CD are generally used in the form of powder or crosslinked polymeric granules that create restriction during their applications [90, 91, 94, 107, 108, 113]. In our pioneer previous studies, we represented a handy solution to this challenge by producing polymer-free nanofibers from three different chemically modified CD: hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD), and methyl- β -cyclodextrin (M β CD) [129, 130]. The modified CD have very high solubility when compared to native CD (α -CD, β -CD, and γ -CD); therefore, the preparation of highly concentrated modified CD solutions in water or polar organic solvents was possible, and the electrospinning of nanofibers from these solutions were successful. However, the electrospinning of native CD still remains a challenge due to their low solubility when compared to that of chemically modified CD. Native CD are soluble in water, yet, their solubility is rather limited due to the presence of intramolecular H-bonding within the CD molecule, which prevents the formation of H-bond with surrounding water molecules [93, 95]. Nevertheless, in this study, we were able to obtain highly concentrated homogeneous solutions of α -CD (120% up to 160%, w/v) and β -CD (120% up to 150%, w/v) by using 10% (w/v) NaOH aqueous solvent system, as well as, γ -CD (120% up to 140%, w/v) by using dimethyl sulfoxide (DMSO)/water (50/50 ratio, v/v) solvent mixture [131, 132]. Our efforts on electrospinning of nanofibers from native CD without using any carrier polymer matrix were quite successful by using these highly concentrated CD solutions. The morphological characterizations of nanofibers were performed by scanning electron microscope (SEM), beside the detailed investigations were carried out by rheology, dynamic light scattering (DLS), transmission electron microscope (TEM), high resolution transmission electron microscope (HR-TEM) and X-ray diffractometer (XRD) measurements. The electrospinning of γ -CD nanofibers was successfully achieved in the large amount. So, we have also studied the molecular entrapment capability of γ -CD nanofibers by capturing the toxic volatile organic molecules (VOCs) (aniline and toluene) from the surrounding and compared with its

powder form [132]. Moreover, we carried out the Brunauer-Emmett-Teller (BET) surface area analyses to investigate and compare the surface areas of γ -CD powder and γ -CD nanofibers.

5.1. Electrospinning of nanofibers from native CD (α -CD, β -CD and γ -CD)

Highly concentrated α -CD (120% up to 160%, w/v) and β -CD (120% up to 150%, w/v) solutions were prepared by dissolving the CD in 10% (w/v) NaOH aqueous solution. On the other hand, the electrospinning solutions were obtained by dissolving γ -CD in DMSO/water (50:50 ratio, v/v) solvent mixture at the concentration range of 120% (w/v) up to 140% (w/v). The characteristics of the CD solutions, the morphology and the average fiber diameters of the electrospun CD nanofibers are summarized in Table 8. The SEM images of the electrospun CD (α -CD, β -CD and γ -CD) nanofibers produced from different solution concentrations are depicted in Figure 27, 28 and 29. The electrospinning of CD solutions resulted in different average fiber diameters and morphologies depending on the CD type and CD solution concentrations. We observed that the electrospinning of native CD is quite similar to polymeric systems in which the solvent type, the solution concentration/viscosity, and the solution conductivity played a key role for the electrospinnability of CD nanofibers. That is, only the CD solutions having optimal concentration/viscosity and conductivity values were able to be electrospun into uniform nanofibers without any bead structure. In addition, we observed that the morphology and the diameter of the resulting electrospun nanofibers significantly vary with the type of CD since the viscosity and conductivity of the solutions were different from each other. In our previous studies, similar findings were also observed in the case of electrospinning of chemically modified CD (HP β CD, HP γ CD, and M β CD) [130].

Table 8. The characteristics of CD solutions (DLS measurements of α -CD and β -CD solutions at 25 °C summarizing the average diameter (nm) and polydispersity index (PDI) of CD aggregates), average fiber diameter, fiber diameter range and fiber morphology of the electrospun CD nanofibers. (Copyright © 2013, Elsevier. Reproduced with permission from Ref.[131] and Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[132])

Solutions	Viscosity (Pa•s)	Conductivity (mS/cm)	Intensity -average diameter /d (nm) - PDI	Average fiber diameter (fiber diameter range) (nm)	Fiber morphology
120% α -CD	0.16	14.33	5.50 / 0.55	-	Bead structures
130% α -CD	0.20	11.22	6.04/ 0.47	-	Bead structures with few fiber formation
140% α -CD	0.26	9.06	6.38/ 0.40	-	Bead structures with fiber formation
150% α -CD	0.32	7.42	7.30/ 0.70	180±80 (50-560)	Beaded nanofibers
160% α -CD	0.43	5.93	8.29/ 0.48	375±150 (80-940)	Bead-free nanofibers
160% α -CD + 20% urea	0.33	4.42	6.04/ 0.81	-	Bead structures with few fiber formation
120% β -CD	0.13	12.05	4.98/ 0.36	-	Bead structures
130% β -CD	0.16	9.77	5.14/ 0.53	-	Bead structures with fiber formation
140% β -CD	0.24	8.21	5.27/ 0.46	175±70 (90-420)	Beaded nanofibers
150% β -CD	0.33	7.25	5.96/ 0.43	220±90 (90-460)	Bead-free nanofibers
150% β -CD + 20% urea	0.15	5.53	4.91/ 0.92	-	Bead structures
120% γ -CD	0.55	2.23*	-	-	Bead structures
130% γ -CD	0.78	2.20*	-	-	Beaded nano and micro fibers
140% γ -CD	1.15	1.68*	-	1155±515 (200-2900)	Bead-free nano and micro fibers
140% γ -CD + 20% urea	0.52	2.45*	-	-	No fiber formation, only splashes

* conductivity unit is μ S/cm

For α -CD, vastly beaded structure along with very few nanofiber structures was obtained when 120% (w/v) α -CD solution was electrospun (Figure 27(a)). The bead structures were gradually eliminated as the α -CD concentration was increased from 120% through 140% (w/v) (Figure 27(b-c)), and nanofibers having very few

beads were obtained at 150% (w/v) concentration (Figure 27(d)). Finally, bead-free and uniform α -CD nanofibers (Figure 27(e)) having fiber diameter in the range of 80-940 nm (Figure 27(g)) with an average fiber diameter (AFD) of 375 ± 150 nm were produced from the electrospinning of 160% (w/v) α -CD solution. Likewise, we have also optimized the electrospinning of modified CD (HP β CD, HP γ CD, and M β CD) in water at 160% (w/v) CD concentration for obtaining bead-free nanofibers in our previously study [130]. The bead structures at lower concentrations were due to the low solution viscosity and the presence of inadequate amount of α -CD aggregates, and therefore, mostly beads were formed instead of fully stretched fibers. This is because of the destabilization of the electrified jet during the electrospinning process. Bead-free nanofibers were obtained from 160% (w/v) α -CD, suggesting that this is the optimal concentration where the solution viscosity and the amount and the size of the CD aggregates were sufficient for the electrospinning of bead-free and uniform nanofiber. This finding is very similar to electrospinning of polymeric systems in which low concentration of polymer solution yielded beaded fiber structure due to the lack of polymer chain entanglements and overlapping, and mostly higher polymer concentrations are required for uniform fiber formation [1, 2, 19]. The DLS and rheology measurements (Figure 30 and 31) indicated that as the concentration of α -CD increased from 120% through 160% (w/v), the solution became more viscous and considerable amount of CD aggregates was formed, and therefore, bead-free α -CD nanofibers were successfully obtained.

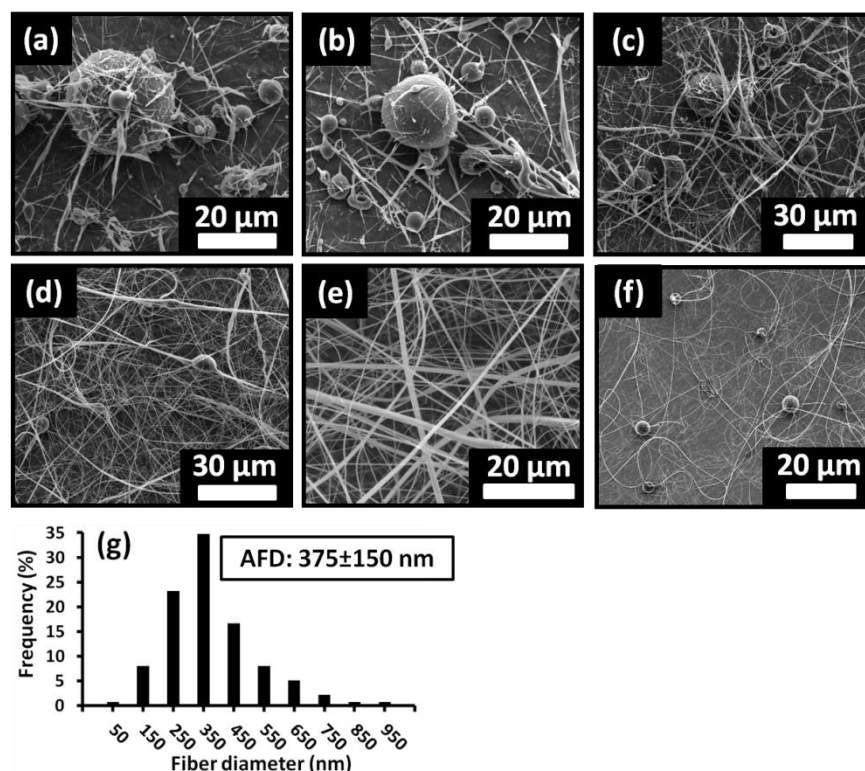


Figure 27. The representative SEM images of α -CD nanofibers obtained from 10% (w/v) NaOH aqueous solution at (a) 120% (w/v), (b) 130% (w/v), (c) 140% (w/v), (d) 150% (w/v), (e) 160% (w/v) α -CD concentrations and (f) the SEM image of bead structures with few fiber formation as a results of adding 20% (w/w) urea to the 160% (w/v) α -CD solution. (g) Fiber diameter distribution of electrospun nanofibers produced from 160% (w/v) α -CD concentration. (Copyright © 2013, Elsevier. Reprinted with permission from Ref.[131])

Similarly, the electrospinning of β -CD solutions at low concentration (120% through 140%, w/v) yielded beaded nanofibers (Figure 28(a–c)), but bead-free uniform β -CD nanofibers were achieved from the electrospinning of 150% (w/v) β -CD solution (Figure 28(d)). The nanofiber electrospun from 150% (w/v) β -CD solution has AFD of 220 $\pm$ 90 nm and the fiber diameter was in the range of 90–460 nm (Figure 28(f)). In the case of γ -CD, at 120% (w/v) γ -CD solution, highly beaded structure along with very few nanofiber structures was obtained (Figure 29(a)). When the concentration was increased to 130% (w/v), the nanofibers having few beads were observed (Figure 29(b)). Finally, the beads were eliminated for 140% (w/v) concentration and uniform nanofibers having AFD of 1155 $\pm$ 515 nm in the range 200–2900 nm were produced (Figure 29(c–d)). We have shown that the morphologies and the diameters of the electrospun CD fibers were very much

dependent on the CD type, CD concentration, and solvent type since the aggregation; viscosity, viscoelastic properties, and the solution conductivity were varied for each CD system. Here, it was also evident that electrospinning of native CD was similar to chemically modified CD where the fiber morphologies and the diameters were vary depending on the CD type and CD concentration. The optimal concentration for obtaining bead-free nanofibers was found as 160%, 150% and 140% for α -CD, β -CD and γ -CD, respectively. In this study, urea was added (20% (w/w) with respect to optimized concentration of native CD solutions and this caused significant decrease in the viscosity and aggregate size (Table 8), hence only beaded fibers, beads or splashes were observed instead of fiber formation (Figures 27(f), 28(e) and 29(d)). Since urea can interrupts the H-bonds between CD molecules [138, 146] and reduces the intermolecular interactions that ensure the self-association, aggregation and therefore disrupt the fiber formation during the electrospinning.

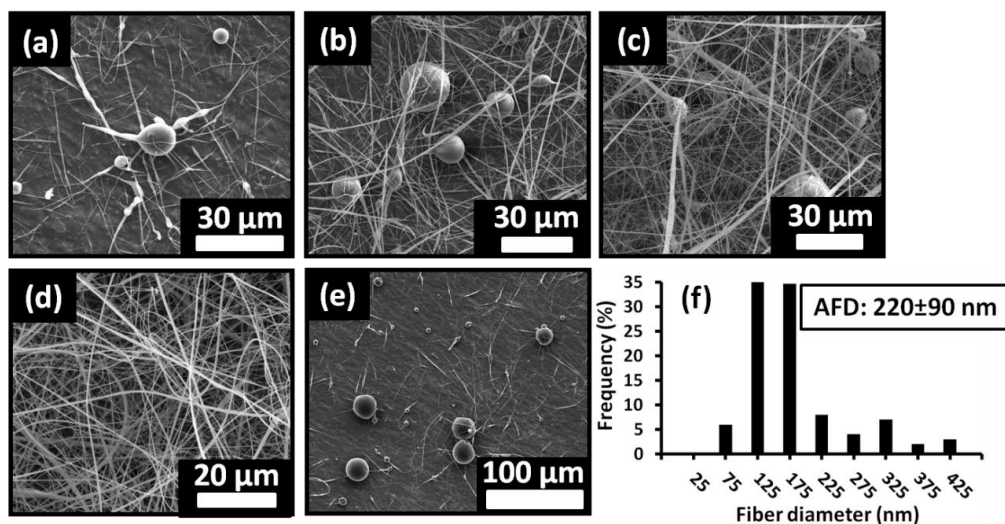


Figure 28. The representative SEM images of β -CD nanofibers obtained from 10% (w/v) NaOH aqueous solution at (a) 120% (w/v), (b) 130% (w/v), (c) 140% (w/v), (d) 150% (w/v) β -CD concentrations and (e) the SEM image of bead structures as a results of adding 20% (w/w) urea to the 150% (w/v) β -CD solution. (f) Fiber diameter distribution of electrospun nanofibers produced from 150% (w/v) β -CD concentration. (Copyright © 2013, Elsevier. Reprinted with permission from Ref.[131])

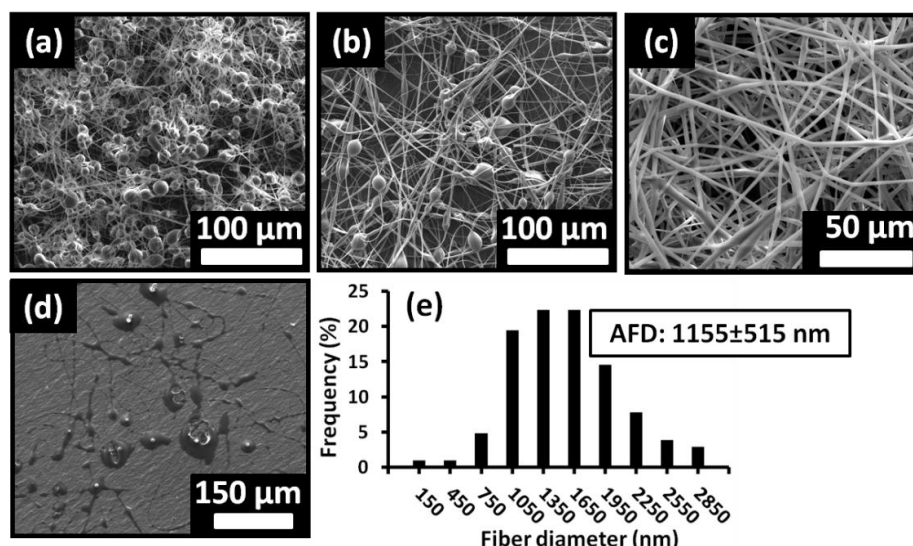


Figure 29. The representative SEM images of γ -CD nanofibers obtained from DMSO/water (50/50 ratio, v/v) solvent mixture at (a) 120% (w/v), (b) 130% (w/v), (c) 140% (w/v) γ -CD concentrations and (d) the representative SEM image of splashed area as a results of adding 20% (w/w) urea to the 140% (w/v) γ -CD solution. (e) Fiber diameter distribution of electrospun nanofibers produced from 140% (w/v) γ -CD concentration. (Copyright © 2013, Elsevier. Reprinted with permission from Ref.[131])

5.2. CD aggregation and rheology of CD solutions

The DLS measurements were performed in order to investigate the aggregation of CD in their highly concentrated solutions. The size distribution of CD aggregates measured by DLS for α -CD and β -CD solutions is given in Figure 30, and the data are summarized in Table 8. However, because of the yellowish color of γ -CD solution we could not manage to carry out the DLS measurements. The results of DLS elucidated the presence of self-aggregated α -CD molecules in their concentrated solutions (Figure 30(a) and Table 8). The size of the α -CD aggregates increased from 5.5 nm to 8.29 nm as the concentration was increased from 120% to 160% (w/v). The size of the aggregates decreased from 8.29 nm to 6.04 nm for the urea-added 160% (w/v) α -CD solution confirming the depletion of the α -CD aggregates with the addition of urea. In the case of β -CD, the aggregate size was increased from 4.98 nm to 5.96 nm as the β -CD concentration was increased from 120% to 150% (w/v) (Table 8 and Figure 30(b)). The size of the α -CD aggregates was slightly bigger than the size of the β -CD aggregates in the same solution concentration. The DLS and

viscosity data are in good agreement with each other, and slight higher viscosity values were recorded for α -CD solutions when compared to β -CD solutions owing to the higher amount of CD aggregates and their growing sizes as the concentration of the CD increased in the solution. In brief, the DLS measurements confirmed that the CD molecules form substantial amount of aggregates in their high concentrations, and this resulted in full stretching of electrified jet yielding bead-free uniform fiber formation without using any polymeric carrier.

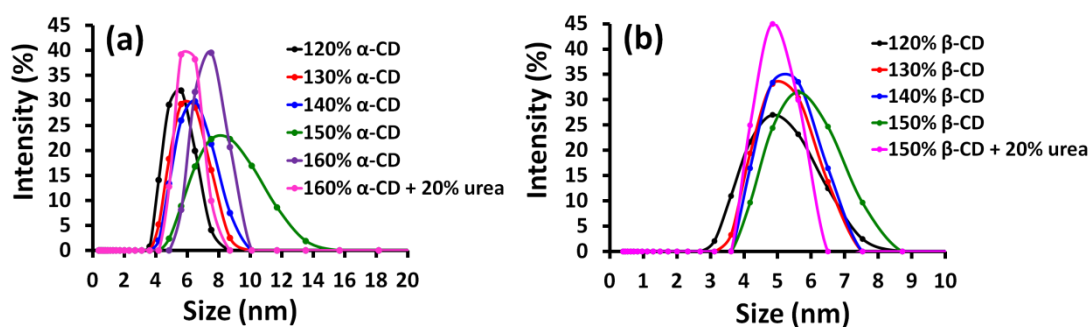


Figure 30. Size distribution of (a) α -CD aggregates for 120%, 130%, 140%, 150%, 160% (w/v) α -CD and 20% (w/w) urea-added 160% (w/v) α -CD in 10% (w/v) NaOH aqueous solution; (b) 120%, 130%, 140%, 150% (w/v) β -CD and 20% (w/w) urea-added 150% (w/v) β -CD in 10% (w/v) NaOH aqueous solution. (Copyright © 2013, Elsevier. Reprinted with permission from Ref.[131])

The rheological properties of CD solutions were examined by performing shear rate sweep viscosity and frequency sweep oscillation tests. Both of these tests were run for CD solutions having 120% (w/v) concentration up to the optimal concentration level (160%, 150% and 140% (w/v) for α -CD, β -CD and γ -CD, respectively) in which the bead-free nanofibers were obtained. The viscosity of CD solutions as a function of shear rate was displayed in Figure 31. It was observed that the viscosity of CD solution for the same concentration was being independent of shear rate indicating that the CD systems show characteristic of a Newtonian fluid. In addition, the solution viscosity of CD increases with the increasing CD concentration due to the presence of higher number of aggregates and their growing sizes. While the viscosity of 120% (w/v) α -CD solution was measured as 0.16 Pa•s, it reached to 0.43 Pa•s for the 160% (w/v) α -CD. The viscosity of β -CD solution was increased from 0.13 Pa•s (120%, w/v) to 0.33 Pa•s (150%, w/v) and the viscosity of γ -CD

solution at 120% (w/v) increased from 0.55 Pa•s to 1.15 Pa•s for 140% (w/v). As mentioned previously, the addition of urea reduces H-bonding between CD molecules and therefore disturbs the CD aggregation [138, 146]. As it is observed the viscosity levels of the α -CD and β -CD solutions were very similar and therefore fiber diameters close to each other were obtained, yet, β -CD nanofibers were somewhat thinner than the α -CD nanofibers since β -CD solution has lower concentration/viscosity and high conductivity values and therefore the electrified jet was subjected to more stretching during the electrospinning process [1, 2]. In the case of γ -CD, nano and micron sized fibers were obtained due to the higher viscosity and very low conductivity of the solutions. These findings elucidated that electrospinning of CD is quite similar to polymeric systems where the high solution concentration/viscosity is crucial for producing bead-free nanofibers from CD. Here, the addition of 20% (w/w) urea (with respect to CD) to the optimized concentrations of CD caused significant decline in their viscosity levels. The viscosity of the CD solutions was decreased from 0.43 Pa•s to 0.33 Pa•s; 0.33 Pa•s to 0.15 Pa•s and 1.15 Pa•s to 0.52 Pa•s for α -CD, β -CD and γ -CD, respectively (Table 8). Similarly, the size of the CD aggregates measured by DLS was decreased from 8.29 nm to 6.04 nm and 5.96 nm to 4.91 nm for α -CD and β -CD solutions containing urea, respectively. SEM images (Figures 27(f), 28(e) and 29(d)) clearly showed that the electrospinnability of CD solutions was significantly affected with the addition of urea. Beads along with few fiber structures and splashes were obtained from the electrospinning of urea-containing α -CD, β -CD and γ -CD solutions (Figures 27(f), 28(e) and 29(d)). It was also worth mentioning that the electrospinning of fibers from urea-containing CD solutions became much difficult since the jet breakup observed very frequently and much less fibers were deposited on the collector.

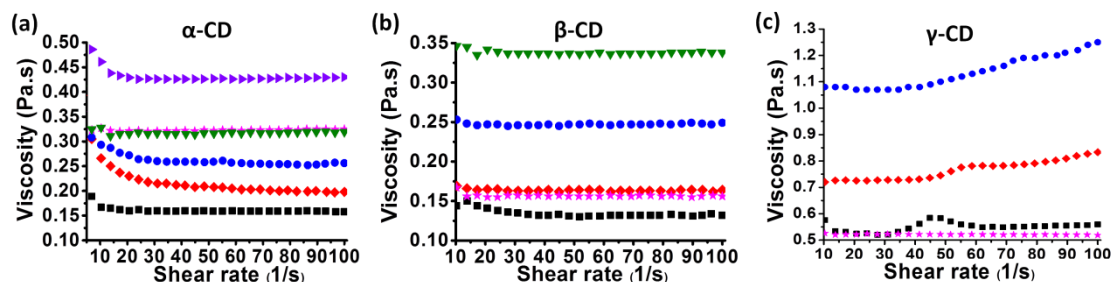


Figure 31. Viscosity versus shear rate graphs of (a) 120% (■), 130% (◆), 140% (●), 150% (▼), 160% (▲) and 20% (w/w) urea-added 160% (w/v) (★) α -CD solutions; (b) 120% (■), 130% (◆), 140% (●), 150% (▼) and 20% (w/w) urea-added 150% (w/v) (★) β -CD solutions; (c) 120% (■), 130% (◆), 140% (●), and 20% (w/w) urea-added 140% (w/v) (★) γ -CD solutions. (Copyright © 2013, Elsevier. Reproduced with permission from Ref.[131] and Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[132])

The viscoelastic properties of the CD solutions were studied by the frequency sweep oscillation measurements. Figure 32 shows the storage and loss modulus of CD solutions as a function of frequency. For all CD solutions at given concentration, the storage modulus was higher than that of the loss modulus in the whole frequency range indicating that these highly concentrated CD solutions behave as a viscoelastic solid [175]. At a fixed CD concentration, both storage and loss modulus were steady under the applied frequency range, but increasing the concentration of CD solutions resulted in higher storage and loss modulus values. We have observed no cross-over point between storage and loss modulus. In addition, the storage modulus was always higher than the loss modulus elucidated that CD solutions show predominantly solid-like behavior for CD systems in all studied concentrations. Moreover, at higher CD concentrations, the gap between storage and loss modulus became larger. This is mostly because the solid-like part becomes more pronounced as the concentration increases due to the increasing aggregation. Moreover, as seen in Figure 32 (a-b) the viscoelastic properties of α -CD and β -CD solutions were almost the same with the similar modulus value for the same concentration. On the other hand, γ -CD solutions showed higher modulus owing to bigger aggregations and showing distinctively higher viscosity when compared to α -CD and β -CD solutions. The oscillation tests were also applied to urea-added CD solutions, and the significant decrease for the modulus values was observed for the optimized concentrations of both CD types. As

mentioned before, the addition of urea disturbs the H-bonding among the CD molecules, so the size of the aggregates get smaller which results in solid density depression in the solution that supplies the elastic property. The modulus of urea-added 160% (w/v) α -CD and 150% (w/v) β -CD solutions was decreased significantly and reached to the modulus value similar to their 120% (w/v) concentration level for α -CD and β -CD. So, as expected, the electrospinning of the urea-added 160% (w/v) α -CD and 150% (w/v) β -CD solutions resulted in similar fiber morphologies when compared to their 120% (w/v) solutions. In the case of γ -CD, the modulus of urea added 140% (w/v) γ -CD solution showed a massive decrease and much lower than its 120% (w/v) solutions, so the electrospinning of the urea-added 140% (w/v) γ -CD solution yielded mostly splashes without any fiber formation. In brief, the electrospinning of the urea-added CD solution did not result in uniform and bead-free nanofiber formation simply because of the break up of the electrified jet due to the presence of insufficient CD aggregates (Figures 27(f), 28(e) and 29(d)). Therefore, it is evident that the presence of substantial amount of CD aggregates via H-bonding plays a key role for the electrospinning of uniform and bead-free nanofibers from CD solutions.

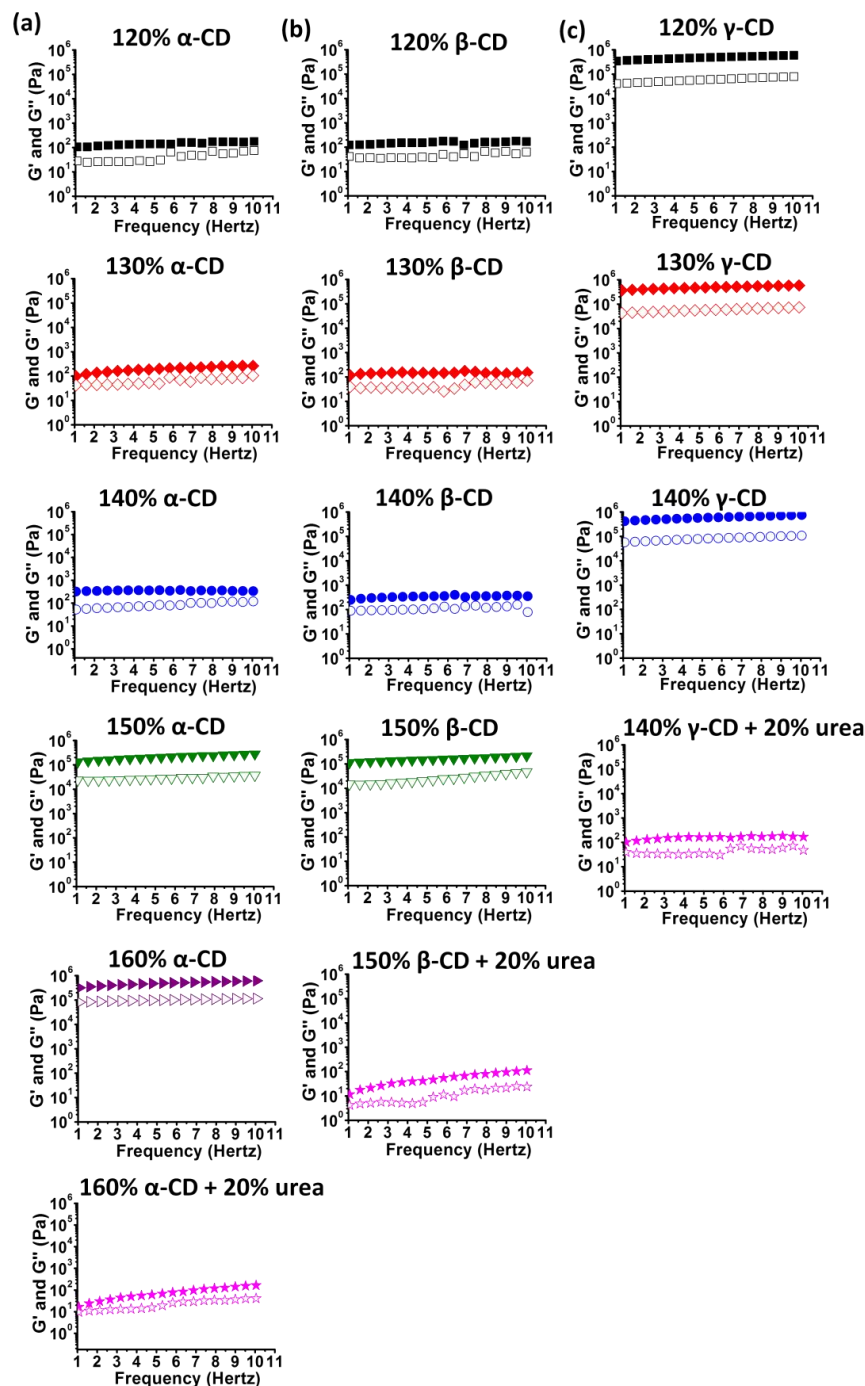


Figure 32. Frequency depended storage modulus G' (filled symbols) and loss modulus G'' (open symbols) graphs of , (a)120% , 130%, 140%, 150%, 160% and 20% (w/w) urea-added 160% (w/v) α -CD solutions; (b) 120% , 130%, 140%, 150% and 20% (w/w) urea-added 150% (w/v) β -CD solutions; (c) 120% , 130%, 140%, and 20% (w/w) urea-added 140% (w/v) γ -CD solutions. (Copyright © 2013, Elsevier. Reproduced with permission from Ref.[131] and Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[132])

5.3. Structural characterization of the electrospun native CD nanofibers

The α -CD, β -CD and γ -CD are crystalline material having crystal structures referred to as cage or channel type [92]. In the cage type packing, the CD molecules are in arrangement in which the cavity of each CD molecule is blocked by neighboring molecules. In the case of channel type packing, the CD molecules are aligned and stacked on top of each other forming long cylindrical channels, and this channel type packing is commonly observed when CD form inclusion complexes (IC) with guest molecules [92]. Here, we have performed the structural analyses of CD nanofibers by XRD. The as-received α -CD, β -CD and γ -CD in powder form are crystalline having a cage type packing (Figure 33(a))[92]. However, the XRD data of electrospun α -CD, β -CD and γ -CD nanofibers showed that the diffraction peaks were absent and only halo XRD pattern was observed indicating that these CD nanofibers have amorphous structure without any particular crystal formation (Figure 33(b)). The HR-TEM further proved that CD molecules were randomly distributed without showing any presence of particular orientation or crystalline aggregation in the fibers (Figure 34). It is likely that CD molecules could not pack into crystal structure because of the rapid evaporation of solvent along with the very fast and continuous stretching of the jet during the electrospinning process. We have also performed the XRD study for these CD nanofibers after 1 year of their production, and we observed that the amorphous structure was protected for α -CD, β -CD and γ -CD nanofibers, and no transformation to cage type packing occurred which is the most stable crystalline form for native CD [92].

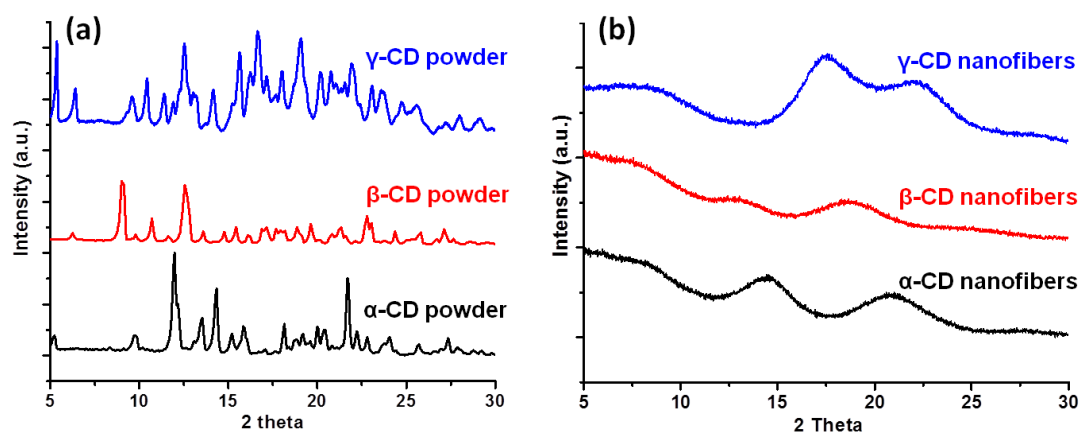


Figure 33. XRD patterns of as-received (a) α -CD, β -CD, γ -CD powder and (b) α -CD, β -CD, γ -CD nanofibers. (Copyright © 2013, Elsevier. Reproduced with permission from Ref.[131] and Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[132])

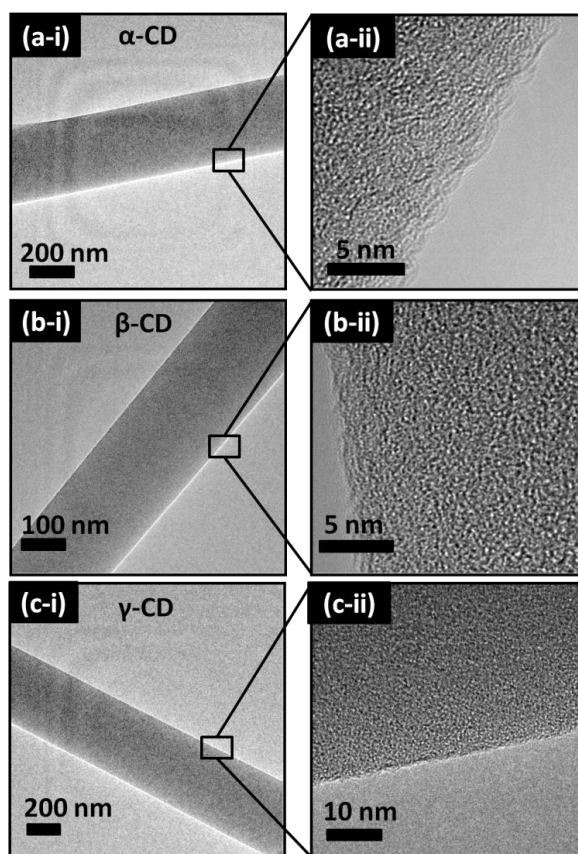


Figure 34. TEM and HR-TEM images of electrospun (a-i,ii) α -CD, (b-i,ii) β -CD and (c-i,ii) γ -CD nanofiber. (Copyright © 2013, Elsevier. Reproduced with permission from Ref.[131] and Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[132])

5.4. Entrapment of organic vapors by γ -CD nanofibrous web

Before the entrapment test, BET analysis was performed to investigate the surface area of γ -CD powder and γ -CD nanofibers, comparatively. The multipoint BET surface area for γ -CD powder was calculated as $1.46 \text{ m}^2/\text{g}$ which correlates with the literature report [170, 171]. On the other hand, the surface area of γ -CD nanofibers was determined as $4.38 \text{ m}^2/\text{g}$ and this proved the increase of surface area as a result of electrospinning process. So, electrospinning of γ -CD nanofibers can be considered as an advantage for obtaining higher surface area which can benefit the filtration application of these supramolecular structures.

As it is mentioned before, CD can form non-covalent host-guest inclusion complexes (IC) with variety of organic molecules and it has been shown that CD can be quite effective for the removal of hazardous organic molecules by inclusion complexation [113]. In this study, we have achieved to obtain γ -CD nanofibrous web in more efficient amount compared to other native CD (α -CD and β -CD) nanofibers, so, the molecular filtration capability of electrospun γ -CD nanofibrous web was tested by the entrapment of organic waste vapors (aniline and toluene) from the surrounding by inclusion complexation. For this, γ -CD nanofibers was placed in a desiccators saturated with aniline or toluene vapor. For a comparison study, the as-received γ -CD powder was also placed in the same environment. The analyses of γ -CD nanofibrous web after exposure to organic vapors were performed by ^1H NMR (Figure 35). We observed that γ -CD nanofibers were quite effective for entrapping aniline and toluene; on the contrary, the γ -CD powder form could not entrap these molecules from the surrounding. The as-received γ -CD powder was in cage type packing in which each CD molecules are blocked by neighboring molecules and therefore CD cavity could not be available for the complexation with aniline and toluene. However, in the case of γ -CD nanofibers, CD molecules were in amorphous phase without forming any particular crystalline packing structure. Therefore, it is likely that the cavity of γ -CD was accessible for aniline and toluene molecules for the complexation. Moreover, γ -CD nanofibrous web has higher surface area compared to γ -CD powder as proven by BET analysis. With the higher surface area

of γ -CD nanofibrous web, the contact points of CD molecules are higher and they become more available to entrap vapours of organic molecules from the environment. From NMR study, the molar ratio of γ -CD to aniline and toluene was calculated about 1:1 and 1:0.7, respectively (Figure 35). This suggests that the entrapping efficiency of γ -CD nanofiber mat for the aniline was better than the toluene which may be due to the better size match between γ -CD cavity and guest molecule [172]. On the other hand, the γ -CD powder form could not entrap these organic molecules so we could not observe the characteristic shifts of aniline and toluene at the aromatic region for this sample. As mentioned earlier, generally γ -CD adopts channel type packing when crystallized from its solution of IC with guest molecules [92, 172]. After the entrapment experiment, we analyzed γ -CD nanofibers by XRD and it was observed that γ -CD nanofibers still kept their amorphous nature even after the complexation with aniline and toluene. In brief, our findings suggest that these electrospun CD nanofibers can be very promising candidates for functional filtering nanomaterials and can be used as molecular filters and/or nanofilters for the removal of organic VOCs from the environment.

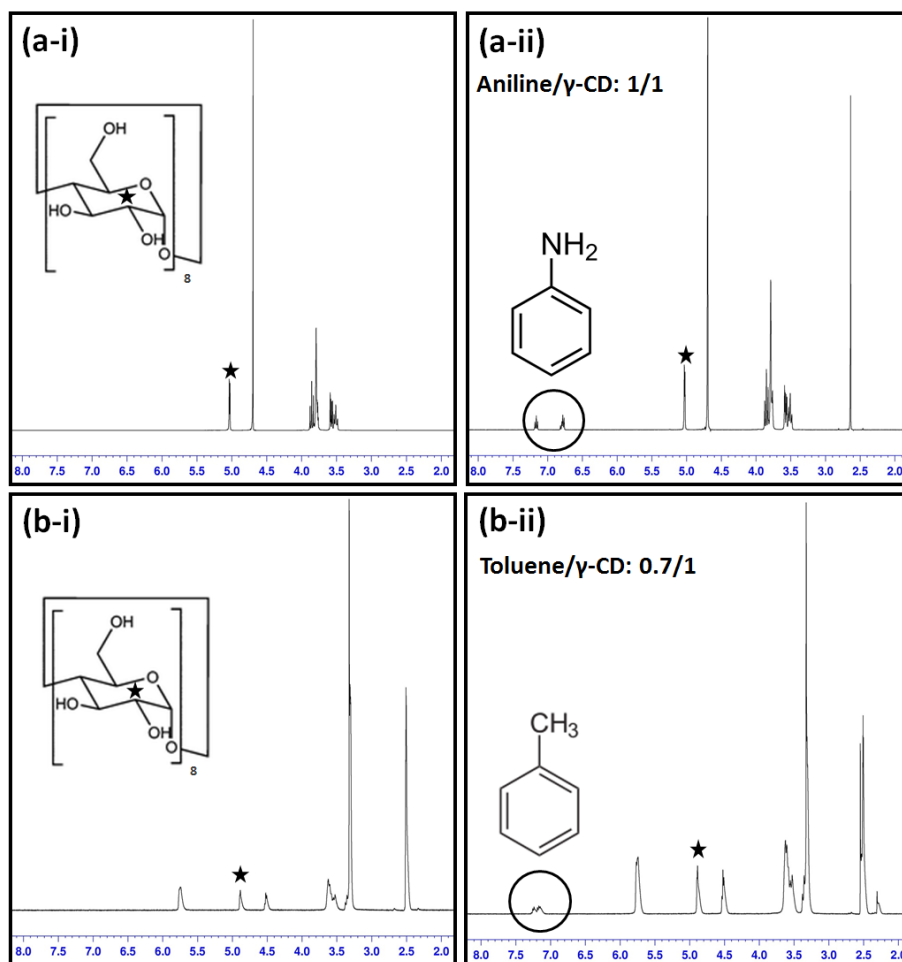


Figure 35. ^1H NMR spectra of (a-i) aniline exposed γ -CD powder and (ii) aniline exposed γ -CD nanofibers in D_2O ; (b-i) toluene exposed γ -CD powder and (ii) toluene exposed γ -CD nanofibers in d_6 -DMSO. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[132])

We have successfully produced nanofibers from native CD of α -CD, β -CD and γ -CD via electrospinning technique without using any carrier polymeric matrix. At lower CD concentrations, beaded nanofibers were obtained, but, as the CD concentrations were increased, the transformation from beaded to bead-free nanofibers was observed. The optimal concentrations for producing bead-free nanofibers were 160%, 150% and 140% (w/v) for α -CD, β -CD and γ -CD, respectively. The DLS and rheology measurements indicated the presence of self-associated CD aggregates in the solutions. It was found that the high solution viscosity and viscoelastic solid-like behavior of CD solutions played a key role for the electrospinning of bead-free nanofibers from native CD types. The size of CD

aggregates got smaller, and the viscosity of the CD solutions decreased significantly with the addition of urea. This situation affected the electrospinnability of CD solutions and beaded fibers, beads or splashes were obtained. The XRD and HR-TEM studies revealed that electrospun CD nanofibers were in amorphous state. The native BET analysis showed that, the surface area of γ -CD nanofibrous web was three times higher than γ -CD powder form. In addition, electrospun γ -CD nanofibers were tested for the entrapment of the VOCs (aniline and toluene) from the surrounding due to their high production amount. It was found that γ -CD nanofibers were quite successful for entrapping aniline and toluene by inclusion complexation whereas γ -CD in powder form did not show any entrapment capability. This suggest that electrospun γ -CD nanofibers are also very promising candidates as filtering material for the removal of organic waste vapours from the environment due to their very high surface area along with their inclusion complexation capability. These three native CD (α -CD, β -CD and γ -CD) have different cavity size which can allow selective inclusion complexation with various molecules of different sizes. Therefore, with the more efficient production amount of other two native CD (α -CD and β -CD), these nanofibers can be quite applicable for air filtration purposes as well as for separation/purification processes by the spesific and selective removing the organic waste from the surroundings just like polymer-free nanofibers obtained from modified CD types.

CHAPTER-2: ELECTROSPINNING OF CYCLODEXTRIN/INCLUSION COMPLEX NANOFIBERS

6. Electrospinning of Polymer-free Nanofibers from Antibacterial (Triclosan)/Cyclodextrin Inclusion Complexes

Electrospun nanofibers having antibacterial functionality can be achieved by incorporating certain types of antibacterial agents in the polymeric nanofibers matrix during the electrospinning process. As a polymeric nanofibers matrix, natural polymers or biocompatible and biodegradable synthetic polymer types are often chosen for the electrospinning. The resulting nanofibrous webs having antibacterial properties can be quite applicable in biomedical practices such as wound dressing. For instance, Nitanan et al. obtained electrospun poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA)/polyvinyl alcohol (PVA) blend nanofibers which was loaded with antibacterial agent neomycin [176]. In another study, Unnithan et al. produced antibacterial electrospun scaffolds by the electrospinning of dextran, polyurethane (PU) and ciprofloxacin HCl (CipHCl) including solution [177]. In the study of Karami et al. the electrospun poly(ϵ -capro-lactone) (PCL), poly(lactic acid) (PLA), and their 50/50 hybrid nanofibrous mats were obtained with the incorporation of herbal agent thymol [178]. In another related study, Lin et al. developed biocompatible nanofibrous membranes by the co-electrospinning of collagen/zein proteins which contain antibacterial agent berberine [179]. One of the associated study, Merrell et al. reported the electrospinning of curcumin loaded PCL nanofibers [180]. While Qi et al. obtained antimicrobial nanofibers by the combination of tetracycline hydrochloride (TCH) and halloysite nanotubes/poly(lactic-co-glycolic acid) (PLGA) composites [181], Nirmala et al. achieved the production of this functional nanofibers by mixing triethylbenzylammonium chloride (TEBAC) into rosin nanofibers [182]. In all the studies mentioned above, the antibacterial activity and/or the wound healing performance of these functional nanofibers were investigated and it was revealed that, antibacterial agent incorporated electrospun nanofibers mats have high potential for the wound dressing purposes.

Cyclodextrin (CD) molecules can form non-covalent host-guest inclusion complexes (IC) with drugs and antibacterials [90, 94, 96]. Such cyclodextrin

inclusion complexes (CD-IC) of bioactive agents are quite useful in medical application since CD-IC provide enhanced functionality by improving the stability, solubility, reactivity, and controlled release of the drugs and antibacterials [90, 91, 94]. In the literature, there are also reports about the incorporation of CD-IC of antibacterial and drug into polymeric matrix to utilize from the inclusion complexation property of CD molecules and to render them into more applicable form [183-187]. Huang et al. embedded neomycin sulfate and its β -CD-IC into PLLA and PCL films [183]. In another study, the mucoadhesive Buccal films (chitosan, KollicoatIR, glycerol) were developed by the IC of HP β CD and poorly soluble anti-inflammatory drug, flufenamic acid for the topical administration [184]. In the study of Sreenivasan, the salicylic acid/ β -CD-IC were loaded into PVA hydrogel film [185]. Plackett et al. produced IC of α -CD and β -CD with an antibacterial agent allyl isothiocyanate (AITC) and encapsulated into polylactide-copolycaprolactone films for the use of cheese packaging [186]. In another related study, the antibacterial agent triclosan/ β -CD-IC were incorporated into biodegradable PCL films [187]. Instead of film, electrospun nanofibers are better candidate as the carrier matrix for CD-IC of bioactive agents such as drugs and antibacterials. Since, very high surface area and highly porous structures of nanofibers provide advantage during the release of these active agents and also by this functionalization, the unique properties of CD molecules were combined with the above mentioned features of nanofibers. There are few studies regarding to the incorporation of CD-IC of bioactive agents into the electrospun nanofibers matrix. For instance, Vega-Lugo et al. obtained antibacterial nanofibers by the electrospinning of AITC/ β -CD-IC including protein isolate (SPI)/poly(ethylene oxide) (PEO) blend and PLA solutions [88]. In another study, the curcumin/ β -CD-IC loaded electrospun PVA nanofibers were produced by Sun et al. [188]. In our research group, PLA nanofibers incorporating IC of triclosan with native CD (α -CD, β -CD, and γ -CD) were obtained successfully [42], in addition, AITC/ β -CD-IC were incorporated into PVA nanofibers demonstrating efficient antibacterial property [58].

Triclosan is a kind of hydrophobic antibacterial agent having very low water solubility [189, 190]. There are studies in the literature about the enhancement of

triclosan solubility by forming IC with various kinds of CD and CD polymers [191-194]. The β -CD and HP β CD are one step ahead through the other CD types owing to providing best improving results in solubility. From this point of view, triclosan was chosen as a model antibacterial agent to observe easily the alteration in solubility and we have reported preliminary findings on electrospun nanofibers from the IC of triclosan and CD without using polymer carrier matrix [133]. Firstly, we achieved the electrospinning of polymer-free nanofibers from IC of triclosan and hydroxypropyl- β -cyclodextrin (HP β CD) and the complexation of triclosan with HP β CD was studied by isothermal titration calorimeter (ITC), turbidity measurements, Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Secondly, polymer-free nanofibers were also produced by using HP γ CD and we have compared these two triclosan/CD-IC nanofibers from the point of inclusion complexation efficiency and antibacterial property against Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria in conjunction with the structural characterizations [134].

6.1. Electrospinning and structural characterization of HP β CD nanofibers and triclosan/HP β CD-IC nanofibers

Studies have shown that triclosan can form IC with different types of CD including β -CD, [191, 195] HP β CD, [194] and M β CD [194]. Here, we have studied the inclusion complexation of triclosan with HP β CD by using ITC. ITC is a powerful and highly sensitive technique for studying the interactions between the guest molecules and the host molecules in the CD-IC systems [196, 197]. ITC measurements give thermodynamic and kinetic information as well as the molar stoichiometry of the CD-IC. The ITC analyses (Figure 36, Table 9) indicated that the standard formation enthalpy (ΔH°) of the inclusion complexation between HP β CD and triclosan was $-521.9 \text{ kJmol}^{-1}$, signifying that the complex formation is an exothermic process. In addition, the negative nature of enthalpy changes indicated that the inclusion complexation process is enthalpy-driven [196]. The entropy effect ($T\Delta S$) was also negative, so the complexation between HP β CD and triclosan is

entropically unfavorable [196]. The high value of the association constant ($K_s = (9.6 \pm 4.2) \times 10^6 \text{ M}^{-1}$) suggested strong host-guest interactions. Moreover, the stoichiometry of the complexation between HP β CD and triclosan was calculated to be $\sim 1:1$ mol/mol from the ITC data ($N = 0.98$).

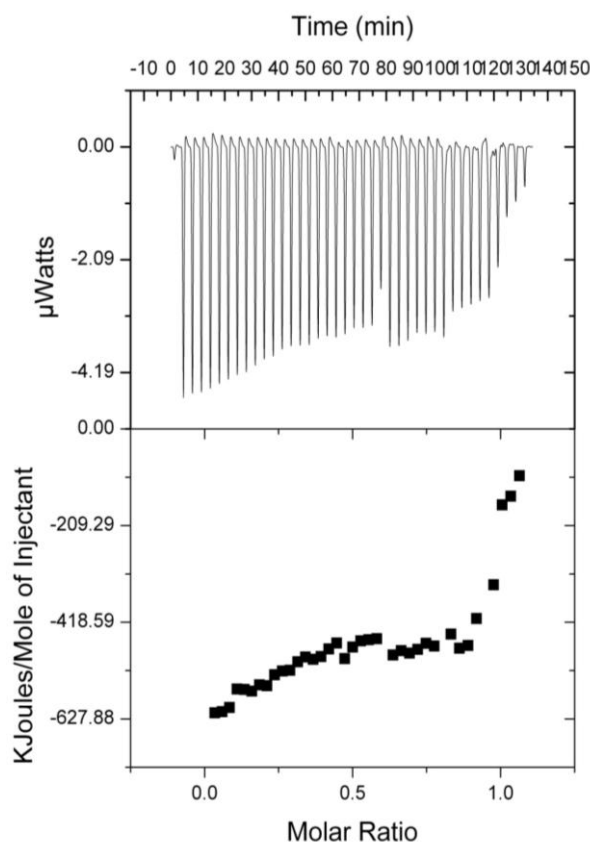


Figure 36. Isothermal calorimetric titration of triclosan with HP β CD in water at 25 °C: (upper) raw data for 40 injections of HP β CD solution into triclosan solution; (lower) titration curve obtained from the integration of the calorimetric traces. (Copyright © 2011, American Chemical Society. Reprinted with permission from Ref.[133])

Table 9. Thermodynamic Parameters Obtained from ITC Measurements. Stoichiometry (N), complex stability constants (K_s/M^{-1}), standard enthalpy changes ($\Delta H^\circ/\text{kJ mol}^{-1}$), and entropy changes ($T\Delta S^\circ/\text{kJ mol}^{-1}$) for inclusion complexation of the triclosan with HP β CD in water at 298 K. (Copyright © 2011, American Chemical Society. Reprinted with permission from Ref.[133])

Triclosan (mM)	HP β CD (mM)	N	$K_s (\text{M}^{-1}) \times 10^6$	$\Delta H^\circ (\text{kJ/mol})$	$T\Delta S^\circ$ (kJ/mol)
0.025	0.25	0.98	9.6 ± 4.2	-521 ± 9	-478

The optimized concentration of HP β CD was determined from the previous study (see 2.2.1.) as 160% (w/v) for the electrospinning of IC nanofibers. The inclusion complexation of triclosan with highly concentrated HP β CD (160%, w/v) was studied visually and by turbidity measurements performed with UV-vis spectrometer (Figure 37). Triclosan is insoluble in water and forms dispersion; however, when 160% (w/v) HP β CD was added, the solution became clear and transparent because triclosan become water soluble as a result of the inclusion complexation with HP β CD (Figure 37(a.i)). Because the mixing continued for a longer time (1-15 h), the solution became very turbid because of the aggregation of triclosan/HP β CD-IC (Figure 37(a, ii-vi)). Figure 37(b) clearly shows the increasing absorbance values as a function of time for the triclosan/HP β CD-IC solution as the solution became more turbid. This behavior is typically observed for CD-IC systems as the solubility of CD decreased substantially when complexed with guest molecules and therefore results in very turbid solutions [194, 198, 199]. These turbid triclosan/HP β CD-IC solutions were electrospun into nanofibers by themselves without the addition of any carrier polymeric matrix. Figure 38 indicates the schematic representation of inclusion complexation and electrospinning of triclosan/HP β CD-IC nanofibers. The discussion of morphological characterization belongs to HP β CD and triclosan/HP β CD-IC nanofibers will be mentioned in detailed later, however as it is seen in Figure 41, both nanofibers have uniform and bead-free morphology. Here, the urea (20% (w/w)) was added to triclosan/HP β CD-IC suspension and splashes were obtained instead of fibers (data is not given) indicating that the urea disrupted the HP β CD aggregates and therefore the breakup in the electrospinning jet was inevitable. So the electrospinnability of IC nanofibers also depends on the sufficient intermolecular interaction and aggregates in the electrospinning solution.

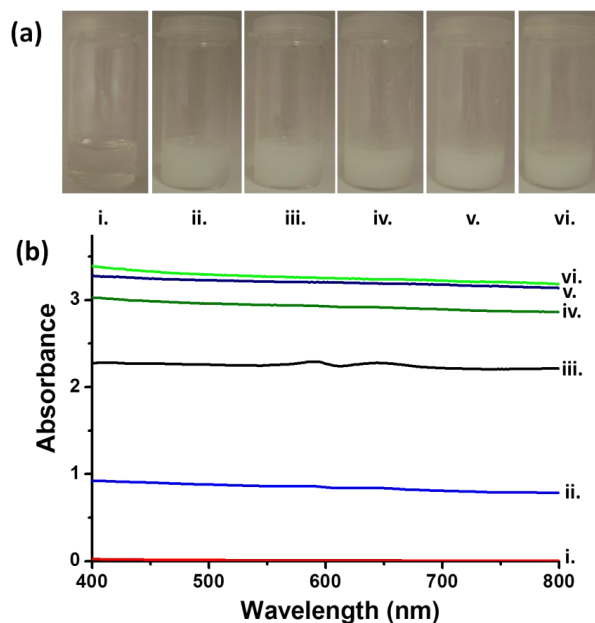


Figure 37. (a) Visual observation of a triclosan/HP β CD-IC (1:1 molar ratio) solution after mixing of the two components for (i) 1, (ii) 3, (iii) 6, (iv) 9, (v) 12, and (vi) 15 h. (b) UV-vis spectrum of the same triclosan/HP β CD (1:1 molar ratio) solution after (i) 1, (ii) 3, (iii) 6, (iv) 9, (v) 12, and (vi) 15 h. (Copyright © 2011, American Chemical Society. Reprinted with permission from Ref.[133])

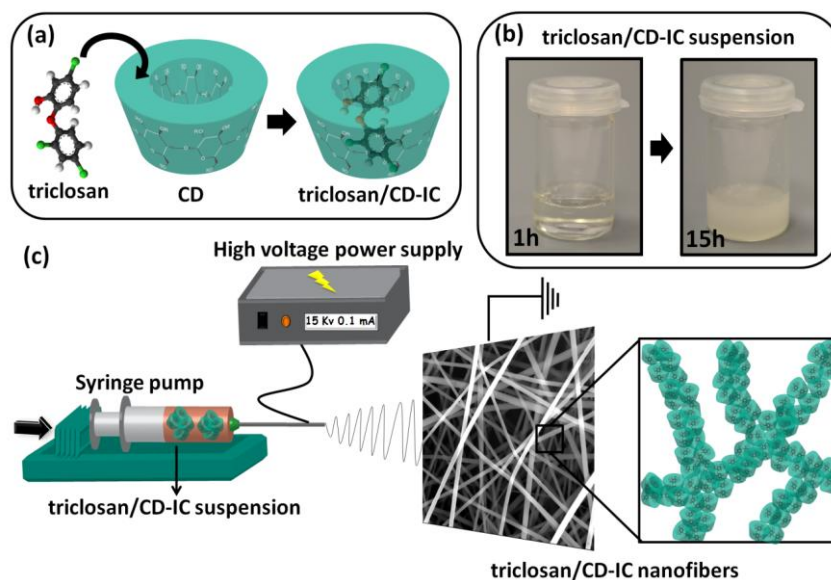


Figure 38. Schematic representation of (a) IC formation between CD and triclosan. (b) The photograph of triclosan/HP β CD-IC suspension for 1h and 15h periods. (c) Illustration of electrospinning of triclosan/HP β CD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

Here, firstly, the comparative FTIR, XRD and DSC characterizations were performed for the triclosan/HP β CD-IC nanofiber and its physical mixture to prove the inclusion complexation between HP β CD and triclosan. The FTIR spectra of pure triclosan, HP β CD nanofibers, triclosan/HP β CD physical mixture, and triclosan/HP β CD-IC nanofibers are depicted in Figure 39. In the FTIR spectrum of the HP β CD nanofibers, the salient absorption bands at around 1020 and 1070 cm^{-1} correspond to the coupled C-C and C-O stretching vibrations, and the absorption band at around 1150 cm^{-1} is attributed to the anti-symmetric stretching vibration of the C-O-C glycosidic bridge [42, 97]. The FTIR spectrum of pure triclosan exhibited characteristic peaks at 1598, 1579, 1507, 1471, 1417, and 1392 cm^{-1} corresponding to vibrations involving C-C stretching inside the benzene ring [42, 190, 191]. The peaks in the region from 1300 to 1000 and 900 to 750 cm^{-1} are due to in-plane and out-of-plane bending of the aromatic ring C-H bonds, respectively [191]. For the triclosan/HP β CD physical mixture, the characteristic peaks for both HP β CD and triclosan were present without any shifts in the absorption bands. However, in the case of triclosan/HP β CD-IC nanofibers, characteristic bands of triclosan such as those at 1471 and 1417 cm^{-1} shifted to 1474 and 1420 cm^{-1} , respectively suggesting the host-guest interactions between HP β CD and triclosan in the electrospun nanofibers. Similar peak shifts were also reported in the literature for triclosan/CD-IC [42, 192]. In addition, the characteristic peaks of triclosan were suppressed in triclosan/HP β CD-IC nanofibers when compared to those of its physical mixture. The attenuation of the absorption bands of guest molecules are typically observed for the CD-IC systems because the IC of guest molecules in the CD cavity hinder their molecular vibrations; therefore, the intensity of their absorption bands is diminished [192, 200]. In brief, the shifts in the characteristic bands of triclosan and their attenuation suggested strong host-guest interactions in triclosan/HP β CD-IC nanofibers.

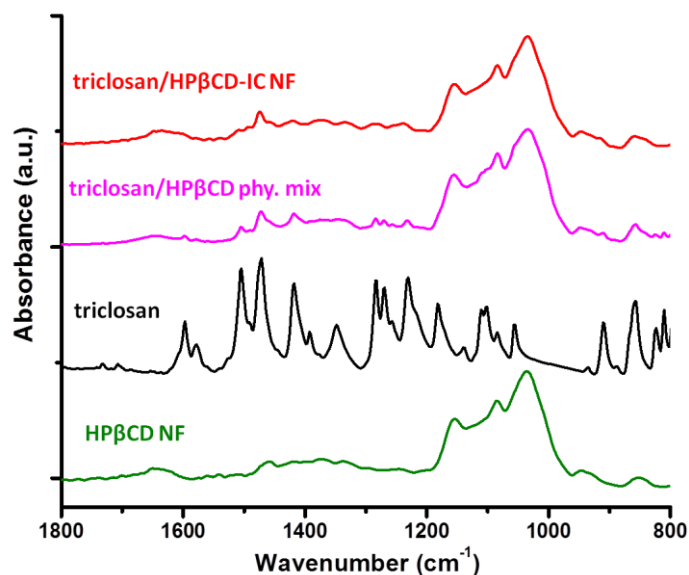


Figure 39. FTIR spectra of HP β CD nanofibers, pure triclosan, triclosan/HP β CD physical mixture, and triclosan/HP β CD-IC nanofibers.

Triclosan is a crystalline material having major diffraction peaks at $2\theta=8.2^\circ$, 24.4° and 25.4° . The XRD patterns of the triclosan/HP β CD-IC nanofibers are very similar to those of pure HP β CD nanofibers having amorphous structures (Figure 40(a)). In the CD-IC, the guest molecules are isolated from each other by the CD cavities; therefore, they cannot form crystals [42, 97, 201]. The XRD of triclosan/HP β CD-IC nanofibers (Figure 40(a)) has shown no diffraction pattern for triclosan, suggesting that the triclosan molecules were included inside the HP β CD cavity. However, the physical mixture of triclosan/HP β CD has diffraction peaks for uncomplexed triclosan (Figure 40(a)).

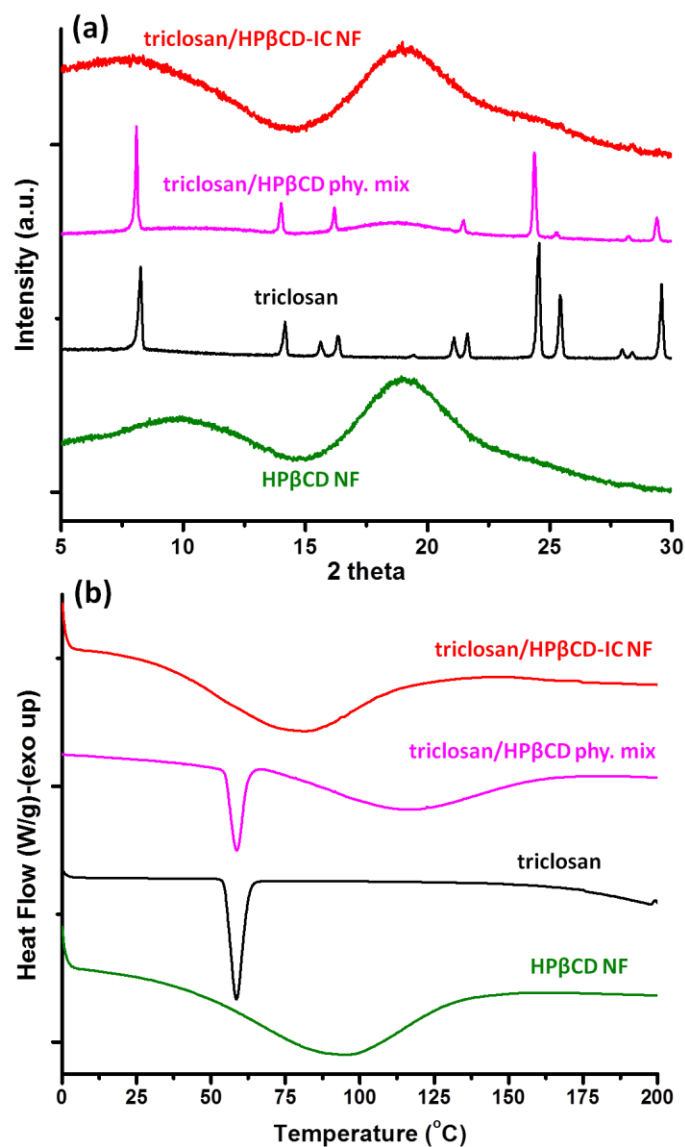


Figure 40. (a) XRD patterns and (b) DSC thermograms of HPβCD nanofibers, pure triclosan, triclosan/HPβCD physical mixture and triclosan/HPβCD-IC nanofibers.

DSC is a useful technique for determine whether the guest molecules are included inside the CD cavities [200, 201]. In the case of complexation generally, the thermal transition of guest molecules such as melting or sublimation can shift or disappear [42, 97]. The melting point (T_m) for guest molecules would be observed if there are any free uncomplexed guests molecules present in the CD-IC system. DSC scans of pure triclosan (Figure 40(b)) and the physical mixture of triclosan/HPβCD (Figure 40(b)) exhibited a melting point for triclosan at around 60 °C whereas no melting point was observed for the triclosan/HPβCD-IC nanofibers (Figure 40(b)),

suggesting that the triclosan molecules were included inside the HP β CD cavity. In short, the absence of a thermal event such as T_m for guest molecules in triclosan/HP β CD-IC nanofibers is evidence of true inclusion complexation. These findings suggest that the electrospinning of nanofibers from triclosan/HP β CD-IC having a 1:1 molar ratio is optimal for obtaining triclosan/HP β CD-IC nanofibers without any free guest molecules [195, 202].

6.2. Electrospinning and structural characterization of triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers

We used the optimized concentration; 160% (w/v) for also the electrospinning of triclosan/HP γ CD-IC suspensions and we were quite successful for the electrospinning of bead-free nanofibers from IC of HP γ CD systems just like HP β CD. The representative SEM images of HP β CD, HP γ CD, triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers were displayed in Figure 41(a-d). Bead-free nanofibers with smooth morphology attained for all samples proved the reproducibility of CD and CD-IC nanofibers. While the bead-free HP β CD nanofibers were obtained with AFD of 695 $\pm$ 335 nm, the HP γ CD nanofibers were obtained with AFD of 1355 $\pm$ 475 nm. Although the viscosity of IC suspensions are higher than the pure HP β CD and HP γ CD solutions, the triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers were obtained with the thinner AFD values of 520 $\pm$ 250 nm and 1100 $\pm$ 660 nm, respectively (Table 10). The reason for this situation can be possibly because of the higher conductivity of IC solutions compared to HP β CD and HP γ CD solutions that leads more stretching of jets, so thinner fiber formation during the electrospinning [1, 19]. Additionally, the HP γ CD based nanofibers are than the HP β CD based ones for both pure CD and IC systems owing to the considerably lower conductivity and higher viscosity levels of HP γ CD solutions. In addition, the high viscosity of IC solutions also suggest that a considerable number of aggregates were present in triclosan/CD-IC solutions and therefore resulted in bead-free nanofibers when electrospun. Figure 41(e-h) indicates the photographs of HP β CD, HP γ CD, triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibrous webs. As is seen

from the observations, both CD and CD-IC nanofibers can be easily handled as a free-standing web and have some mechanical integrity and flexibility.

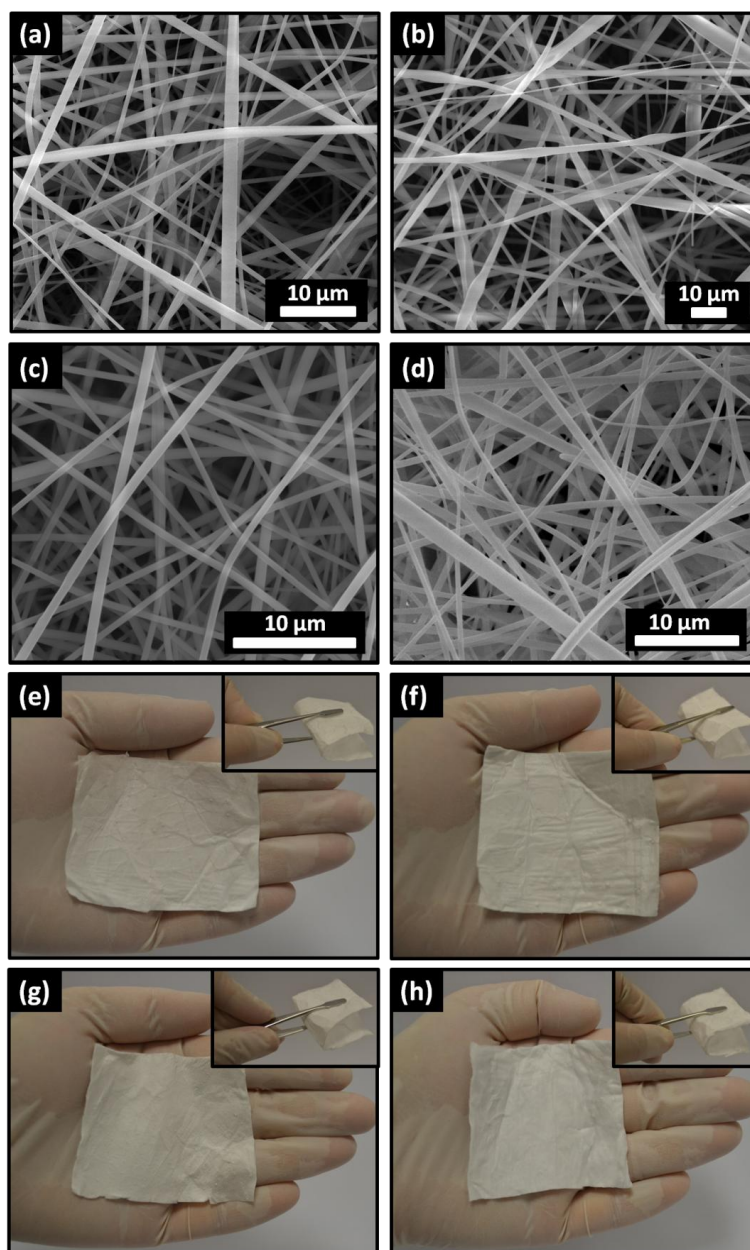


Figure 41. Representative SEM image of electrospun nanofibers obtained from (a) HP β CD, (b) HP γ CD solutions, (c) triclosan/HP β CD-IC, and (d) triclosan/HP γ CD-IC suspensions. The photographs of nanofibrous webs which can be easily handled and folded; (e) HP β CD nanofibers, (f) HP γ CD nanofibers, (g) triclosan/HP β CD-IC nanofibers, and (h) triclosan/HP γ CD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

Table 10. The characteristics of HP β CD, HP γ CD solutions, triclosan/HP β CD-IC and triclosan/HP γ CD-IC suspensions and the properties of resulting electrospun nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

Solution	Viscosity* (Pa•s)	Conductivity* (μ S/cm)	Fiber morphology	Average fiber diameter (nm)	Fiber diameter range (nm)
HP β CD	0.26 $\pm$ 0.01	197.00 $\pm$ 1.52	bead-free nanofibers	695 $\pm$ 335	240-1700
HP γ CD	0.34 $\pm$ 0.06	4.89 $\pm$ 1.11	bead-free nanofibers	1355 $\pm$ 475	505-2300
triclosan/HP β CD-IC	0.86 $\pm$ 0.10	249.00 $\pm$ 8.88	bead-free nanofibers	520 $\pm$ 250	250-1100
triclosan/HP γ CD-IC	1.29 $\pm$ 0.26	6.74 $\pm$ 0.07	bead-free nanofibers	1100 $\pm$ 660	300-2100

* The measurements were repeated three times (n=3) and the average results were given with standard deviations.

As it is mentioned, the antibacterial property of triclosan/CD-IC nanofibers were comparatively investigated for both HP β CD and HP γ CD systems. Therefore, before the antibacterial test, the structural characterizations were performed for triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers by using FTIR, ^1H NMR, XRD, TGA and DSC techniques. Here, we aimed to determine the efficiency differences between these two modified CD in terms of inclusion complexation and to observe its effect on the antibacterial property. Figure 42 shows the FTIR spectra of the electrospun triclosan/CD-IC nanofibers samples and pure triclosan. As shown in Figure 39, some characteristic peaks of triclosan can shift to the higher wavenumber owing to IC formation between HP β CD molecule and triclosan [42, 133, 192]. We have also observed the same small shifts for triclosan peaks in FTIR spectra of triclosan/HP γ CD-IC nanofibers, from 1471 and 1417 cm^{-1} to 1474 and 1420 cm^{-1} , respectively (Figure 42(b)). So, the FTIR study suggested again the presence of host-guest interactions between CD cavity and triclosan in triclosan/HP γ CD-IC nanofiber samples.

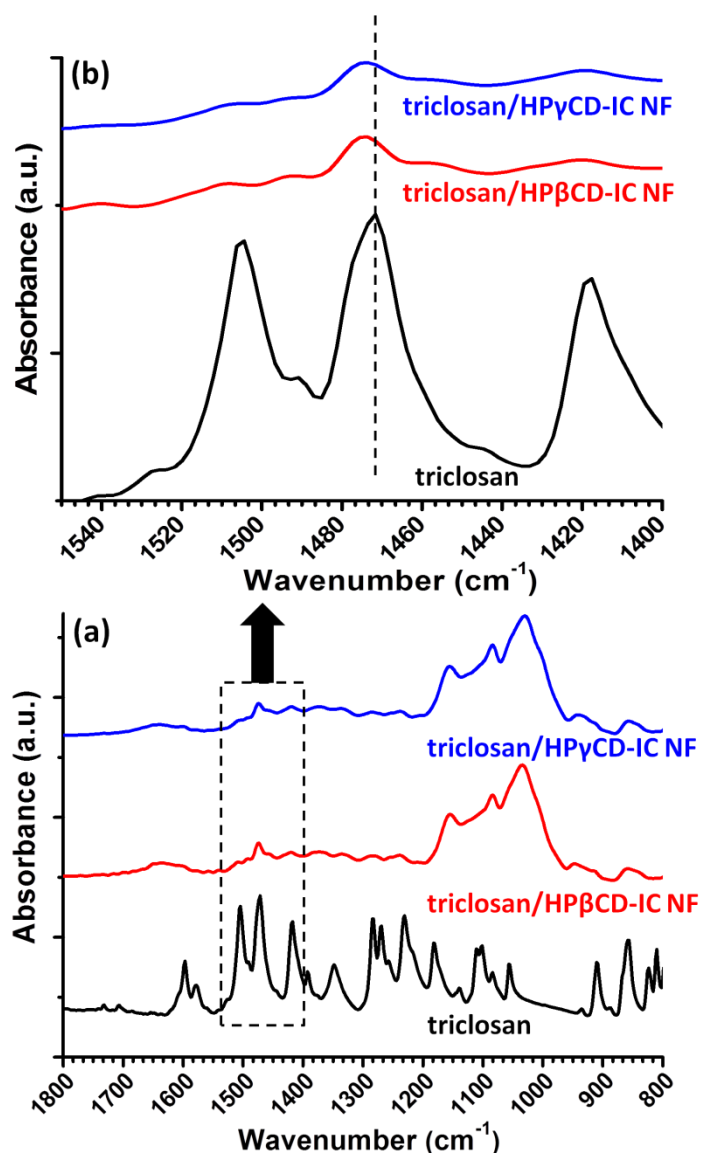


Figure 42. FTIR spectra of pure triclosan, triclosan/HP β CD-IC nanofibers and triclosan/HP γ CD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

The presence of triclosan and the molar ratio between triclosan and CD (HP β CD and HP γ CD) in nanofibers samples were determined by ^1H NMR study (Figure 43). The molar ratio was calculated by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to triclosan, HP β CD and HP γ CD by using the NMR software. The molar ratios were calculated by taking account the integration of triclosan aromatic peak at about 6.7 ppm [194] and the CD's characteristic peak at about 1 ppm [203]. It was found from the calculation that the triclosan:CD molar ratio in triclosan/HP β CD-IC nanofibers and triclosan/HP γ CD-IC

nanofibers was 1:1 and 0.7:1, respectively. The triclosan:HP β CD 1:1 molar ratio for triclosan/HP β CD-IC nanofibers was quite well agrees with our initial 1:1 mixing ratio in the solution. This indicates that triclosan was fully complexed with HP β CD and its loss was protected by inclusion complexation during the electrospinning process and/or during storage. However, in the case of triclosan/HP γ CD-IC nanofibers, the triclosan:HP γ CD molar ratio in nanofibers (0.7:1) was lower than the initial ratio (1:1) and this is probably because of some uncomplexed triclosan in triclosan/HP γ CD-IC suspension that could not be effectively preserved and some amount of triclosan was lost during the electrospinning process and/or during storage.

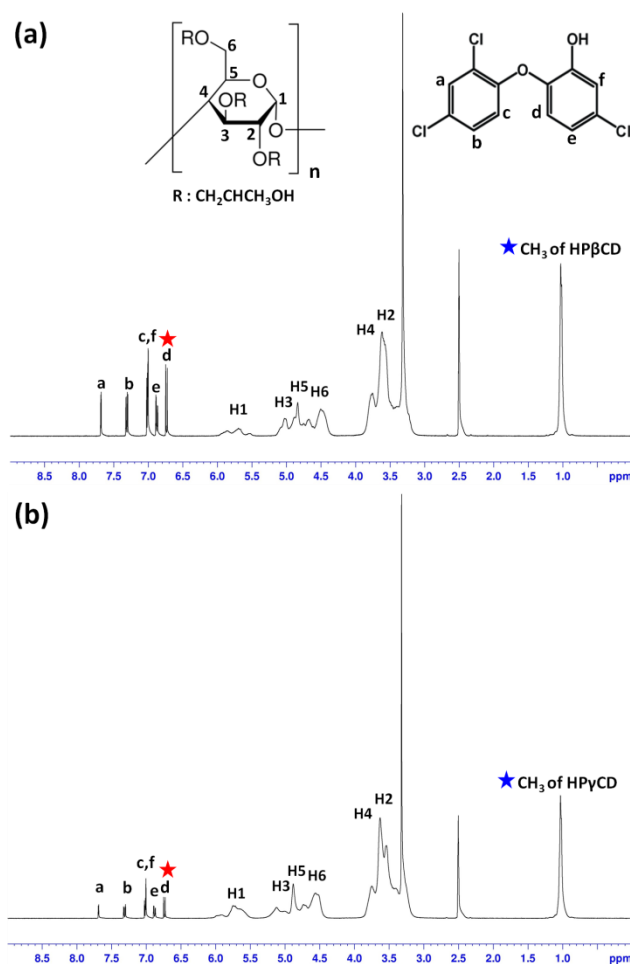


Figure 43. ^1H NMR spectra of (a) triclosan/HP β CD-IC nanofibers and (b) triclosan/HP γ CD-IC nanofibers dissolved in d_6 -DMSO (red and blue stars are assigned for the calculated peak of triclosan and CD, respectively.) (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

TGA thermograms of pure triclosan powder and triclosan/CD-IC nanofibers are shown in Figure 44. The thermal evaporation/degradation of triclosan started at about 140 °C (Td onset) and continued till 250 °C. For triclosan/HP β CD-IC nanofibers, three stages of weight losses were observed between 25 °C and 400 °C. The weight losses at 100 °C and 300 °C correspond to the water loss and main thermal degradation of HP β CD, respectively (Figure 44). On the other hand, triclosan/HP β CD-IC nanofibers have additional weight loss having onset point (Td onset) at 150 °C and belong to the evaporation/degradation of triclosan. The Td onset for pure triclosan was 140 °C, however, in the case of triclosan/HP β CD-IC, Td onset of triclosan slightly shifted to the higher temperature (150 °C) suggesting the complexation between triclosan and HP β CD. The triclosan amount in triclosan/HP β CD-IC nanofibers was calculated as ~10 % (w/w, with respect to HP β CD) that is correlated with the 1:1 molar ratio complexation and proved the preservation of triclosan during the electrospinning. This result was also supported by the ^1H NMR analysis. For triclosan/HP γ CD-IC nanofibers, four stages of weight losses are observed; the initial step below 100 °C belongs to water loss, the second step started at about 140 °C corresponds to uncomplexed triclosan degradation, the third step having onset point at 210 °C due to degradation of complexed type of triclosan, in last step, the main degradation of the HP γ CD is observed at about 300 °C. From TGA data of triclosan/HP γ CD-IC nanofibers, we have detected the existence of triclosan which could not make IC and wane at the triclosan amount during the electrospinning because the total of the calculated triclosan from TGA thermogram (~7.5%-w/w, with respect to HP γ CD) is less than the used quantity (~9%-w/w, with respect to HP γ CD for the 1:1 molar ratio). This finding indicates that, certain parts of the guest molecule formed IC and the other part could not be preserved because of the uncomplexation. The obtained TGA outcomes also clarified the results taken from ^1H NMR analysis for triclosan/HP γ CD-IC nanofibers in terms of molar ratio (1:0.7). Furthermore, for triclosan/HP γ CD-IC nanofibers, the thermal degradation of complexed triclosan delayed to the higher temperature (210 °C) compared to complexed triclosan which existence in triclosan/HP β CD-IC nanofibers, indicating that the interaction between triclosan and HP γ CD was much stronger in comparison with HP β CD.

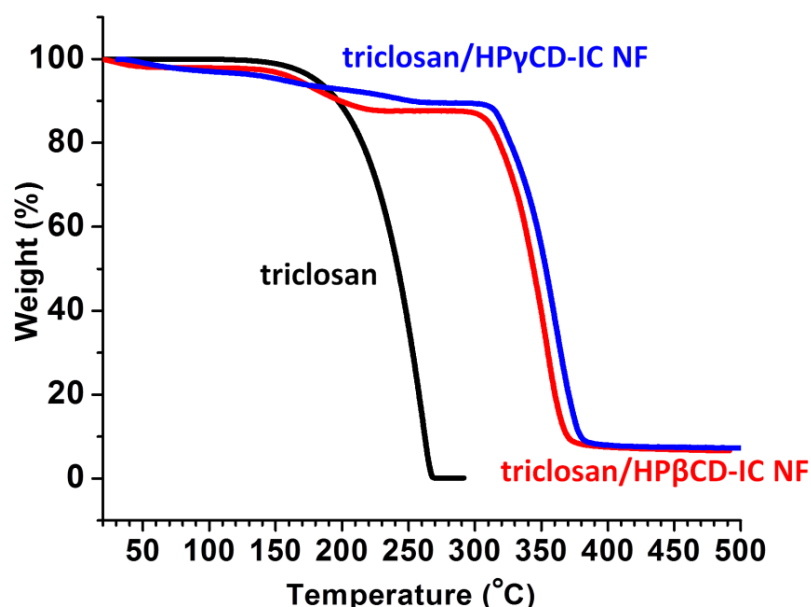


Figure 44. TGA thermograms of pure triclosan, triclosan/HPβCD-IC nanofibers and triclosan/HPγCD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

As it is observed in Figure 45(a), while triclosan/HPβCD-IC nanofibers represent totally amorphous XRD pattern, triclosan/HPγCD-IC nanofibers have diffraction peak with low intensity for the uncomplexed triclosan part, additively to the amorphous HPγCD pattern and this situation also supported the TGA results. The DSC graphs of triclosan powder, triclosan/HPβCD-IC nanofibers and triclosan/HPγCD-IC nanofibers are given in Figure 45(b). Unlike, triclosan/HPβCD-IC nanofibers, for triclosan/HPγCD-IC nanofibers, the melting point of triclosan ($T_m \sim 60^\circ\text{C}$) was observed that is originated from the uncomplexed triclosan part, so DSC also proved the existence of uncomplexed triclosan in the triclosan/HPγCD-IC nanofibers. In brief, TGA, XRD and DSC measurements demonstrated that, triclosan/HPγCD-IC nanofibers have some uncomplexed triclosan molecules unlike triclosan/HPβCD-IC nanofibers. So it can be said that, while the initial molar ratio 1:1 was protected and optimal for triclosan/HPβCD-IC nanofibers, this ratio was excess and caused the uncomplexed triclosan existence for triclosan/HPγCD-IC nanofibers. In addition, from the TGA data, we observed that the HPγCD make more influential interaction with triclosan compared to HPβCD, most probably due to the better size match between HPγCD and triclosan molecules [91].

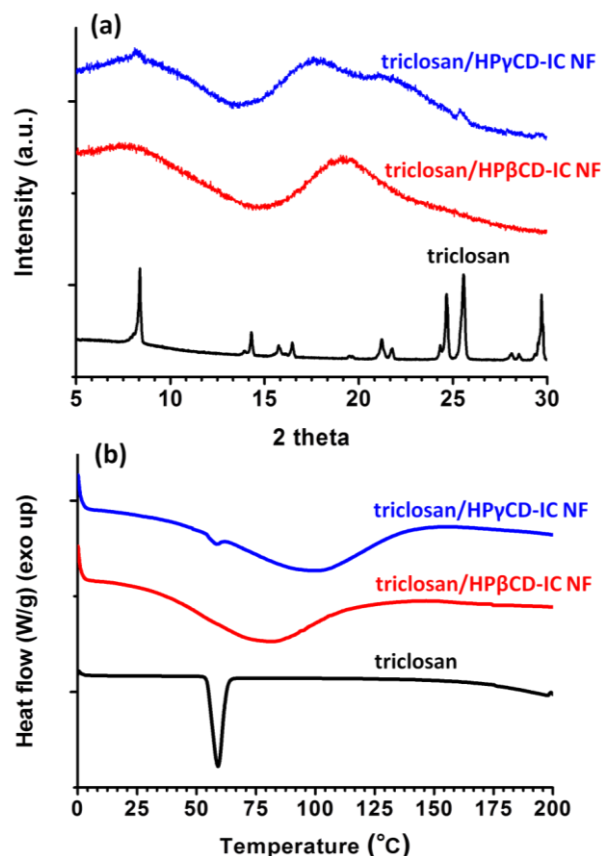


Figure 45. (a) XRD patterns and (b) DSC thermograms of pure triclosan, triclosan/HPβCD-IC nanofibers and triclosan/HPγCD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

6.3. Antibacterial activity of triclosan/HPβCD-IC nanofibers and triclosan/HPγCD-IC nanofibers

The antibacterial activity of triclosan/HPβCD-IC and triclosan/HPγCD-IC nanofibers were investigated against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. Pure HPβCD and HPγCD do not have antibacterial activity so their nanofibers were not compared [204]. Figure 46 indicates the representative photographs of antibacterial test plates with the average inhibition zone calculations for zero and 24h time intervals. It was observed that triclosan/HPβCD-IC nanofibers and triclosan/HPγCD-IC nanofibers show efficient antibacterial activity against both of the bacteria type. In the pure triclosan plates, the inhibition zones were measured as 4.00 ± 0.00 cm and 5.00 ± 0.00 cm for *E. coli* and *S. aureus* bacteria, respectively. For triclosan/HPβCD-IC nanofibers, the inclusion zones were wider, 5.33 ± 0.57 cm

and 6.35 ± 0.55 cm for *E. coli* and *S. aureus* bacteria, respectively. The inhibition zones are smaller in triclosan/HP γ CD-IC nanofibers plates, and they were determined to be 4.83 ± 0.29 cm for *E. coli* and 5.85 ± 0.30 cm for *S. aureus*. The increased antibacterial activity of triclosan is caused by the IC mechanism that increases the solubility and therefore provided efficient release of the hydrophobic agent in the agar medium. Triclosan/HP γ CD-IC nanofibers contain uncomplexed triclosan part, so the solubility improvement could not be very efficient and this lead to a slightly smaller inhibition zone compared to triclosan/HP β CD-IC nanofibers. The stronger interaction between HP γ CD and triclosan molecules could be another reason for the lower antibacterial activity, which results in a delay of the release of triclosan. Furthermore, the inhibition zone areas are larger for *S. aureus* compared to *E. coli* due to the cellular wall content differences between Gram negative and Gram positive bacteria [205].

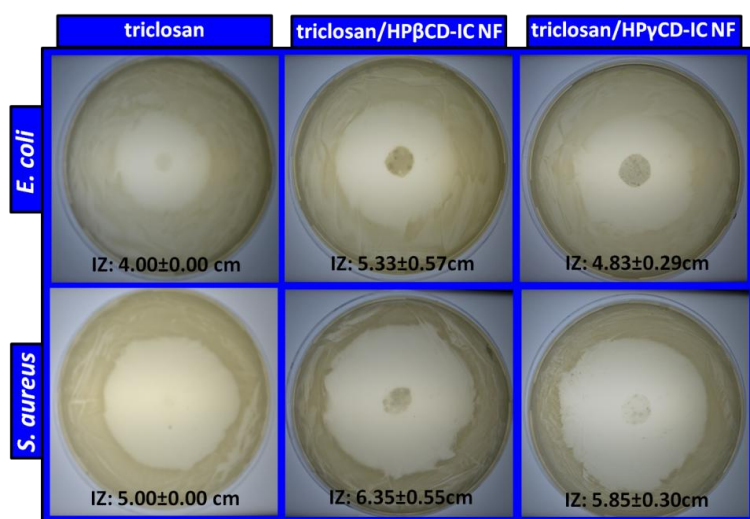


Figure 46. The representative photographs of antibacterial test plates with the average inhibition zone (IZ) and standard deviation calculations for *E. coli* and *S. aureus* treated with pure triclosan, triclosan/HP β CD-IC nanofibers and triclosan/HP γ CD-IC nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[134])

In this study, we report the first results on the electrospinning of nanofibers from CD-IC without the use of any polymeric carrier matrix. A widely used antibacterial agent (triclosan) was chosen as guest molecule and complexed with HP β CD and HP γ CD, then electrospun into uniform nanofibers. The ITC, turbidity

test performed with UV-vis-spectroscopy, FTIR, XRD and DSC analyses suggested the presence of a host-guest interaction between triclosan and HP β CD in the electrospun nanofibers. Here, it was also aimed to demonstrate the application potential of triclosan/CD-IC nanofibers by comparative antibacterial test between HP β CD and HP γ CD based samples. So FTIR, ^1H NMR, TGA, XRD and DSC analyses were performed for triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers, separately to indicate the structural and complexation efficiency differences between these two CD types. It was observed that triclosan was fully complexed having 1:1 molar ratio of triclosan:HP β CD in triclosan/HP β CD-IC nanofibers. Yet, in the case of triclosan/HP γ CD-IC nanofibers, some uncomplexed triclosan was detected for this sample and the 1:1 initial molar ratio of triclosan:HP γ CD could not be protected during the electrospinning. We have performed the antibacterial tests for triclosan/CD-IC nanofibers against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. We have observed more efficient antibacterial effect for triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers against *E. coli* and *S. aureus* compared to pure triclosan powder owing to improved solubility of agent that provides higher release through the medium. Electrospun CD-IC nanofibers are very intriguing materials owing to the unique properties by combination of very high surface area and the specific functionalities of CD-IC supramolecular structures. Moreover, CD-IC nanofibers can exhibit higher content of active component compared to polymer-template nanofibers without raising an issue during the electrospinning. Thus, superior bioactivity may be provided in the course of use depending on the higher agent content. The nanofiber type of CD-IC also eliminates the use challenges that are originated from the powder form and render them into more applicable state. As a result, due to the non-toxic nature of CD, the high functionality of CD-IC and practicable structure of CD nanowebs, the electrospun triclosan/CD-IC nanofibers or CD-IC nanofibers containing other types of bioactive agents would be applicable in biotechnology area such as wound dressing and drug delivery, etc.

7. Electrospinning of Polymer-free Nanofibers from Vanillin/Cyclodextrin Inclusion Complexes

Vanillin (4-hydroxy-3-methoxybenzaldehyde), which is the main component of natural vanilla, is widely used as a flavoring additive in the food industry [206-208]. The antioxidant and antimicrobial properties of vanillin also make this agent a good candidate as a food preservative [206, 208]. In addition, vanillin is used as a fragrance component in the cosmetics and textile industries [206, 209]. Unfortunately, a short shelf life is a significant restriction for vanillin due to its thermal instability and volatile nature. Cyclodextrin (CD) molecules are capable of forming inclusion complex (IC) with food additives such as flavors/fragrances which are generally sensitive to heat, oxygen and light. This inclusion complexation is very efficient way for the stabilization/protection and controlled/sustained release of these functional additives [200, 210]. There are studies in the literature regarding to complexation between vanillin and different kinds of CD types [208, 211, 212]. Even, we have reported the detailed investigation of solid state vanillin/CD-IC by using native CD (α -CD, β -CD and γ -CD) in one of the related study and in this report, the enhancement of thermal stability and sustained release of vanillin were shown obviously. [97].

Electrospun nanofibers have received great attention in functional food and active food packaging applications [88, 213], due to their extremely high surface area and high encapsulation efficiency. Consequently, the integration of the vanillin/CD-IC with nanofibers can be considered as a good alternative to improve the shelf-life and stability of this active compound by combining the high surface area of nanofibers with the specific features of vanillin/CD-IC. In our previous study, we have produced functional polyvinyl alcohol (PVA) electrospun nanofibers incorporating vanillin/CD-IC by using three types of CD (α -CD, β -CD and γ -CD) and high thermal stability, enhanced durability as well as a carrier template were provided for vanillin and its IC [31]. However, in this study, the content of the vanillin in nanofibers is limited with the amount of CD-IC which does not cause a problem during the electrospinning. Although the PVA is a water soluble and

biocompatible polymer, it can be also a concern about the practices for food applications.

In this study, the polymeric template was totally removed and polymer-free nanofibers were produced from vanillin/CD-IC by using three CD types (hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD)). Thereby, we supposed to attain more appropriate materials for the food applications along with the non-toxic and edible nature of CD. Here, the IC solutions were prepared in three different solvents; water, dimethylformamide (DMF) and dimethylacetamide (DMAc) to observe the morphological differentiation depending on the solvent types. The morphology analysis of ultimate nanowebs was performed by scanning electron microscope (SEM). Then, vanillin/CD-IC nanofiber produced with water was selected for the investigation of the application potential of these IC nanofibers due to its more proper features for food purposes originated from the water usage. The detailed characterization of water based IC nanofibers were carried out by using Fourier transform infrared spectrometer (FTIR), X-ray diffractometer (XRD), differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA). The molar ratios between vanillin and CD (HP β CD, HP γ CD and M β CD) were calculated by using proton nuclear magnetic resonance (^1H NMR) technique. Moreover, high performance liquid chromatography (HPLC) technique was used for the comparative determination of the vanillin solubility for CD-IC nanofibers and pure agent.

7.1. Electrospinning of vanillin/CD-IC nanofibers

In this study, we used the same concentrations of CDs with the previous studies[130], for the electrospinning of vanillin/CD-IC systems and we have successfully obtained bead-free nanofibers from all IC except vanillin/HP γ CD-IC nanofibers produced in DMAc (Figure 47). The properties of the vanillin/CD-IC solutions and the ultimate nanofibers were also summarized in Table 11. In the case of vanillin/HP β CD-IC nanofibers, the AFD values were calculated as 540 ± 130 nm, 750 ± 125 nm and 1450 ± 310 nm for water, DMF and DMAc based systems, respectively. On the other hand, the AFD were determined as; 1665 ± 435 nm for

vanillin/HP γ CD-IC (water) and 3510 $\pm$ 930 nm for vanillin/HP γ CD-IC (DMF). As it is observed, the vanillin/HP γ CD-IC nanofibers have significantly higher fiber diameter values compared to vanillin/HP β CD-IC nanofibers, and this is originated from the higher viscosity value of vanillin/HP γ CD-IC solutions that leads to less stretching, so thicker fiber formation during the electrospinning. The more viscous characteristic of HP γ CD solutions probably arise from the bigger HP γ CD aggregates size [130]. In addition, the lower conductivity of the HP γ CD systems compared to HP β CD solutions can be the other effective factor about the thicker HP γ CD fibers [130]. Even, for vanillin/HP γ CD-IC nanofibers obtained in DMAc, we only observed bead structures and could not be able to obtain nanofibers. The reason for this situation can be possibly the extremely high viscosity (Table 11) and low conductivity [130] of DMAc systems that did not allow the morphology transition from beads to the fiber structures because of the inadequate stretching during the process. Otherwise, vanillin/M β CD-IC nanofibers have AFD values, 210 $\pm$ 330 nm, 1070 $\pm$ 490 nm and 1285 $\pm$ 350 nm for water, DMF and DMAc solvents, respectively. The viscosity of vanillin/M β CD-IC solutions are higher than vanillin/HP β CD-IC solutions, however, AFD are not considerably different from each other. This is probably due to the higher conductivity of M β CD solutions compared to HP β CD ones, that eliminate and dominate the effect of higher viscosity level and provide more stretching of electrospinning jet[130].

Table 11. Properties of the vanillin/CD-IC solutions and the resulting nanofibers.

Solutions	% CD (w/v)	Viscosity (Pa.s)	Average fiber diameter (nm)	Fiber diameter range (nm)
vanillin/HP β CD-IC-water	160	0.1040	540 $\pm$ 130	195-1950
vanillin/HP β CD-IC-DMF	120	0.3850	750 $\pm$ 125	230-1750
vanillin/HP β CD-IC-DMAc	120	0.6700	1450 $\pm$ 310	425-1990
vanillin/HP γ CD-IC-water	160	0.2200	1665 $\pm$ 435	565-2980
vanillin/HP γ CD-IC-DMF	125	0.6130	3510 $\pm$ 930	1320-5200
vanillin/HP γ CD-IC-DMAc	125	1.8500	-	-
vanillin/M β CD-IC-water	160	0.1600	155 $\pm$ 100	50-550
vanillin/M β CD-IC-DMF	160	0.8200	1070 $\pm$ 490	150-3880
vanillin/M β CD-IC-DMAc	160	1.0100	1285 $\pm$ 350	650-1920

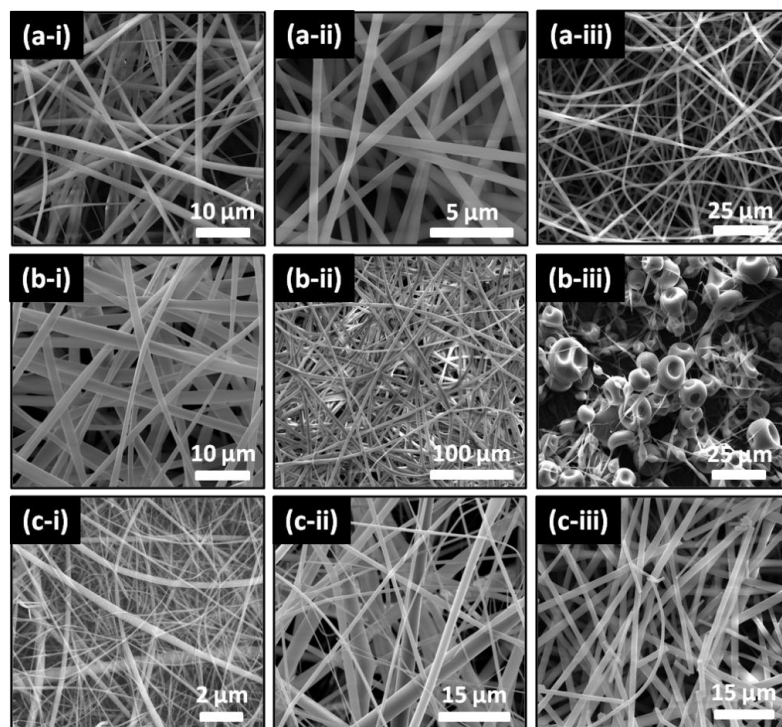


Figure 47. Representative SEM images of electrospun (a) vanillin/HP β CD-IC, (b) vanillin/HP γ CD-IC and (c) vanillin/M β CD-IC nanofibers obtained in (i) water, (ii) DMF and (iii) DMAc.

7.2. Structural characterizations and solubility investigation of vanillin/CD-IC nanofibers

After we have obtained vanillin/CD-IC nanofibers from all solvent systems (water, DMF and DMAc), we have selected IC nanofibers produced in water to investigate the water solubility of nanofibers that is an essential issue for the food applications. Depending on this, we have performed the structural characterization for water based IC nanofibers before the solubility test to determine the differences between these CD types in terms of IC efficiency and thermal properties.

The FTIR spectra of the electrospun vanillin/CD-IC nanofibers and pure vanillin are depicted in Figure 48. We observe prominent absorption peak at around 1020, 1070 and 1150 cm^{-1} that correspond to the coupled C–C/C–O stretching vibrations and the anti-symmetric stretching vibration of the C–O–C glycosidic bridge of CD molecules, respectively for vanillin/CD-IC nanofibers [42, 97]. On the other hand, the FTIR spectrum of pure vanillin exhibited characteristic peaks at

1510, 1590, and 1665 cm^{-1} corresponding to stretching absorption of benzene ring and stretching of C=O of the aldehyde group[214]. All vanillin/CD-IC nanofibers spectrum include the characteristic absorption bands of vanillin demonstrating the existence of vanillin inside the CD-IC nanofibers (Figure 48). Besides, inclusion complexation can cause some shift to the higher/lower wavenumber of compounds characteristic peaks at the FTIR spectra [42, 133, 192]. We have also observed small shifts for the characteristic peaks of vanillin in FTIR spectra of vanillin/CD-IC nanofibers as shown in Figure 48. So, the host-guest interactions between CD cavity and vanillin in nanofiber structures were proved by FTIR study.

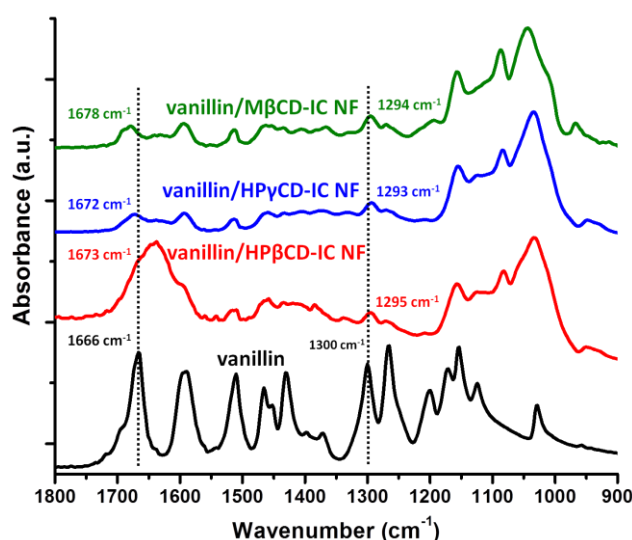


Figure 48. FTIR spectra of pure vanillin and vanillin/CD-IC nanofibers obtained in water.

XRD measurements were performed to investigate the crystalline structure of vanillin/CD-IC nanofibers (Figure 49(a)). Vanillin is a crystalline material having a distinct diffraction centered at $2\theta=13^\circ$ (Figure 49(a)). On the other hand, the XRD graphs represent that the vanillin/CD-IC nanofibers have amorphous pattern just like uncomplexed HP β CD, HP γ CD and M β CD nanofibers [130]. This proves the inclusion complexation between vanillin and CD (HP β CD, HP γ CD and M β CD), because the encapsulation of vanillin molecules inside the CD cavity prevent the formation of crystalline structure by separating guest molecules from each other [42, 97]. The DSC thermograms of pure vanillin and vanillin/CD-IC nanofibers were depicted in Figure 49(b). There is a melting point at 82 $^\circ\text{C}$ for pure vanillin at its

graph, on the other hand, the DSC spectrum of IC nanofibers do not show any endothermic peak at this point, so DSC also suggest the fully complexation of vanillin with CD (HP β CD, HP γ CD and M β CD) just like XRD (Figure 49(b)).

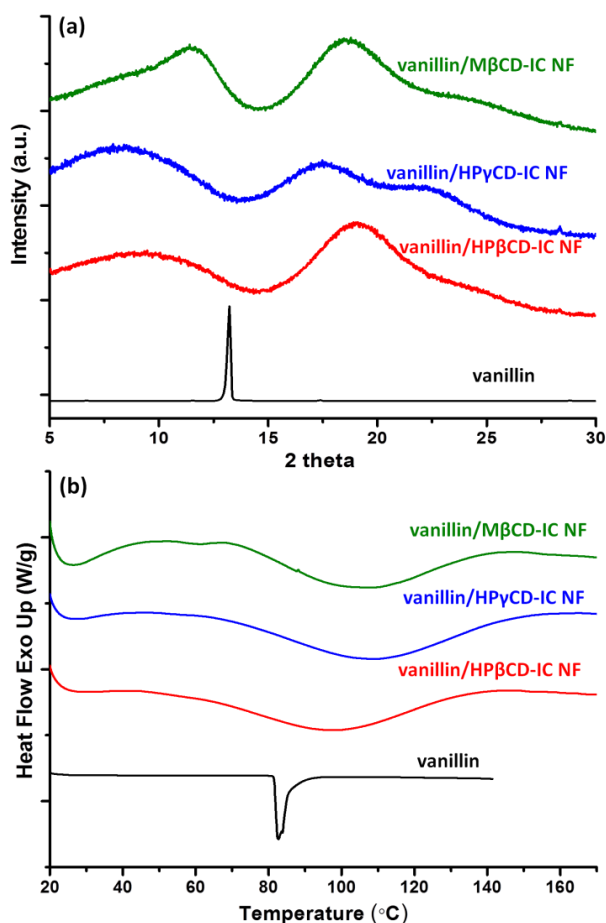


Figure 49. (a) XRD patterns and (b) DSC thermograms of pure vanillin and vanillin/CD-IC nanofibers obtained in water.

Figure 50 depicts the TGA thermograms of pure vanillin powder and vanillin/CD-IC nanofibers. The thermal evaporation/degradation of vanillin started at about 80°C (Td onset) and continued till 195 °C showing that vanillin has a volatile nature. The TGA thermograms of vanillin/CD-IC nanofibers are composed of three main stages of weight losses between 25 °C and 400 °C; the initial weight loss below 100 °C is due to water loss, the second weight loss between 150 and 250 °C is due to the evaporation/degradation of vanillin, and the major weight loss above 300 °C corresponds to the main thermal degradation of CD (Figure 50). The degradation of

pure vanillin complete at about 195 °C, however, in the case of vanillin/CD-IC it is shifted to higher temperature confirming that the thermal stability of vanillin increased due to inclusion complexation with CD. For vanillin/HP β CD-IC nanofibers and vanillin/HP γ CD-IC nanofibers, the degradation is over at about 240 °C and 245 °C, respectively suggesting the complexation. On the other hand, there is an additional weight loss step for vanillin/M β CD-IC nanofibers apart from other three stages (Figure 50). The degradation of vanillin is observed in two steps in the case of M β CD based IC nanofibers; the initial step is slightly higher than the degradation of vanillin, the second step completed at about 270 °C. So it can be considered that, the M β CD form IC in two different way with vanillin and this situation can be demonstrated by modeling study. Furthermore, the second type of complexation between vanillin and M β CD is much stronger in comparison to other CDs, since the thermal degradation of complexed vanillin is delayed to extremely higher temperature (270 °C) as regards to HP β CD and HP γ CD. The amount of vanillin in CD-IC nanofibers was calculated as ~8.5%, ~8.7% and ~11.9% (w/w, with respect to CD) for vanillin/HP β CD-IC, vanillin/HP γ CD-IC and vanillin/M β CD-IC, respectively, which slightly lower compared to the initial amount of vanillin (9.8%, ~9.2% and ~12%, respectively) used for the complex formation. This finding indicates that, the most of guest molecules formed IC and they were preserved owing to complexation. At the same time, ¹H NMR analysis was also performed to determine the vanillin content in the IC nanofibers in terms of molar ratio. The molar ratio of vanillin:CD are calculated as; 0.7:1, 0.8:1 and 0.95:1 for vanillin/HP β CD-IC, vanillin/HP γ CD-IC and vanillin/M β CD-IC, respectively. The calculated molar ratio are faintly lower than the initial 1:1 molar ratio, which was also supported by the TGA analysis. As TGA and NMR data confirmed, very few amount of vanillin could not be preserved during electrospinning or storage in vanillin/CD IC nanofibers.

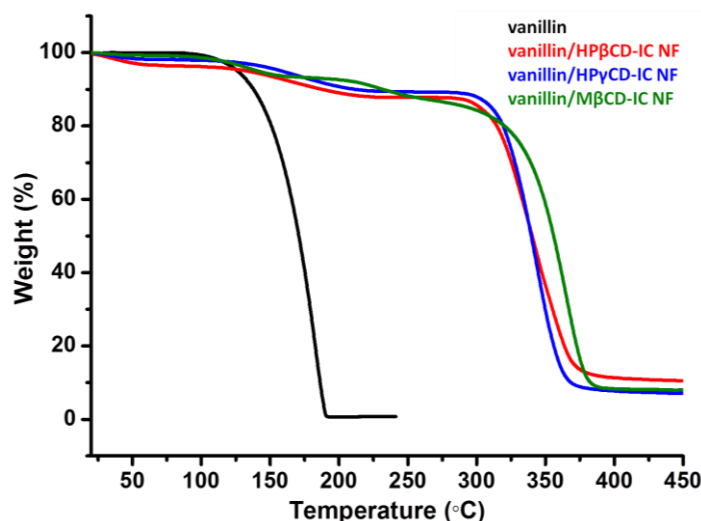


Figure 50. TGA thermograms of pure vanillin and vanillin/CD-IC nanofibers obtained in water.

Vanillin is a widely used compound in food industry as flavor/fragrance agent. Its solubility is not so low; however it can be considered limited depending on the purpose and this can be a drawback during its usage. Here, in addition to thermal property enhancement, the solubility of the vanillin is also improved by forming IC with CD molecules. The solubility of the vanillin encapsulated in CD-IC nanofibers was determined by HPLC technique. For this purpose, the pure vanillin and the IC nanofibers which include the same concentration (20 mg/mL) of vanillin are dissolved in water. While the vanillin/CD-IC nanofibers were solved in water immediately, there were still vanillin powders in the pure vanillin solution even after stirring over-night. The HPLC results of the filtrated solution of pure vanillin and vanillin/CD-IC nanofibers demonstrated that, in the case of pure vanillin, the solubility value is at 10.2 ± 0.02 mg/mL correlated with the literature limit. Otherwise, the solubility of vanillin encapsulated in vanillin/CD-IC nanofibers were determined as; 20.6 ± 0.2 , 21.6 ± 0.7 and 20.4 ± 0.2 for vanillin/HPβCD-IC, vanillin/HPγCD-IC and vanillin/MβCD-IC, respectively. These results revealed that, we have obtained a full dissolution for the vanillin that we used during the test and the water solubility of vanillin was improved remarkably owing to inclusion complexation. It can also be expected that, as the higher amounts of nanoweb are dissolved during the solubility test, we may detect much more solubility enhancement for vanillin.

In this part, the electrospinning of nanofibers from vanillin/CD-IC were achieved without using a carrier polymeric matrix. The IC solutions were prepared by using three CD types (HP β CD, HP γ CD and M β CD) in three different solvent systems (water, DMF and DMAc). Except the vanillin/HP γ CD-IC nanofibers produced in DMAc, all IC nanofibers were obtained with uniform morphology. After morphological characterization, vanillin/CD-IC nanofibers produced in water were chosen for the further analysis and water solubility test. Since, the water based systems are more suitable for the food applications owing to non-toxic nature of the solvent. FTIR, XRD, DSC and TGA analyses demonstrated the existence of vanillin in nanofibers and IC formation between vanillin and CD (HP β CD, HP γ CD and M β CD). Besides, ^1H NMR technique was used to determine the molar ratios between vanillin and CD. As a result of the analyses, only slight decrease was observed at initial amount of vanillin after the electrospinning, so approximately all vanillin was protected in IC nanofibers due to the inclusion complexation. While 5% (w/w, with respect to polymer) vanillin content was provided in the previous PVA study[31], here it reached to almost 10% (w/w, with respect to CD) without disturbing the electrospinning process. So we have shown that, the amount of active compound can be significantly increased by the direct electrospinning of IC systems. Furthermore, solubility test indicate that, the water solubility of vanillin can be provided at least double times higher compared to pure vanillin by the inclusion complexation. In the previous part, we mentioned the electrospinning of antibacterial triclosan/CD-IC nanofibers without using polymeric matrix. In this study, we have produced IC nanofibers of vanillin which is a widely using food ingredient as flavor/fragrance. Hence, the vanillin/CD-IC nanofibers would be rather attractive in food applications along with the non-toxic nature of CD and high surface area of electrospun nanofibers. Moreover, vanillin/CD-IC was turned into more applicable form by the electrospinning, compared to its powder state with the uppermost active agent content and improved solubility.

8. Electrospinning of Polymer-free Nanofibers from Essential Oils/Cyclodextrin Inclusion Complexes

Essential oils (EOs) are aromatic products which are extracted from natural plants and contain a huge number of components (thymol, eugenol, citral, camphor, cineole, cymene, geraniol etc.) [106, 215]. These molecules represent several significant properties such as; antibacterial, antifungal, antioxidant, anti-inflammatory, antiseptic, antiviral, anticancer, insect repellent, as well as flavor/fragrance [215, 216]. Owing to written features, these functional compounds are widely used in food manufacturing (flavoring and preservation), cosmetic (soaps, colognes, perfumes, etc.) and medical purposes [216, 217]. However, their high volatility and reactivity cause limitations during their use especially in food applications.

Cyclodextrins (CD) are also able to form inclusion complexes (IC) with EOs [106, 218-220]. The molecular encapsulation of these components in the CD cavity provide solubility enhancement, stability against oxidation, light, heat, chemicals or modification at taste and odor [90, 91, 95, 218-220]. So, CD are commonly employed for the food application to improve the stability (evaporation, degradation and oxidation) and product shelf-life of the sensitive ingredients. On the other hand, electrospun nanofibers, particularly produced by using biodegradable and edible polymers[86, 221, 222], also have great potential for the functional and smart food applications along with their large surface area, nanoscale porosity, and high encapsulation efficiency. So, the incorporation of these nanofibers with the active agents (essential oils) extremely improves their performance depending on the required features [6, 223-225]. From this point of view, the addition of cyclodextrin inclusion complexes (CD-IC) into electrospun nanofibers can be more functional due to the integration of unique properties of nanofibers with the specific properties of CD-IC. In the related studies of our research group, we have reported the electrospinning of menthol/CD-IC [226, 227], vanillin/CD-IC [31] , eugenol/CD-IC [40] and geraniol/CD-IC [41] incorporated polymeric nanofibers. We have

demonstrated that, prolonged shelf-life and high thermal stability are provided for the menthol, vanillin, eugenol and geraniol in the ultimate nanofibers.

In our recent study, we have eliminated the polymeric template and produced nanofibers from EOs/CD-IC without using a carrier polymer matrix. Thus, we have assumed to obtain more proper materials for the food applications along with the non-toxic and edible nature of CD. For this, six types of EO (thymol, eugenol, citral, camphor, cineole and cymene) and three different CD types (hydroxypropyl- β -cyclodextrin (HP β CD), hydroxypropyl- γ -cyclodextrin (HP γ CD) and methyl- β -cyclodextrin (M β CD)) were used for the production of IC nanofibers. Scanning electron microscope (SEM) characterization was performed for the morphology analysis of obtained nanowebs. Moreover, Fourier transform infrared spectrometer (FTIR), thermogravimetric analyzer (TGA) and X-ray diffractometer (XRD) were used to prove the existence of EOs and host-guest IC formation. The molar ratios between EOs and CD were calculated by using proton nuclear magnetic resonance (^1H NMR) technique.

8.1. Electrospinning of EOs/CD-IC nanofibers

From our previous studies, we have determined the optimum concentrations of HP β CD, HP γ CD and M β CD for formation of bead-free nanofiber (*see 2.2.1.*) [130]. Here, we used the same concentration (160% CD, w/v) for the electrospinning of EOs/CD-IC systems and we have successfully obtained bead-free nanofibers from all IC systems. In this study, we have prepared IC solutions from all EO compounds (thymol, eugenol, citral, camphor, cineole and cymene) for each CD types (HP β CD, HP γ CD and M β CD). On the other hand, while we have achieved to produce IC nanofibers of thymol, eugenol and citral for three types of CD (HP β CD, HP γ CD and M β CD), we were able to produce IC nanofibers of camphor, cineole and cymene for two types of CD; HP β CD and HP γ CD. Since, the IC solutions of M β CD precipitated during the process for camphor, cineole and cymene, so we could not manage to obtain nanofibers from these systems. Figure 51 and 52 display the representative SEM images of EOs/CD-IC nanofibers. As it is seen, uniform, bead-free nanofibers with smooth morphology were attained for all samples.

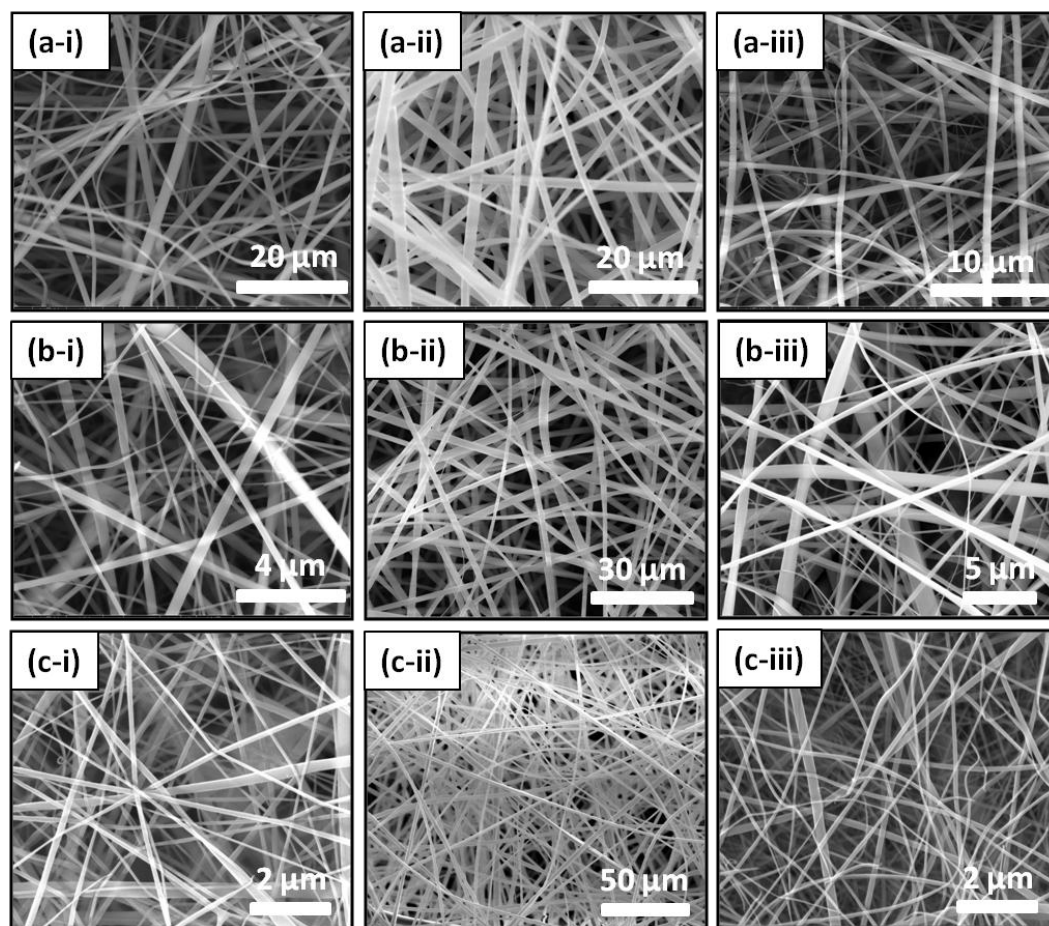


Figure 51. Representative SEM image of electrospun nanofibers obtained from IC of (a) thymol, (b) eugenol and (c) citral with (i) HP β CD, (ii) HP γ CD and (iii) M β CD.

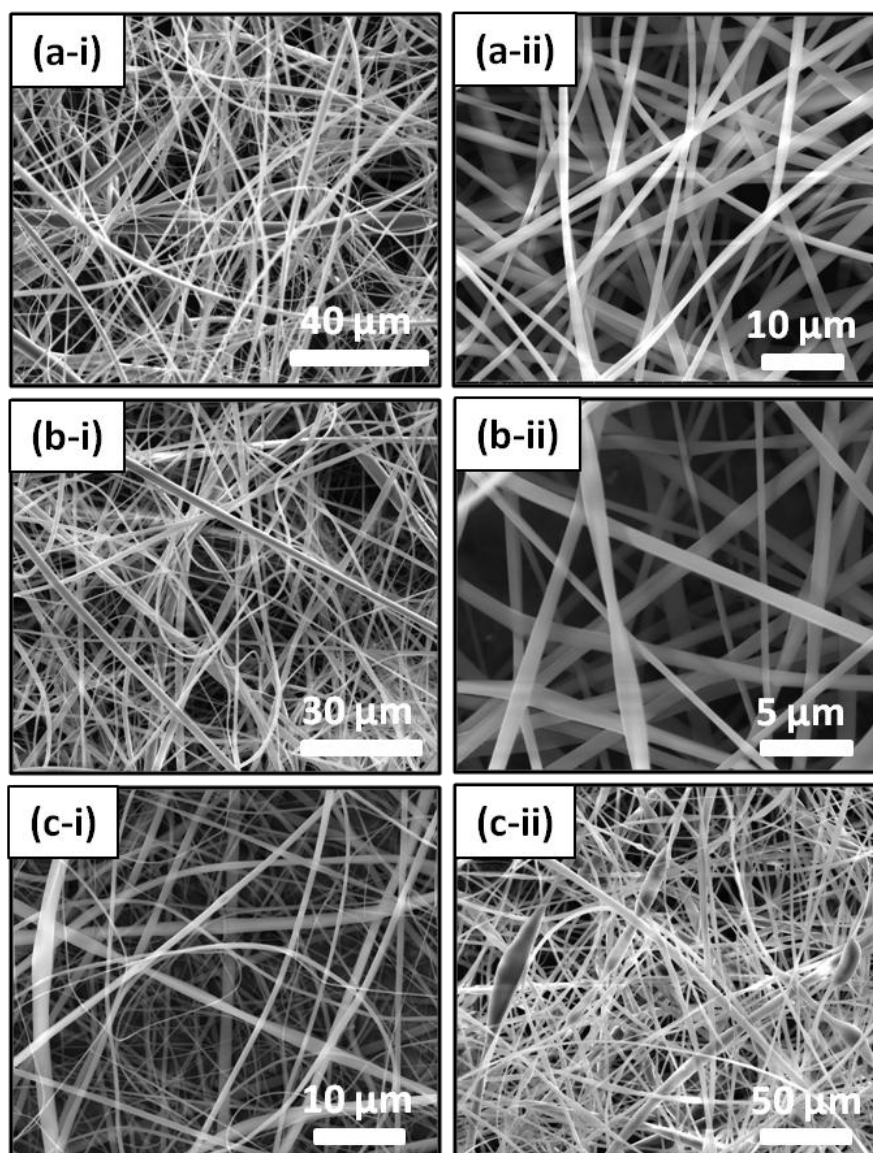


Figure 52. Representative SEM image of electrospun nanofibers obtained from IC of (a) camphor, (b) cineole and (c) cymene with (i) HP β CD and (ii) HP γ CD.

8.2. Structural and thermal characterizations of EOs/CD-IC nanofibers

The structural and thermal characterizations of the EOs/CD-IC nanofibers were carried out by using FTIR, ^1H NMR, XRD and TGA techniques. The FTIR spectra of the electrospun EOs/CD-IC nanofibers and pure EOs are depicted in Figure 53. For all, EOS/CD-IC nanofibers we observe prominent absorption peak at around 1020, 1070 and 1150 cm^{-1} that correspond to the coupled C–C/C–O stretching vibrations

and the anti-symmetric stretching vibration of the C–O–C glycosidic bridge of CD molecules, respectively [42, 97]. All EOs/CD-IC nanofibers spectrum indicate the characteristic absorption bands of related EOs which they include and this situation proves the existence of these functional agents inside the CD-IC nanofibers (Figure 53). In company with the inclusion complexation, some characteristic peaks of organic compounds can shift to the higher/lower wavenumber at the FTIR spectra [42, 133, 192]. From this point of view, we have also observed small shifts for the characteristic EOs peaks in FTIR spectra of EOs/CD-IC nanofibers as depicted in Figure 53. So, we can say that, the FTIR study proved the presence of host-guest interactions between CD cavity and EOs in EOs/CD-IC nanofibers samples.

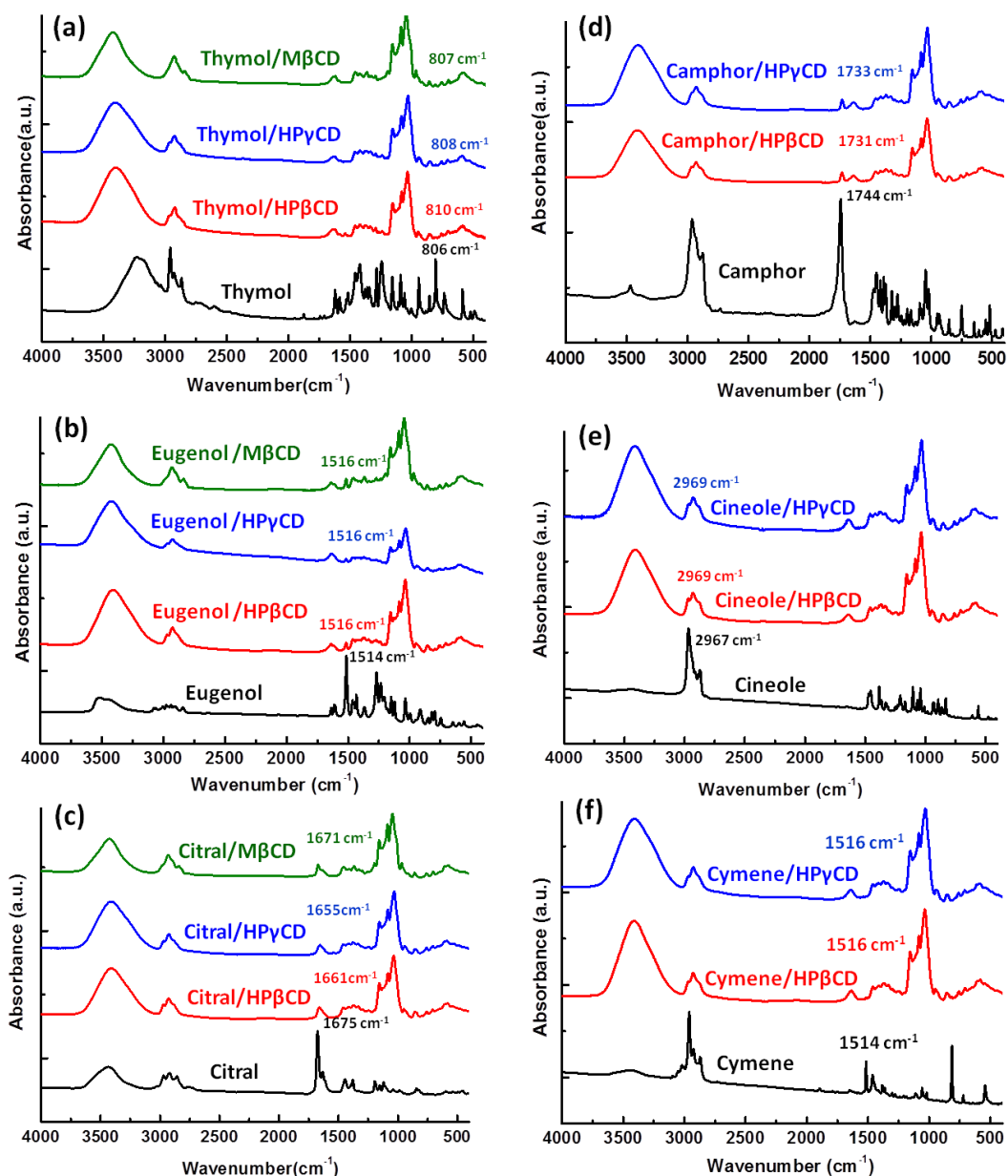


Figure 53. FTIR spectra of pure EOs and the EOs/CD-IC nanofibers of (a) thymol, (b) eugenol, (c) citral, (d) camphor, (e) cineole and (f) cymene with HPβCD, HPγCD and MβCD.

TGA is useful technique to detect the inclusion complexation between guest molecule and CD. Figure 54 shows the TGA thermograms of pure EOs and EOs/CD-IC nanofibers. For IC nanofibers, the weight loss observed at about 350 °C corresponds to main thermal degradation of CD molecules. The additional weight loss of the thermograms belongs to the evaporation/degradation of EOs in the nanofiber structures. When we compare the degradation temperature of pure EOs

with the EOs included in the nanofibers, we have observed significant shifts to the higher temperature for the Td onset (eugenol) or Td maximum (thymol, citral, camphor, cineole and cymene) values of the EOs (Figure 54). This situation also suggests the complex formation between EOs and CD molecules.

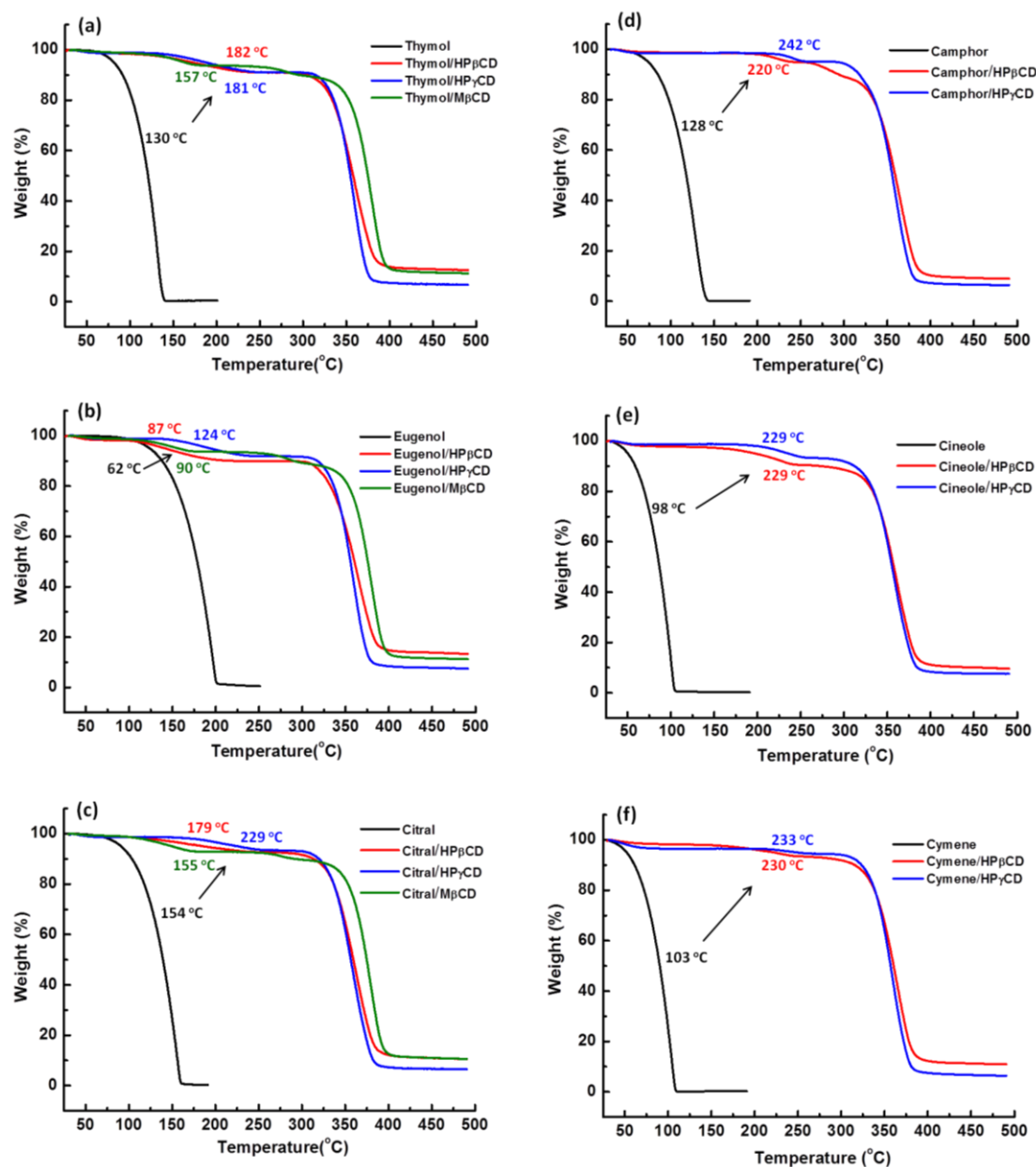


Figure 54. TGA thermograms of pure EOs and EOs/CD-IC nanofibers of (a) thymol, (b) eugenol, (c) citral, (d) camphor, (e) cineole and (f) cymene with HPβCD, HPγCD and MβCD.

^1H NMR technique was used to indicate the presence of EOs in nanofibers and to determine the molar ratio between EOs and CD (HP β CD, HP γ CD and M β CD). The molar ratio was calculated by integrating the peak ratio of the characteristic chemical shifts (δ) corresponding to EOs and CD by using the NMR software. The calculation results of molar ratios for all EOs/CD-IC nanofibers are listed at Table 12. It was found that, the molar ratio values of thymol/CD nanofibers are almost agrees with the initial 1:1 mixing ratio in the solution. This shows that thymol was fully complexed with CD and its loss was protected by inclusion complexation during the electrospinning process. On the other hand, in the case of eugenol, camphor and cineole, the molar ratio between EOs and CD are lower compared to initial ratio (1:1) (Table 12). This situation is probably originated from some uncomplexed EOs in EOs/CD-IC suspension that could not be effectively preserved and some amount of them lost during the electrospinning process and/or during storage. Even, these molar ratios significantly decrease to lower value for citral and cymene due to their more volatile nature compared to other EOs.

Table 12. The molar ratio values and the percentage conversions (% (w/w)) of EOs:CD calculated from ^1H NMR measurements.

	Thymol/CD	Eugenol/CD	Citral/CD	Camphor/CD	Cineole/CD	Cymene/CD
HPβCD	0.88/1 (8.6%)	0.69/1 (7.5%)	0.25/1 (2.7%)	0.64/1 (6.5%)	0.61/1 (6.3%)	0.50/1 (4.5%)
HPγCD	1.00/1 (8.7%)	0.66/1 (6.4%)	0.25/1 (2.4%)	0.89/1 (7.5%)	0.72/1 (6.6%)	0.40/1 (3.3%)
MβCD	1.00/1 (10.2%)	0.94/1 (10.5%)	0.46/1 (5.0%)	-	-	-

The XRD measurement was only performed for thymol and camphor based samples which have crystalline structure that we can easily examine by XRD technique. Figure 55 shows the XRD pattern of pure thymol, camphor and EO/CD-IC nanofibers. The uncomplexed HP β CD, HP γ CD and M β CD nanofibers show amorphous structure just like their powder forms [130]. The similar amorphous XRD patterns were also observed for thymol/CD-IC and camphor/CD-IC nanofibers owing

to complexation between CD and EO molecules, since guest molecules are separated from each other inside the CD cavity so they cannot form crystal structure [42, 97].

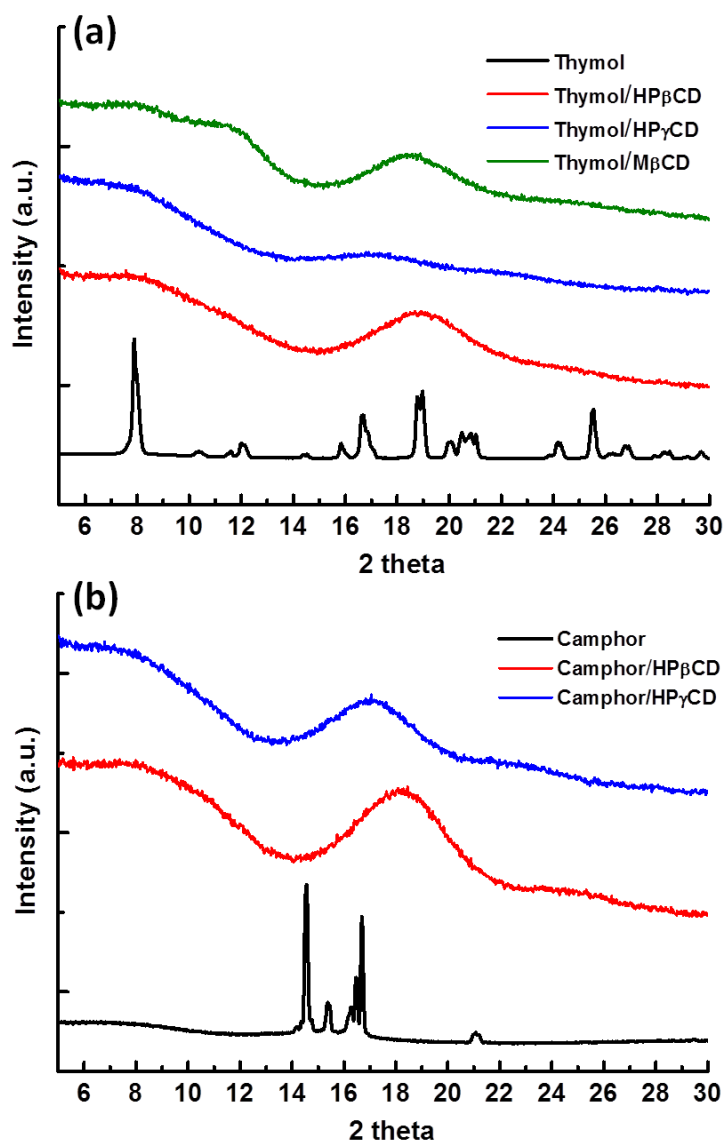


Figure 55. XRD patterns of pure thymol, camphor and their IC nanofibers.

In this study, the electrospinning of nanofibers from EOs/CD-IC were achieved without using a carrier polymeric matrix. Here, the IC systems were formed by using six types of EO (thymol, eugenol, citral, camphor, cineole and cymene) and three different types of CD (HPβCD, HPγCD and MβCD). While all CD (HPβCD, HPγCD and MβCD) were used to produce IC nanofibers from thymol, eugenol and citral, we could not obtain nanofibers from the IC of MβCD for camphor, cineole and

cymene because of the precipitation occurred during the IC formation. The uniform and bead-free morphology of nanofibers were represented by the SEM characterization. In addition, FTIR, TGA and XRD analyses proved the existence of EOs in nanofibers and host-guest IC formation between EOs and CD. Moreover, the molar ratios between EOs and CD were calculated by using ^1H NMR technique. Electrospun CD-IC nanofibers are very fascinating materials due to the integration of very large surface area of the nanofibers with specific functionalities of guest molecules. In one of our previous study, we produced IC nanofibers by using an antibacterial agent; triclosan as a guest molecule and we proved the application potential of these nanowebs by the antibacterial tests against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. In other previous study, we have achieved the production vanillin/CD-IC nanofibers with high solubility property which is a very promising material for the food application purposes. This time, we have produced CD nanofibers from the IC of essential oils which are obtained from the plant by the extraction and well-known with their antiseptic, anesthetic, antimicrobial, antibacterial, antioxidant and flavor/fragrance property. So, the obtained nanofibers would be quite applicable in active and smart food applications depending on the required property along with the non-toxic nature of CD. In addition, the nanofiber type of CD-IC eliminates the use challenges that are originated from their powder form and render them into more applicable state with the highest active agent content and improved solubility. By the elimination of the polymeric carrier matrix, the resulting nanofibers become also edible which is not so possible for the polymer based nanofibers except edible ones (gelatin, starch).

CHAPTER-3: CYCLODEXTRIN NANOFIBERS INCORPORATING METAL NANOPARTICLES

9. One-step Synthesis of Size-Tunable Silver Nanoparticles (Ag-NP) Incorporated in Electrospun PVA/Cyclodextrin Nanofibers

Electrospun nanofibers have design flexibility for particular functionalization which can be performed during the electrospinning process or by applying post-treatment methods. For instance, functional composite nanofibers can be produced by incorporation of metal nanoparticles (NP) into electrospun polymeric nanofibers [228-230]. However, the size and homogeneous distribution of metal NP through the nanofiber matrix should be taken into consideration to achieve high efficiency and effective performance from these nanofibrous composite materials. For example, silver nanoparticles (Ag-NP) have attracted considerable attention due to their unique optical, electronic, catalytic and antibacterial properties [231-233]. Depending on this, functional nanofibrous composites can be obtained by combining the unique properties of nanofibers with that of Ag-NP [229, 234-236]. Yet, the size control and uniform distribution of Ag-NP without aggregation in the polymeric nanofiber matrix is challenging, therefore, a number of different approaches were followed for obtaining electrospun polymer/Ag-NP composite nanofibers [229, 237-240]. However, in these approaches silver salt precursor was directly added to the polymer solution and the synthesis of Ag-NP was carried out through thermal [237] chemical [229, 240] and radiolytic [238] post-treatment of the electrospun nanofibers. So these above mentioned methods are often complex, time-consuming, and mostly require reducing and stabilizing chemicals which are sometimes highly toxic.

Therefore, simple and environmentally friendly approaches are essential for the practical applications of electrospun nanofibers incorporating Ag-NP. For example, one-step synthesis of Ag-NP incorporated in polyethylene oxide (PEO) nanofibers [33] or polyvinyl alcohol (PVA) nanofibers [234] was achieved where the polymer solution was used as both a reducing and protecting agent for Ag-NP and an electrospinning template. In other studies, polymer/Ag-NP composite nanofibers were produced in one-step by using the electrospinning solvent as a reducing agent and the electrospinning polymer matrix as a stabilizing/protective agent [236, 241].

The use of toxic reducing and stabilizing agents for the synthesis of Ag-NP were replaced with so called “green” substances such as natural biomolecules including cellulose, chitosan, polyphenols, ascorbic acid, cyclodextrins (CD) etc. [242-246]. As well, “green” practices started to take their place in the electrospinning process by the use of natural and nonhazardous polymers [234]. Very recently, polymer/CD/AgNO₃ mixtures were electrospun into polymer/Ag-NP composite nanofibers where the CD was used as a stabilizing and reducing agent for the formation of Ag-NP in the polymer matrix [247, 248]. However, polymer used in these studies was dissolved in dimethylformamide (DMF) which is an undesirable solvent type from the point of biomedical applications. On the other hand, CD are natural and non-toxic molecules and they are also very promising candidates for use as reducing and stabilizing agent for the formation of metal NP [246, 249-252].

In this study, we report a one-step synthesis of Ag-NP incorporated into electrospun composite nanofibers [253]. Initially, we used a biocompatible polymer, PVA, as reducing agent to convert silver salt (AgNO₃) into Ag-NP and then we obtained PVA/Ag-NP composite nanofibers via electrospinning. In addition to that, we also used hydroxypropyl-β-cyclodextrin (HPβCD) as both reducing and stabilizing agent to control the size and uniform dispersion of Ag-NP within the electrospun nanofibers. The PVA/HPβCD solution having different amount of HPβCD were prepared to investigate the effect of HPβCD amount on the size of Ag-NP and their dispersion within the nanofiber matrix. It was observed that the size of Ag-NP decreases significantly and homogeneous distribution of Ag-NP without aggregation were achieved in the electrospun PVA/HPβCD nanofibers. The detailed morphological and structural characterizations of the samples were performed by scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffractometer (XRD), UV-vis-NIR spectroscopy, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Surface enhanced Raman scattering (SERS) properties of these electrospun nanofibers incorporating Ag-NP have been investigated. The antibacterial property of Ag-NP is well-known and widely studied [21, 254, 255] Hence, we have also performed antibacterial tests for PVA/Ag-NP and

PVA/HP β CD/Ag-NP composite nanofibrous mats against Gram-negative (*Escherichia coli*) and Gram-positive (*Staphylococcus aureus*) bacteria.

9.1. Electrospinning and morphological characterizations of PVA/Ag-NP and PVA/HP β CD/Ag-NP composite nanofibers

Here, *in situ* reduction of silver nitrate (AgNO₃) into silver nanoparticle (Ag-NP) was achieved in PVA aqueous solution where PVA was acted as reducing agent and stabilizing agent as well as electrospinning polymer matrix for the fabrication of PVA/Ag-NP composite nanofibers. PVA can reduce the Ag⁺ ions into Ag-NP due to the hydroxyl groups on the polymer backbone [234] and also stabilize the Ag-NP by keeping them from aggregation. Yet, in order to control the size and ensure uniform dispersion of Ag-NP in PVA solution, we also used HP β CD as a supplementary reducing and stabilizing agent. The carbohydrates (glucose, starch, etc.) have high potential for the reduction of AgNO₃ to the Ag-NP; however in order to be efficient, NaOH could be added to the system to enhance and accelerate the reduction of Ag⁺¹ to Ag⁰ by releasing the electrons from glucose molecules [145], otherwise, these agents may represent limited reducing effect. So, we have prepared the alkaline conditions by using NaOH (pH ~8.5) to benefit from the reducing potential of HP β CD molecules that have very similar chemical structure with other types of carbohydrates. The concentration of PVA in aqueous solution was adjusted as 7.5% (w/v, with respect to solvent) in order to obtain bead-free and uniform nanofibers by electrospinning. For PVA/HP β CD blend solutions, the concentration of PVA was kept at 7.5% (w/v) and three different concentrations of HP β CD was used; 7.5%, 15% and 25% (w/v). AgNO₃ was added to homogeneous aqueous solutions of PVA and PVA/HP β CD and the dark brown solutions were obtained after overnight mixing indicating the Ag-NP formation in the electrospinning solutions (Figure 56). In each electrospinning solution, the concentration of AgNO₃ was adjusted accordingly to have 1% (w/w, with respect to total PVA or PVA/HP β CD concentration) Ag-NP in the electrospun nanofibers.

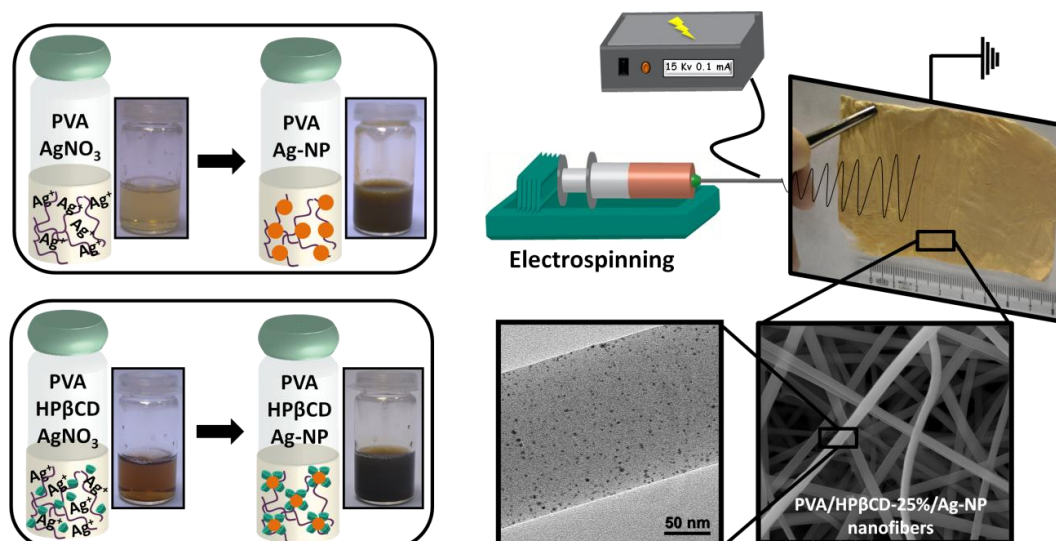


Figure 56. Schematic representation and the photographs of PVA/AgNO₃, PVA/Ag-NP, PVA/HPβCD-25%/AgNO₃ and PVA/HPβCD-25%/Ag-NP solutions. Schematic representation of the electrospinning and the photograph of PVA/HPβCD-25%/Ag-NP nanofibrous mat with the representative SEM and TEM images. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

The electrospinning of PVA/HPβCD/Ag-NP nanofibers was illustrated in Figure 56. The electrospun PVA/HPβCD/Ag-NP composite nanofibrous mats have the characteristic color of Ag-NP and these materials are flexible which can be easily handled as a free-standing mat (Figure 56). The representative SEM images of PVA, PVA/HPβCD, PVA/Ag-NP and PVA/HPβCD/Ag-NP nanofibers were shown at Figure 57 and their AFD were given in Table 13. In all cases, bead-free and uniform nanofibers were obtained elucidating that the concentration and viscosity of the electrospinning solutions were at the optimal level. However, the AFD of the nanofibers were different from each other because of the differences in the viscosity and conductivity values of the solutions (Table 13). In electrospinning, typically high solution viscosity or low solution conductivity yield thicker fibers because of the less stretching of the electrospinning jet [1, 2]. On the contrary, electrospinning of solutions having lower viscosity or higher solution conductivity resulted in thinner fibers because of the more stretching of the electrospinning jet [1, 2]. The electrospun PVA nanofibers have AFD of 290±75 nm and when HPβCD was added to the PVA solution at the highest HPβCD concentration (25%, w/v), PVA/HPβCD-25% nanofibers having AFD of 500±140 nm were obtained. Although the solution

conductivity increased a bit, high solution viscosity of PVA/HP β CD-25% yielded thicker fibers. In the case of electrospun PVA/Ag-NP nanofibers, the AFD decreased to 235 ± 40 nm when compared to PVA nanofibers and this was owing to the presence of Ag-NP which contributed to higher solution conductivity [33] and the viscosity of the solution was also lowered which resulted in more stretching of the electrospinning jet. The PVA/HP β CD/Ag-NP solutions have higher viscosity and conductivity values, in addition, the higher amount of HP β CD, the higher the viscosity of the solutions were obtained and the solution conductivity of the PVA/HP β CD/Ag-NP systems were very close to each other. Therefore, thicker fibers were expected to be produced as the amount of HP β CD increased from 7.5% (w/v) thru 25% (w/v). As expected, we observed that PVA/HP β CD-7.5%/Ag-NP, PVA/HP β CD-15%/Ag-NP and PVA/HP β CD-25%/Ag-NP nanofibers have AFD of 360 ± 70 nm, 400 ± 70 nm and 485 ± 100 nm, respectively.

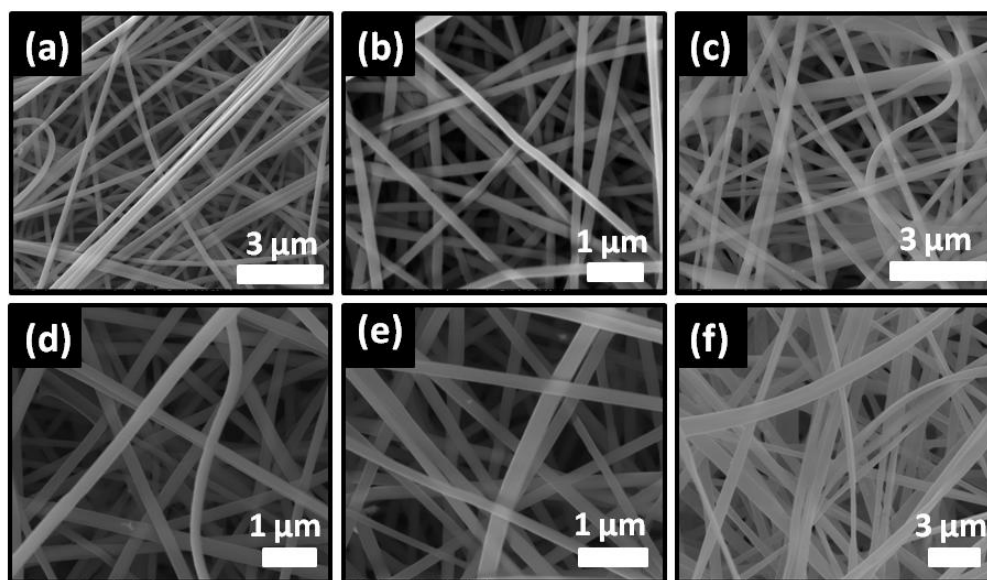


Figure 57. The representative SEM images of electrospun (a) PVA, (b) PVA/HP β CD-25%, (c) PVA/Ag-NP, (d) PVA/HP β CD-7.5%/Ag-NP, (e) PVA/HP β CD-15%/Ag-NP and (f) PVA/HP β CD-25%/Ag-NP nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

Table 13. The properties of the electrospinning solutions and the AFD and the APS of Ag-NP present in the electrospun nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

Sample	Conductivity ($\mu\text{S/cm}$)	Viscosity ($\text{Pa}\cdot\text{s}$)	Average fiber diameter (nm)	Average particle size of Ag-NP (nm)
PVA	525	0.50	290 $\pm$ 75	-
PVA/HP β CD-25%	830	0.60	500 $\pm$ 140	-
PVA/Ag-NP	1415	0.35	235 $\pm$ 40	8.0 $\pm$ 0.5
PVA/HP β CD-7.5%/Ag-NP	1630	0.60	360 $\pm$ 70	2.7 $\pm$ 0.5
PVA/HP β CD-15%/Ag-NP	1625	0.63	400 $\pm$ 70	2.6 $\pm$ 0.5
PVA/HP β CD-25%/Ag-NP	1635	0.70	485 $\pm$ 100	1.8 $\pm$ 0.4

The representative TEM images of PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibers were shown in Figure 58 and the APS of Ag-NP present in the fiber matrix was given in Table 13. Ag-NP were seen as black spherical spots in TEM images of the fiber samples. For PVA/Ag-NP nanofiber sample, the APS of the Ag-NP was 8.0 $\pm$ 0.5 nm but a small number of Ag-NP aggregations were also observed for this sample (Figure 58(a)). On the other hand, it was apparent that Ag-NP have homogenous distribution through the fiber matrix for PVA/HP β CD/Ag-NP samples (Figure 58(b-d)). Additionally, the size of Ag-NP decreases significantly in the PVA/HP β CD/Ag-NP nanofiber samples as the amount of HP β CD increases in the fiber matrix. The APS of the Ag-NP was 8.0 $\pm$ 0.5 nm for HP β CD free PVA/Ag-NP nanofibers whereas the size of the Ag-NP decreased to 2.7 $\pm$ 0.5 nm, 2.6 $\pm$ 0.5 nm and 1.8 $\pm$ 0.4 nm for PVA/HP β CD-7.5%/Ag-NP, PVA/HP β CD-15%/Ag-NP and PVA/HP β CD-25%/Ag-NP nanofiber samples, respectively. Owing to hydroxyl groups, PVA polymer has the ability to reduce Ag salts into Ag-NP, however, with the addition of HP β CD into the PVA solution significant decrease was observed for the size of Ag-NP due to the highly efficient stabilizing and reducing properties of CD molecules [246, 251]. Furthermore, Ag-NP did not aggregate or coagulate locally due to the stabilizing effect of HP β CD that leads to uniform distribution of Ag-NP within the fiber matrix. More importantly, the

size Ag-NP can be controlled by varying the amount of HP β CD, that is, higher the amount of HP β CD, smaller the size of Ag-NP.

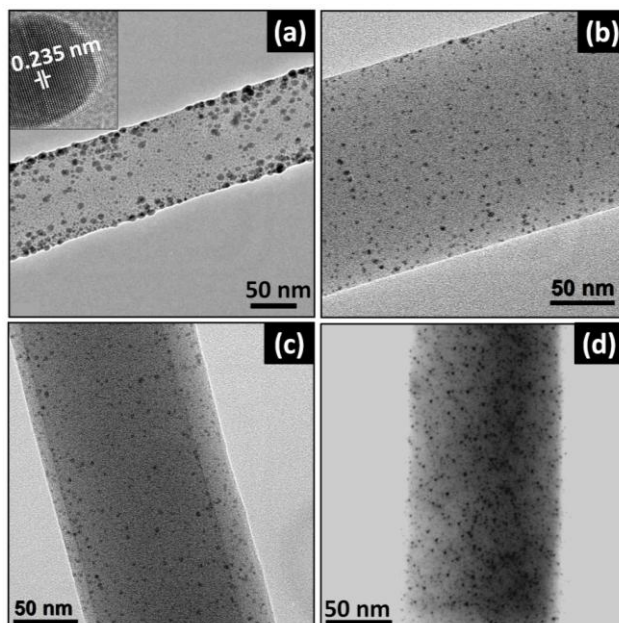


Figure 58. The representative TEM images of electrospun (a) PVA/Ag-NP, (b) PVA/HP β CD-7.5%/Ag-NP, (c) PVA/HP β CD-15%/Ag-NP and (d) PVA/HP β CD-25%/Ag-NP nanofibers. The HR-TEM image of a single Ag-NP indicating the *d*-spacing between Ag (111) planes as inset figure. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253]).

9.2. Structural characterizations of PVA/Ag-NP and PVA/HP β CD/Ag-NP composite nanofibers

The characteristics of Ag-NP were investigated by using HR-TEM and XRD measurements. The representative HR-TEM, given in Figure 58(a) as an inset figure, shows the lattice fringes of Ag-NP in PVA/Ag-NP composite nanofibers and the *d*-spacing was measured to be 0.235 nm from the lattice fringes which corresponded to the lattice spacing of the (111) planes of the fcc Ag [256]. The XRD patterns of the electrospun nanofibrous mats were given in Figure 59. The PVA/Ag-NP sample has diffraction peaks at $2\theta=38.4^\circ$, 44.4° , 64.6° and 77.6° which belong to (111), (200), (220), and (311) crystal planes of Ag, respectively [257, 258]. For PVA/HP β CD/Ag-NP samples same characteristic peaks of elemental Ag were observed, but, there were also additional peaks at $2\theta=28.0^\circ$, 32.4° , 46.4° , 55.0° and 57.9° indicating the

existence of oxidized Ag [258-260]. This is possibly originated from the oxidation of unsaturated outer surface of Ag-NP by the hydroxyl groups of HP β CD molecules [261]. For PVA/HP β CD/Ag-NP samples, we also observed that, as the size of the Ag-NP decreases depending on the increasing amount of HP β CD, the diffraction peak intensities of Ag-NP decreases too.

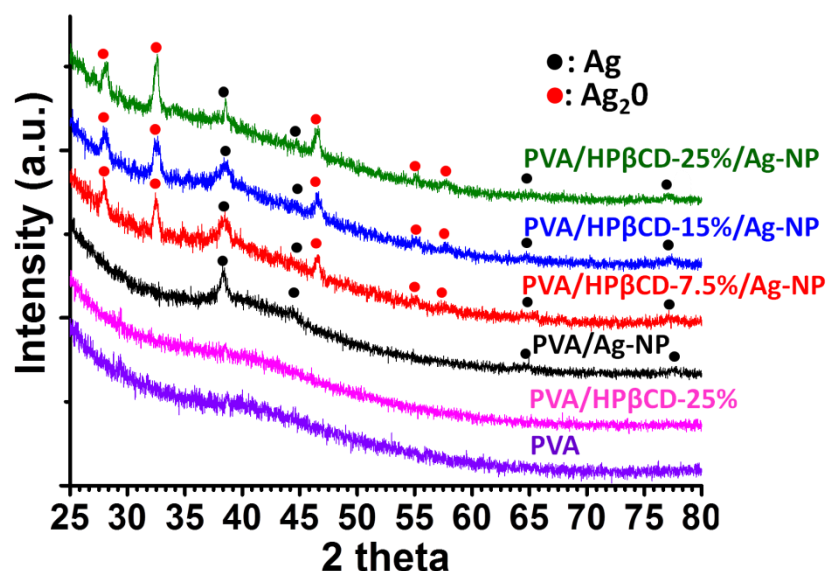


Figure 59. (a) XRD spectra of PVA, PVA/HP β CD-25%, PVA/Ag-NP, PVA/HP β CD-7.5%/Ag-NP, PVA/HP β CD-15%/Ag-NP and PVA/HP β CD-25%/Ag-NP nanofibrous mats. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

The UV-vis absorption measurements of the PVA/Ag-NP and PVA/HP β CD/Ag-NP were obtained from the aqueous solution by dissolving the nanofibrous mats in water (Figure 60). The spectra of all samples show an absorption band in the range of 400-450 nm wavelengths due to the characteristic surface plasmonic resonance (SPR) band for Ag-NP [244, 246]. For PVA/Ag-NP nanofibers the particle size was 8.0 ± 0.5 nm and the maximum absorption value exists at 421 nm. On the other hand, the SPR peak for PVA/HP β CD-7.5%/Ag-NP (APS= 2.7 ± 0.5 nm) was observed at 439 nm. As the HP β CD content increased, blue-shift of absorption peaks to 435 nm and 428 nm for PVA/HP β CD-15%/Ag-NP (APS= 2.6 ± 0.5 nm) and PVA/HP β CD-25%/Ag-NP (APS= 1.8 ± 0.4 nm) were observed, respectively due to the decreasing size of Ag-NP in the fiber matrix. Even though the Ag-NP particle size is distinctively small for the PVA nanofibers

containing HP β CD compared to HP β CD free PVA nanofibers, the absorption peak in the spectrum firstly shows red-shift to the higher wavelength and broadening for PVA/HP β CD/Ag-NP systems. This can be explained by the existence Ag₂O on the Ag-NP that was also proved by the XRD measurements. For the PVA/HP β CD/Ag-NP samples, the Ag₂O layer on the Ag-NP surface results an absorption shoulder in 450-500 nm range and it also causes broadening at the characteristic absorption band of Ag-NP [259].

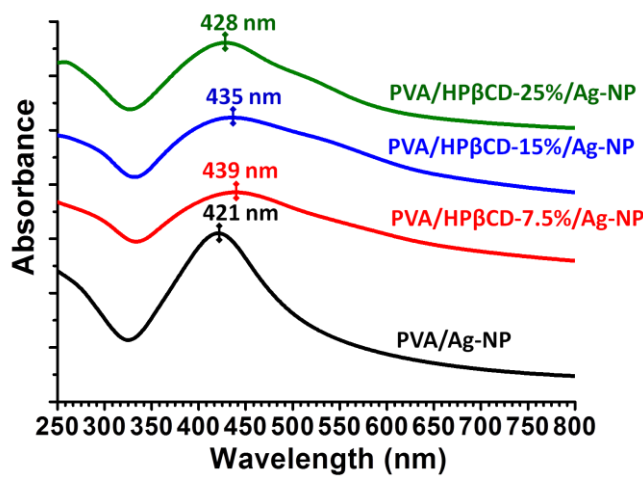


Figure 60. UV-vis spectra taken from the dissolved PVA/Ag-NP, PVA/HP β CD-7.5%/Ag-NP, PVA/HP β CD-15%/Ag-NP and PVA/HP β CD-25%/Ag-NP nanofibers in water. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

Figure 61 shows the XPS spectra of PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibers. The doublet peaks at 368.2 and 374.2 eV are assigned to the binding energies 3d_{5/2} and 3d_{3/2} of Ag 3d core level, respectively [262]. There are merely differences between the binding energy of Ag⁰ and Ag⁺¹, so the ionic type existence cannot be easily noticed from Ag 3d core level which was supported by XRD measurements [257].

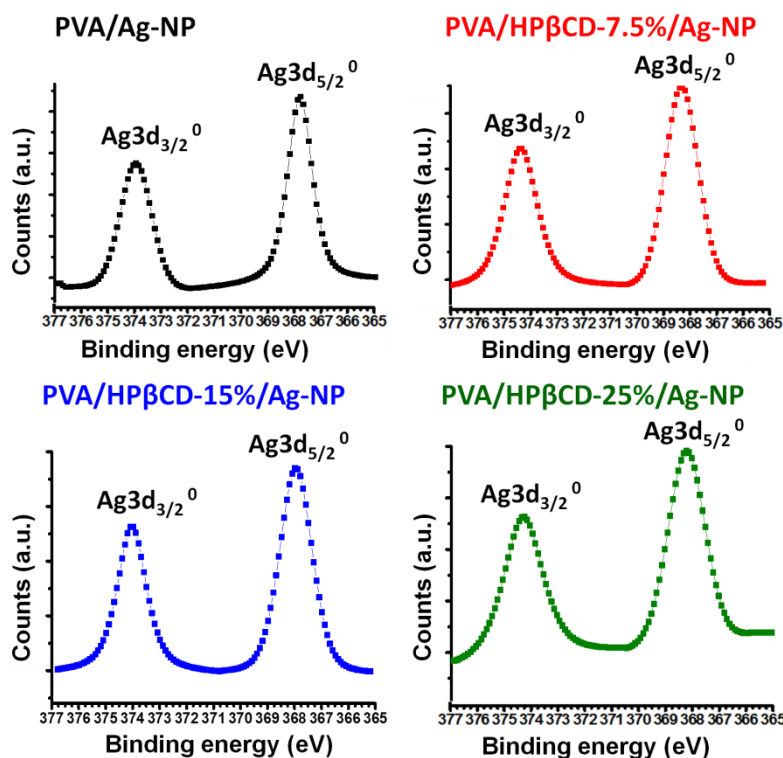


Figure 61. The high resolution XPS of electrospun PVA/Ag-NP, PVA/HPβCD-7.5%/Ag-NP, PVA/HPβCD-15%/Ag-NP and PVA/HPβCD-25%/Ag-NP nanofibers. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

9.3. Surface enhanced Raman scattering (SERS) properties of PVA/Ag-NP and PVA/HPβCD/Ag-NP composite nanofibers

Surface enhanced Raman scattering (SERS) properties of Ag-NP surface-decorated electrospun polymeric nanofibers has been previously demonstrated, resulting in flexible SERS active substrates [263]. We investigated the presence of SERS effects in Ag-NP loaded PVA and PVA/HPβCD nanofibers as shown in Figure 62. Without Ag-NP, the PVA and PVA/HPβCD nanofiber samples exhibited Raman spectra (Figure 62), that are stable in time, even under high excitation powers of 10 mW (Figure 62(b-c)). However, PVA/Ag-NP (Figure 62(d)) and PVA/HPβCD/Ag-NP (Figure 62(e)) nanofibers exhibited fluctuating Raman spectra even at low powers (<1mW) due to the presence of Ag-NP, typical indication of strong SERS effect. Time dependent Raman spectra of PVA/HPβCD-7.5%/Ag-NP sample is given as example in Figure 62(e), but, PVA/HPβCD-15%/Ag-NP and PVA/HPβCD-25%/Ag-NP samples have also shown similar characteristics (data not shown). It has been

also observed that (data not shown), high excitation powers resulted in thermal damage to PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibrous mats due to poor thermal conduction of nanofibers and high absorption of Ag-NP. Fluctuations of the SERS signal for Ag-NP incorporated nanofibers suggest that a thermally activated mechanism is likely to be the source of observed blinking behavior. In short, PVA/Ag-NP and PVA/HP β CD/Ag-NP samples exhibited SERS effect which can be useful for sensing application [263].

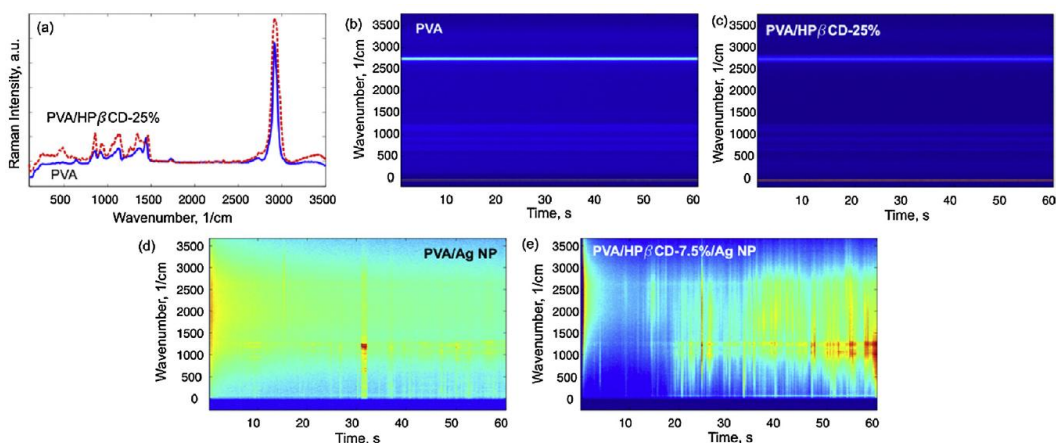


Figure 62. (a) Raman spectra of PVA and PVA/HP β CD-25% nanofibers when illuminated with 532 nm, 10 mW power, 20x objective. (b) Time dependent Raman spectra of pristine PVA nanofibers. (c) Time dependent Raman spectra of PVA/HP β CD-25% nanofibers. When Ag-NP are present in (d) PVA/Ag-NP and (e) PVA/HP β CD-7.5%/Ag-NP nanofibers, time dependent Raman spectra show fluctuations even at low powers (532 nm, 0.5 mW, 20x objective), typical indication of high surface enhancement Raman scattering (SERS). Due to high absorption coefficient and high thermal insulation of free standing fibers, absorption causes thermal damage to sample at high powers (e.g. 10 mW). (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

9.4. Antibacterial properties of PVA/Ag-NP and PVA/HP β CD/Ag-NP composite nanofibers

Here, we investigated the antibacterial effects of PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibrous mats against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. The electrospun PVA and PVA/HP β CD without Ag-NP were also tested for comparison. For the antibacterial test, three samples taken from different locations of the same nanofibrous mat were placed on *E. coli* and *S. aureus* spreaded agar plates

and visualized after incubation for 24 h. The plates were checked for the presence and size of the inhibition zones (Figure 63 and Table 14). We observed that, PVA and PVA/HP β CD nanofibers did not show any antibacterial activity. On the other hand, PVA/Ag-NP nanofibers have shown antibacterial property due to the presence of Ag-NP. Ag-NP has antibacterial property, which is size dependent [255]. So, in the case of PVA/HP β CD/Ag-NP nanofibers, as the size of Ag-NP decreased depending on the HP β CD amount, the inhibition zone became larger indicating enhanced antibacterial activity compared to PVA/Ag-NP nanofibers (Figure 63). Among PVA/HP β CD/Ag-NP samples, the PVA/HP β CD-25%/Ag-NP has shown better antibacterial activity since the Ag-NP has the smallest size in this sample (Table 14). This may be due to the fact that the release of the Ag-NP becomes easier as the particle size decreases, so that Ag-NP can more effectively reach the bacteria region and contact with the bacteria. In addition, owing to the smaller dimensions, higher surface to volume ratios were obtained which also enhances the antibacterial activity of Ag-NP [264, 265]. Similarly, Morones *et al.* reported that bactericidal properties of the Ag-NP are size dependent and smaller Ag-NP were much more effective against Gram-negative bacteria since Ag-NP having a diameter of ~1-10 nm preferentially present a direct interaction with the bacteria [255]. Moreover, we observed that the increase in the inhibition zone was more distinctive for *S. aureus* compared to *E. coli* as the Ag-NP size get smaller and this could be attributed to the cellular wall content differences between Gram-positive and Gram-negative bacteria as discussed by Thiel *et al.* [205].

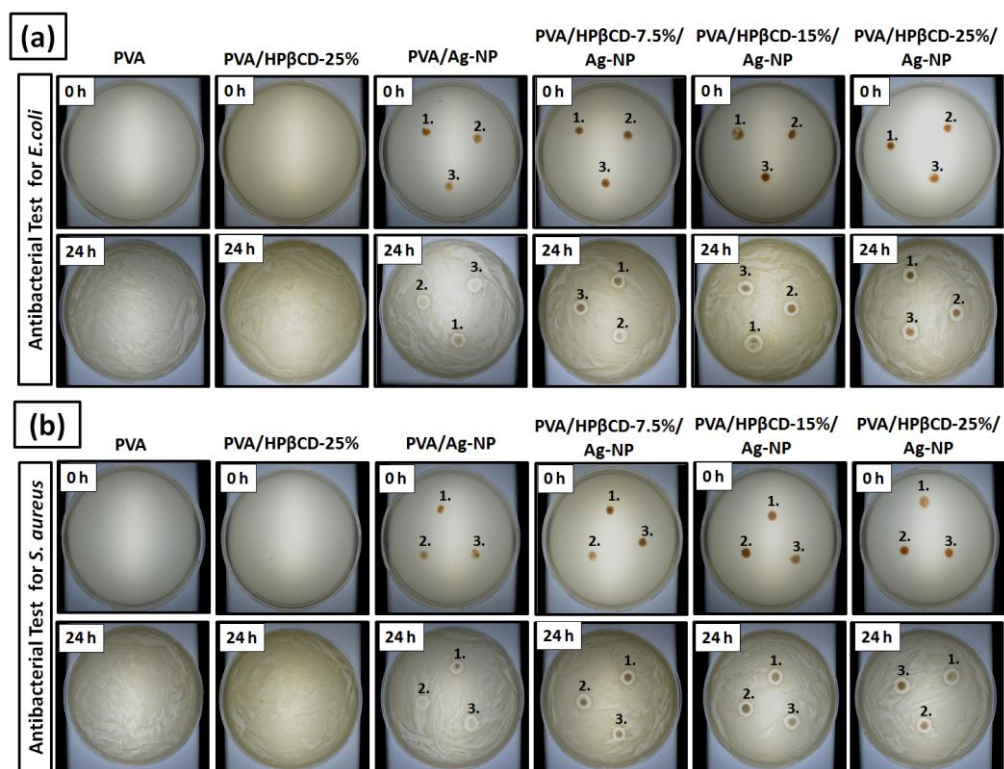


Figure 63. The photographs of antibacterial testing of nanofibrous mats which were performed against (a) *E. coli* and (b) *S. aureus*. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

Table 14. The inhibition zone results taken after 24 h for PVA, PVA/HPβCD-25%, PVA/Ag-NP, PVA/HPβCD-7.5%/Ag-NP, PVA/HPβCD-15%/Ag-NP and PVA/HPβCD-25%/Ag-NP nanofibers against *E. coli* and *S. aureus*. (Copyright © 2014, Elsevier. Reprinted with permission from Ref.[253])

Samples	<i>E. coli</i>		<i>S. aureus</i>	
	0 h (cm)	24 h (cm)	0 h (cm)	24 h (cm)
PVA	0.8	0.8	0.8	0.8
PVA/HPβCD-25%	0.8	0.8	0.8	0.8
PVA/Ag-NP	0.8	1.32±0.00	0.8	1.41±0.15
PVA/HPβCD-7.5%/Ag-NP	0.8	1.55±0.07	0.8	1.62±0.16
PVA/HPβCD-15%/Ag-NP	0.8	1.60±0.03	0.8	1.73±0.21
PVA/HPβCD-25%/Ag-NP	0.8	1.72±0.16	0.8	1.85±0.07

Here, we have achieved one-step synthesis of Ag-NP by reduction of AgNO₃ by using PVA and PVA/HPβCD aqueous solution as reducing and stabilizing medium as well as the electrospinning matrix. For the PVA/Ag-NP

system, Ag-NP with an APS of 8.0 ± 0.5 nm was obtained and a small number of Ag-NP aggregations were observed within the PVA fiber matrix. The size of Ag-NP decreased significantly with the addition of HP β CD to the PVA solution and homogeneous distribution of Ag-NP without aggregation was achieved for the PVA/HP β CD/Ag-NP nanofibers. By increasing the amount of HP β CD in the PVA solution, the size-tunable Ag-NP synthesis was successful owing to the efficient reducing and stabilizing properties of HP β CD. The size of the Ag-NP in PVA/Ag-NP nanofibers was decreased to 2.7 ± 0.5 nm, 2.6 ± 0.5 nm and 1.8 ± 0.4 nm for PVA/HP β CD-7.5%/Ag-NP, PVA/HP β CD-15%/Ag-NP and PVA/HP β CD-25%/Ag-NP nanofibers, respectively. We have observed that, multifunctional PVA/Ag-NP and PVA/HP β CD/Ag-NP nanofibers exhibited SERS effect which might be applicable in sensing applications, in addition, these nanofibrous mats have shown antibacterial effect against *E. coli* and *S. aureus* bacteria. When compared to PVA/Ag-NP, PVA/HP β CD/Ag-NP samples have shown better antibacterial efficiency due to smaller size of Ag-NP. In addition, the PVA/HP β CD-25%/Ag-NP having the smaller Ag-NP has shown better antibacterial efficiency among PVA/HP β CD/Ag-NP samples. In brief, our approach is a “green” and facile method for the fabrication of Ag-NP incorporated functional nanofibrous mats having SERS effect and antibacterial properties. HP β CD is a bio-compatible and non-toxic oligosaccharide and the additional use of hazardous reducing/stabilizing agent for the formation of Ag-NP can be eliminated by using HP β CD. Furthermore, polymer matrix such as PVA is also known for its biocompatible nature and suitable for biomedical applications. Therefore, these electrospun PVA/HP β CD/Ag-NP nanofibrous mats can be quite applicable as a wound healing material, in sensing or other biomedical uses.

10. Green and One-step Synthesis of Metal Nanoparticles Incorporated in Electrospun Cyclodextrin Nanofibers

Metal nanoparticles (NP) have received great attention due to their unique optical, chemical and electronic properties along with their wide range of promising applications in photonics, biomedicine, catalysis, sensing and nanoelectronics, etc. [231, 266]. A variety of approaches can be used for the synthesis of metal NP and the most common one is the wet chemical method by using appropriate reducing agent and stabilizer or templates in order to obtain NP from their salt precursors [233, 267-269]. The wet chemical methods for the synthesis NP are sometimes quite complex, time-consuming, or require strict synthetic conditions and the use of hazardous reducing and stabilizing chemicals, therefore, simple and versatile approaches for the synthesis of size and shape controlled uniform NP are always desired for the practical applications. So, recent studies are more focused on developing environmentally friendly and economically viable methods for the synthesis of NP as well as other nanomaterials. Especially, the revelation of the reducing and stabilizing potential of some biomolecules, accelerate “green” practices for these synthesis. For instance, some biomolecules have been used as environmentally friendly so-called “green” reducing and capping agents for the synthesis of NP. As an alternative to toxic reducing and stabilizing agents, “green” approach was reported by using naturally-occurring macromolecules such as chitosan [242], cellulose [243], cellulose nanocrystal [270] or natural water soluble polyphenols [230, 244, 271] which can be utilized as both reducing agent and stabilizing agents for the synthesis of metal NP. Furthermore, cyclodextrins (CD), which are naturally occurring supramolecular structure, can be used as an effective stabilizing/reducing agent for the size-controlled fabrication of NP from different metal types such as gold, [246, 250, 272-275] silver, [107, 246, 275] palladium [251, 252, 276] and platinum [249].

As it is mentioned before, it is fairly easy to improve the functionality of the electrospun nanofibers by incorporating metal NP which have various applications due to their unique sensing, optical, catalytic and antibacterial properties [33, 67, 74, 75, 82]. In our previous study, we have achieved one-step synthesis of Ag-NP

incorporated into electrospun composite nanofibers by using polyvinyl alcohol (PVA), and hydroxypropyl- β -cyclodextrin (HP β CD) as both reducing and stabilizing agent to control the size and uniform dispersion of Ag-NP within the electrospun nanofibers in the increasing amount of CD (*see Chapter 3.; Part 9.*) [253]. This time, we report the green and one-step synthesis of metal NP (Ag-NP, Au-NP and Pd-NP) incorporating electrospun CD nanofibers without using a carrier matrix by eliminating the polymeric template. For the electrospinning of HP β CD/NP nanofibers, HP β CD was used as reducing; stabilizing agent as well as fiber matrix and no additional chemical was used for the synthesis of metal NP [136]. The composite nanofibers were fabricated by using two different solvent systems (dimethylformamide (DMF) and water) and two different NP loadings (1 wt% and 2 wt%). The detailed structural characterizations of HP β CD/NP nanofibers were performed by scanning electron microscope (SEM), transmission electron microscope (TEM), scanning transmission electron microscope (STEM), UV-vis-NIR spectrophotometer; X-ray diffractometer (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectrometer (FTIR). In addition, the application potential of Pd-NP incorporating nanofibers was investigated for catalyst purposes.

10.1. Electrospinning and characterization of the Ag-NP including HP β CD nanofibers

The uniform Ag-NP incorporated HP β CD nanofibers were obtained from two solvent type (water and DMF) and at two Ag-NP loading concentrations (1 wt% and 2 wt%). The HP β CD concentration in water (160%, w/v) and DMF (120%, w/v) systems were already optimized from our previous study in order to obtain bead-free nanofibers (*see 2.2.1*) [130]. Both the electrospinning solution and ultimate nanofibers have the characteristic color of Ag-NP (Figure 64). Figure 65 indicates the SEM images of uniform nanofibers. In the case of DMF system, HP β CD/Ag-NP-NF containing 1 wt% and 2 wt% Ag-NP have AFD of 145 ± 45 nm and 210 ± 85 nm in the 50-500 nm and 50-300 nm diameter range, respectively (Figure 66). For water system, the AFD values of HP β CD/Ag-NP-NF were 190 ± 125 nm (60-600 nm) and

220±160 nm (60-600 nm) for 1 wt% and 2 wt% Ag-NP, respectively (Figure 66). It was noticed that, HP β CD/Ag-NP-NF obtained in DMF has thinner fiber diameters compared to that of water based nanofibers and this can be originated from the higher concentration of HP β CD solution used for water system. Moreover, as the loading weight of Ag-NP increase from 1% to 2 wt%, the AFD of nanofibers increase merely. Actually, there are slight differences between AFD of nanofibers and this is most probably because of some differences in solution properties such as concentration and viscosity [1].

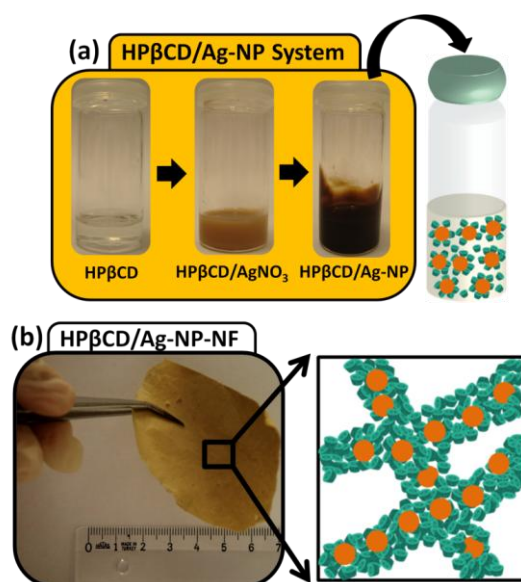


Figure 64. The photographs and the schematic view of (a) the electrospinning solution and (b) the nanofibrous mat which include Ag-NP and having the characteristic color of NP.

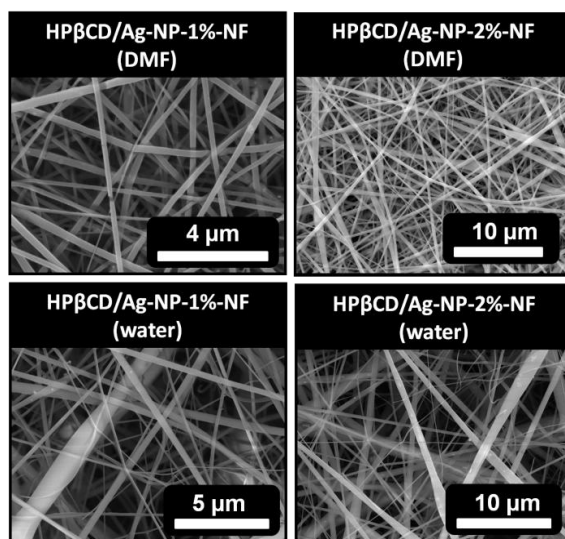


Figure 65. The representative SEM images of electrospun composite nanofibers that were produced in DMF and water at the 1 wt% and 2 wt% Ag-NP concentrations.

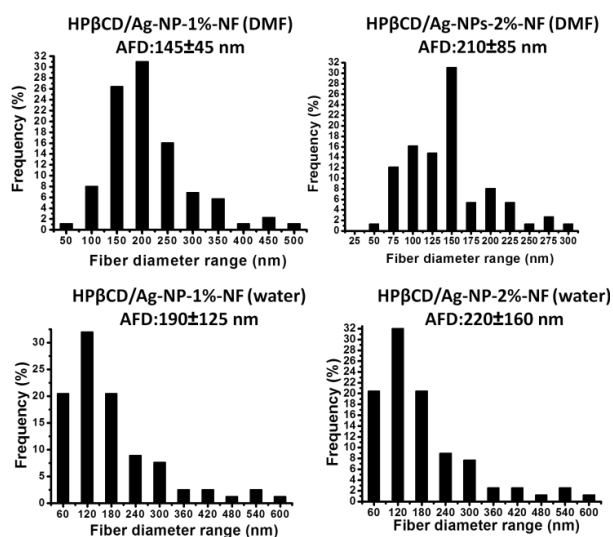


Figure 66. The histograms of fiber diameter distributions and average AFD of HPβCD/Ag-NP-NF.

The TEM, STEM images and APS distributions are shown in Figure 67, 68, 69, respectively. The homogenous dispersion through the HPβCD nanofibers matrix and the narrow size distributions of Ag-NP were easily absorbed from the TEM and STEM micrograms. The APS and the PSD of Ag-NP were determined from TEM images and the variations were observed at these values depending on the wt% loading of NP and the solvent type used. The APS of the Ag-NP in HPβCD/Ag-NP-1%-NF and HPβCD/Ag-NP-2%-NF obtained from DMF were calculated as 3.5 ± 1.0

nm and 4.8 ± 1.4 nm, respectively. On the other hand, the Ag-NP has APS of 1.9 ± 0.5 nm for HP β CD/Ag-NP-1%-NF and 2.3 ± 0.5 nm for HP β CD/Ag-NP-2%-NF for water based system (Figure 69). As it is seen, when the loading of Ag-NP was increased from 1 wt% to 2 wt%, the NP size got larger for both of solvent systems because the Ag atom potential is higher for 2wt% loading in solutions which join the nucleation during the Ag-NP formation and results in bigger NP [277]. In addition, the smaller Ag-NP were obtained in water-based systems compared to DMF ones, and this can be originated from the higher HP β CD concentration of water system that supplies more efficient stabilization and thus smaller Ag-NP.

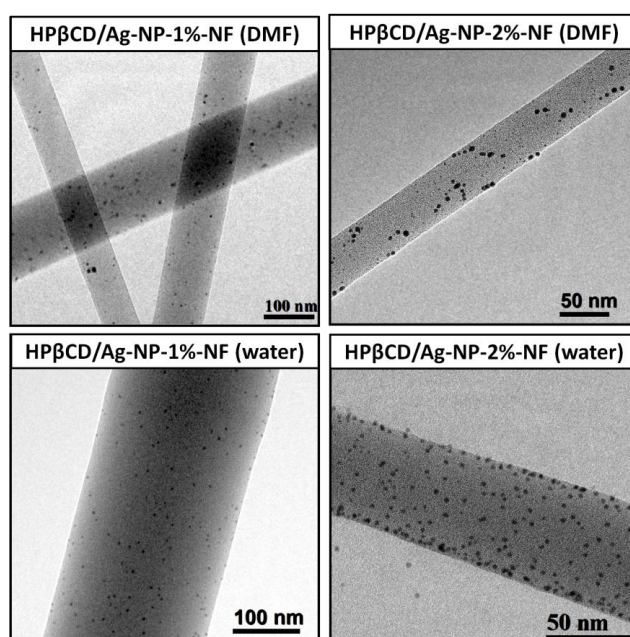


Figure 67. The representative TEM images of electrospun composite nanofibers that were produced in DMF and water at the 1% and 2% Ag-NP concentrations.

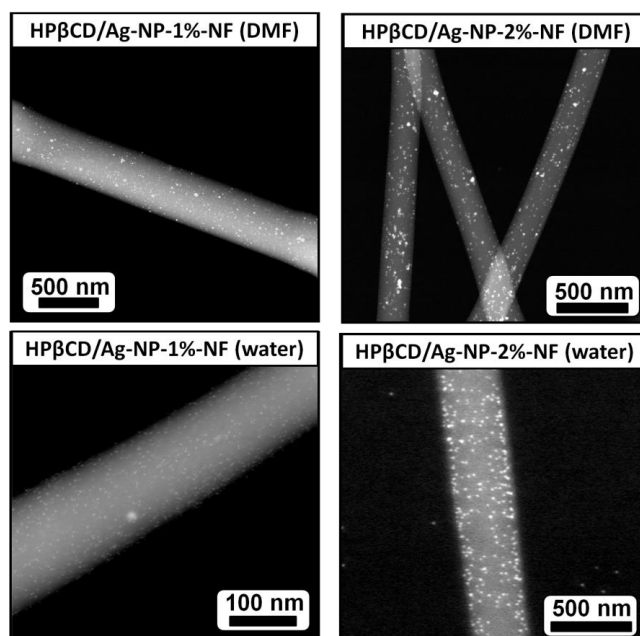


Figure 68. The representative STEM images of electrospun composite nanofibers that were produced in DMF and water at the 1 wt% and 2 wt% Ag-NP concentrations.

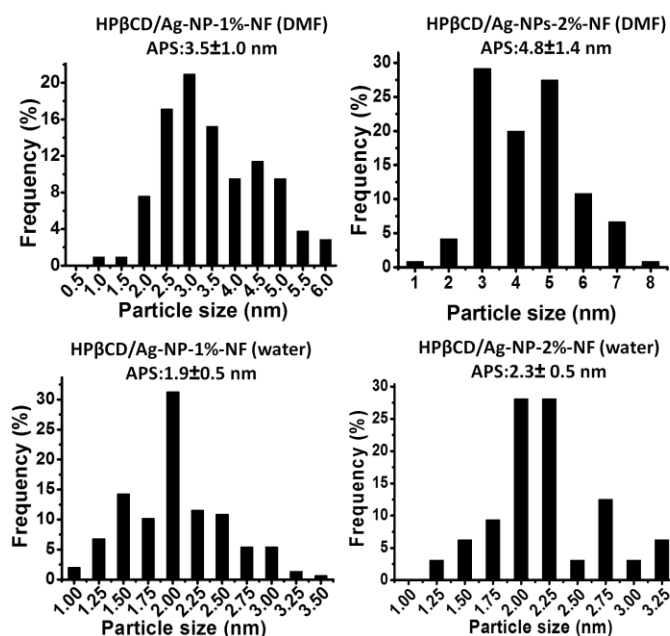


Figure 69. The histograms of APS and their distributions of Ag-NP present in HPβCD/Ag-NP-NF.

The crystalline nature of Ag-NP was confirmed by HR-TEM and XRD measurements. HR-TEM images of Ag-NP which were taken from 2 wt% Ag-NP

loaded samples of DMF and water-based systems were dispatched in Figure 70. It was revealed from the HR-TEM, Ag-NP were polycrystalline and the *d*-spacing was 0.235 nm between lattice fringes which corresponded to the lattice spacing of the (111) planes of the fcc Ag-NP [246, 256, 257]. The XRD spectra of nanofibers were shown in Figure 71 and the broad halo at about $2\theta \approx 18$ is due to HP β CD amorphous structure for all samples [130]. The diffraction patterns that belong to (111), (200), (220) and (311) crystal planes of Ag are observed at $2\theta = 38.3^\circ$, 44.3° , 64.6° and 77.6° , respectively [258]. Moreover, there are additional peaks at $2\theta = 28.0^\circ$, 32.4° , 46.4° , 54.8° and 57.7° which are significant and correspond to existing of Ag₂O [259, 260]. The surface silver atoms of Ag-NP are unsaturated so the outer face of NP reactive for the oxidation [261]. The high OH amounts of CD molecules can cause the oxidation of ionic NP, in addition, it can be more easy to be oxidized in the aqueous medium for NP so the peak intensities of Ag₂O are more dominant for the water-based system compared to DMF-based system. Furthermore, the peak intensities are slightly higher for the HP β CD/Ag-NP-NF containing higher loading of Ag-NP (2 wt%).

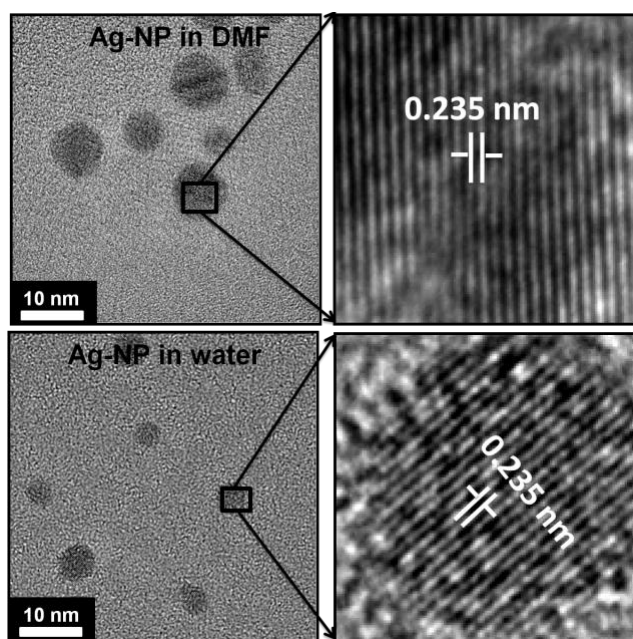


Figure 70. The representative TEM and HR-TEM images of Ag-NP obtained at DMF (2 wt% NP loading) and water (1 wt% NP loading) based system of HP β CD solutions.

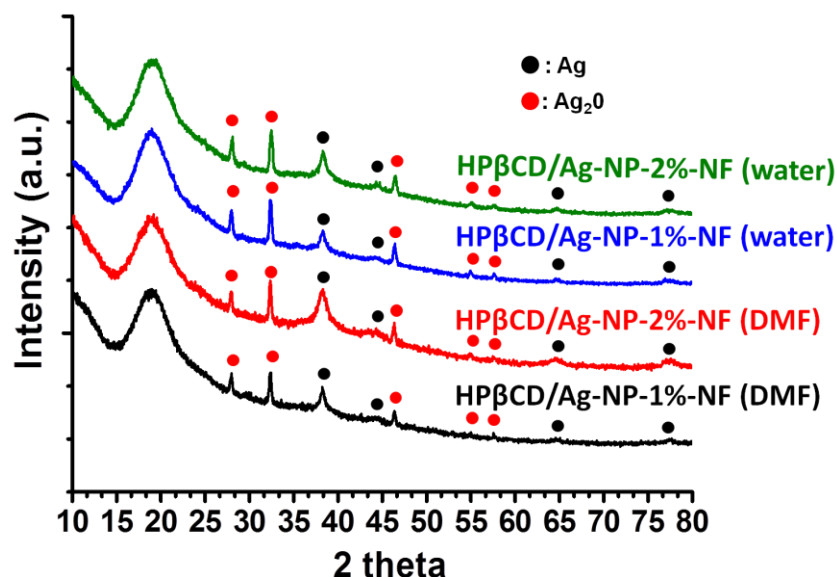


Figure 71. The XRD spectra of electrospun HPβCD/Ag-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt % and 2 wt %).

The solid-state UV-vis absorption spectra of the electrospun HPβCD/Ag-NP-NF are displayed in Figure 72. The characteristic surface plasmonic resonance (SPR) band of metallic Ag-NP displays absorption peaks in the range of 400-450 nm wavelengths for 2 to 50 nm sized NP [244, 275]. In HPβCD/Ag-NP-NF, we observed intense absorption band at about 405-415 nm confirming the successful formation of Ag-NP in the HPβCD nanofibers. In the case of 2 wt% Ag-NP loading concentrations, the SPR band of Ag-NP undergoes to the red-shift due to the growing size of particles [145]. So when the 1 wt% Ag-NP loaded HPβCD nanofibers indicate λ_{max} at about 405 nm, the absorption peaks slightly red-shifted to the 415 nm for the 2 wt% Ag-NP loaded HPβCD nanofibers.

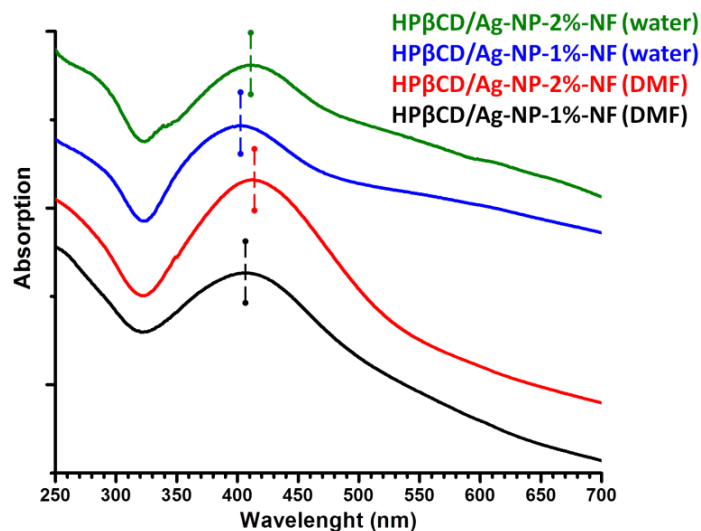


Figure 72. The solid UV-vis spectra of electrospun HPβCD/Ag-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt % and 2 wt %).

Moreover, FTIR study have proved the interaction between HPβCD molecules and Ag-NP by shifts of HPβCD' -OH stretching mode to the lower absorption band (almost 10 cm^{-1}) (Figure 73). The presence of HPβCD molecules around Ag-NP and their interaction can be originated from the oxidized surface of Ag-NP and -OH groups of HPβCD and this provides the stabilization of Ag-NP by inhibiting the particle growing and aggregation during the NP formation.

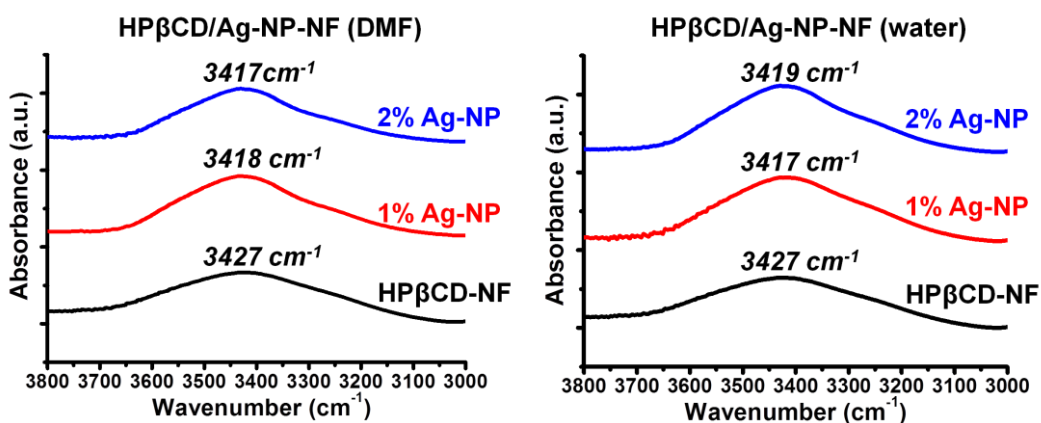


Figure 73. The FTIR spectra of HPβCD-NF and HPβCD/Ag-NP-NF obtained in water and DMF. The zoom out region between $3800\text{--}3000\text{ cm}^{-1}$ at the -OH stretching mode range of HPβCD molecule.

The structural characterizations of Ag-NP in HP β CD nanofibers matrix were also carried out by XPS measurement (Figure 74). The XPS spectra of HP β CD/Ag-NP-NF for the Ag 3d core level have the doublet peaks at 368.2 and 374.2 eV which are assigned to the binding energies of 3d_{5/2} and 3d_{3/2}, respectively [262]. The binding energy difference between Ag⁰ and Ag⁺¹ is insignificant, so the ionic type existence cannot be easily noticed from Ag 3d core level [257]. However, the slight negative shifts [278, 279] were observed at the binding energy for the water based samples compared to DMF based ones due to increasing ratio of Ag₂O in the HP β CD/Ag-NP-NF (water) that was also determined from the XRD data (Figure 71).

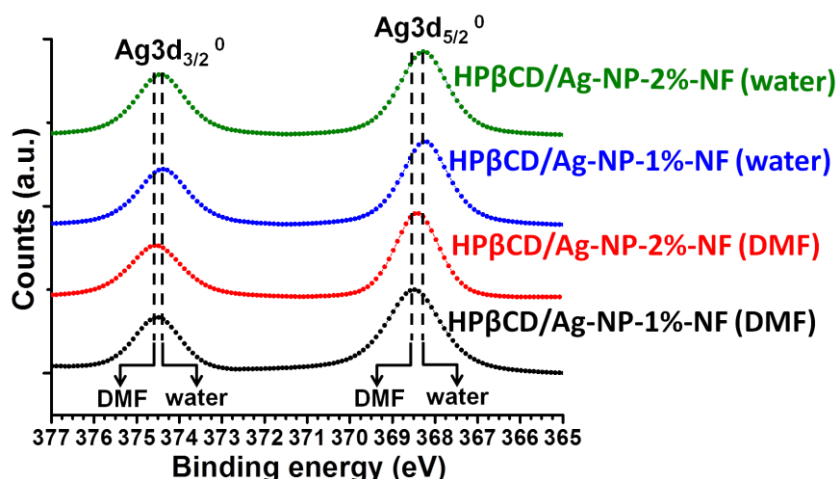


Figure 74. The high resolution XPS of electrospun HP β CD/Ag-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%).

10.2. Electrospinning and characterization of the Au-NP including HP β CD nanofibers

HAuCl₄ was added to highly concentrated HP β CD solution (160% (w/v) in water or 120% (w/v) in DMF). The clear and transparent HP β CD solution became dark purple after mixing over-night indicating the formation of Au-NP (Figure 75(a)). The HP β CD/Au-NP solutions were then electrospun into bead-free nanofibers and the ultimate nanoweb also have the characteristic color of Au-NP (Figure 75(b)). The bead-free HP β CD nanofibers incorporating Au-NP were obtained from both of the

solvent type (water and DMF) and different NP loading (1 wt% and 2 wt%). The SEM images and the AFD distributions of samples are given at Figure 76 and Figure 77, respectively. The HP β CD nanofibers electrospun from DMF solution have AFD of 135 ± 70 nm and 180 ± 60 nm for 1 wt% and 2 wt% Au-NP, respectively. On the other hand, the AFD of water systems were 275 ± 155 nm and 280 ± 170 nm for 1 wt% and 2 wt% Au-NP, respectively. We observed that the HP β CD/Au-NP-NF obtained from DMF solvent system have thinner fiber diameters compared to that of water based system possibly because of the higher concentration of HP β CD solution used for water system. In addition, increasing the weight % of NP from 1% to 2 wt% resulted in slight increase in AFD. In brief, the AFD of samples were not significantly different, but slight variations were observed possibly because of some differences in solution properties such as concentration/viscosity [1].

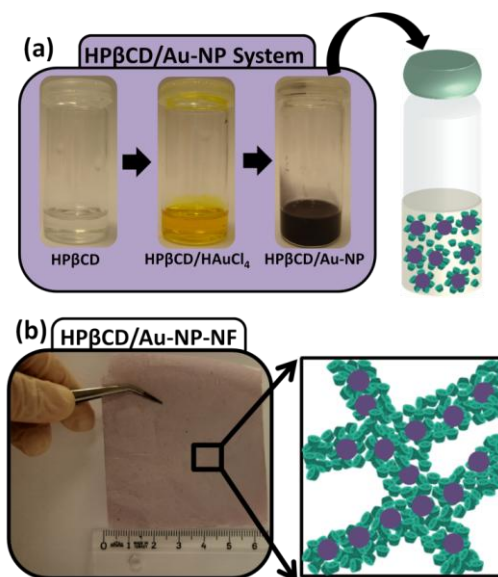


Figure 75. The photographs and the schematic view of (a) the electrospinning solution and (b) the nanofibrous mat which include Au-NP and having the characteristic color of NP. (Copyright © 2013, Royal Society of Chemistry. Reproduced with permission from Ref.[136])

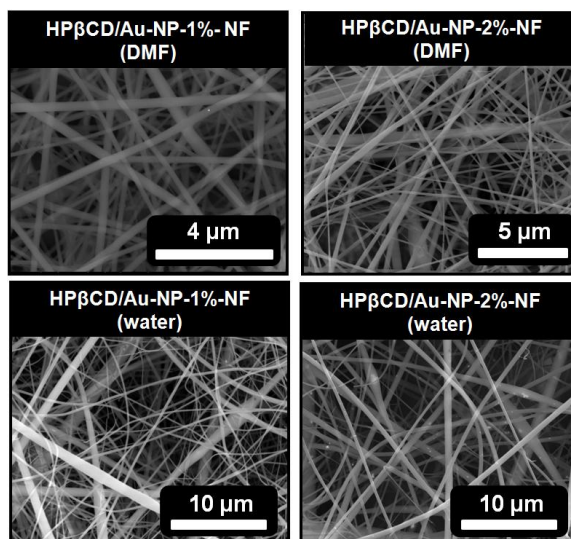


Figure 76. The representative SEM images of electrospun composite nanofibers that were produced in DMF and water at the 1 wt% and 2 wt% Au-NP concentrations. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

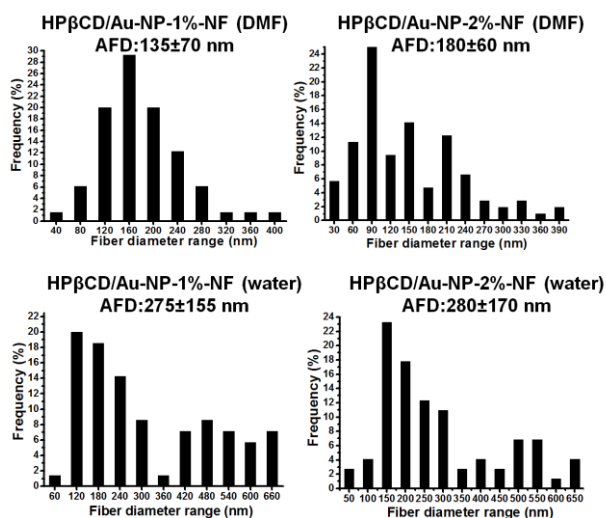


Figure 77. The histograms of average fiber diameter distributions and AFD values of HPβCD/Au-NP-NF. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

The TEM and STEM images and APS distributions of the NP for other samples are given in Figure 78, 79 and 80, respectively. The TEM and STEM images clearly showed that the NP have narrow size distribution and they are homogeneously dispersed in the HPβCD nanofibers matrix without presence of

aggregation except for HP β CD/Au-NP-2%-NF (water) (Figure 78 and 79). The APS and the PSD of the NP were calculated from the TEM images (Figure 80) and they were varied with the wt% loading of NP and the solvent type used. The APS of Au-NP was 8.2 ± 1.8 nm and 9.1 ± 1.4 nm for HP β CD/Au-NP-1%-NF (DMF) and HP β CD/Au-NP-2%-NF (DMF), respectively. In the case of water system, Au-NP has APS of 6.0 ± 1.4 nm for HP β CD/Au-NP-1%-NF. However, for HP β CD/Au-NP-2%-NF, the size of the Au-NP got much bigger having APS of 25.1 ± 11.0 nm and presence of some aggregation was obvious indicating that 2 wt% loading is too much for attaining homogeneously distributed Au-NP in the fiber matrix from water-based system. The NP size got bigger as the loading of Au increased from 1 wt% to 2 wt%. Except for HP β CD/Au-NP-2%-NF (water) in which aggregation occurred, the sizes of the NP are generally smaller for water-based system compared to that of DMF system. One possibility is that water system has higher HP β CD concentration which yielded better stabilization and resulted in smaller NP. On the other hand, we did not come across with the coagulation or local aggregation of Au-NP at higher wt% loading (2 wt%) for the DMF-based system probably due to the reduction ability of DMF [280].

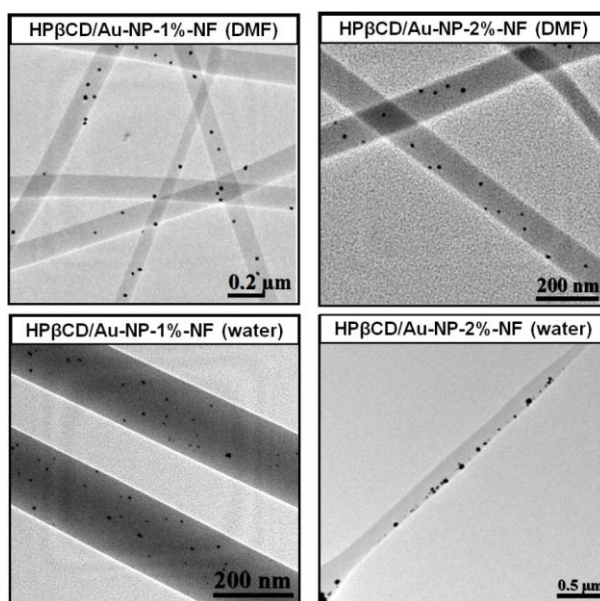


Figure 78. The representative TEM images of electrospun composite nanofibers that were produced in DMF and water at the 1% and 2% Au-NP concentrations. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

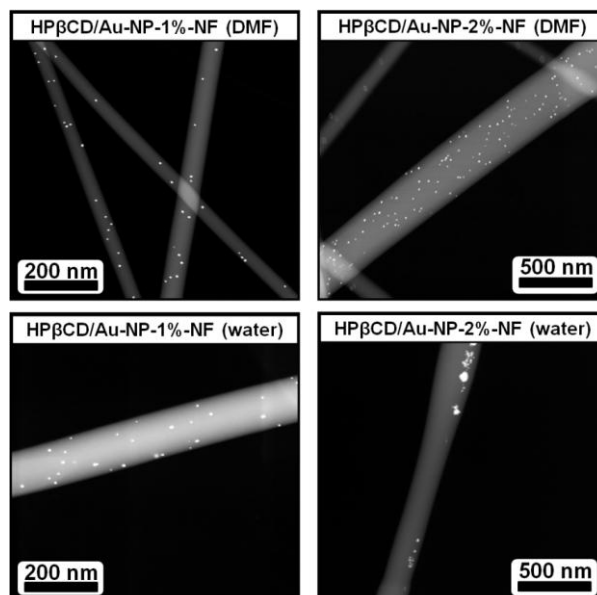


Figure 79. The representative STEM images of electrospun composite nanofibers that were produced in DMF and water at the 1 wt% and 2 wt% Au-NP concentrations. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

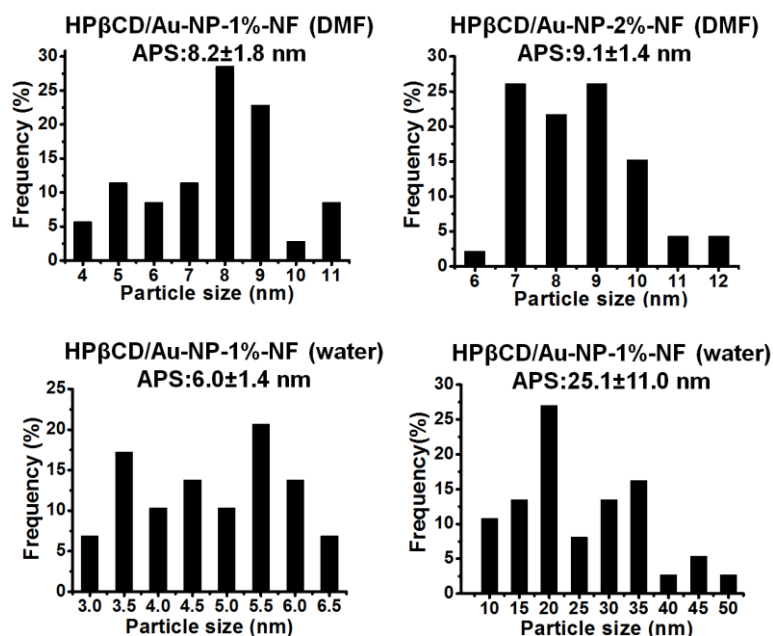


Figure 80. The histograms of APS and their PDS of Au-NP present in HPβCD/Au-NP-NF. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

The crystalline nature of the Au-NP was confirmed by the presence of lattice fringes. From HR-TEM, it was observed that the Au-NP were polycrystalline and *d*-

spacing was measured to be 0.235 nm from the lattice fringes which corresponded to the lattice spacing of the (111) planes of the fcc Au [250] (Figure 81). The crystalline nature of the Au-NP was further confirmed by XRD study. Figure 82 shows XRD patterns of HP β CD/Au-NP-NF and similar to its powder form, the electrospun HP β CD nanofibers having amorphous structure show broad halo in the XRD pattern [130]. For HP β CD/Au-NP-NF, the broad halo having a maximum at $2\theta \approx 18$ is due to HP β CD. The intense diffraction peaks at $2\theta = 38.2^\circ$, 44.4° , 64.6° , and 77.6° are observed, which correspond to the (111), (200), (220), and (311) reflections of Au crystals, respectively [144]. The peak intensities are higher for the HP β CD/Au-NP-NF containing 2 wt% Au-NP. In addition, the intensity of $2\theta = 38.2^\circ$ peak is higher than the other peaks implying a certain predominance of the (111) facets in the formed Au-NP.

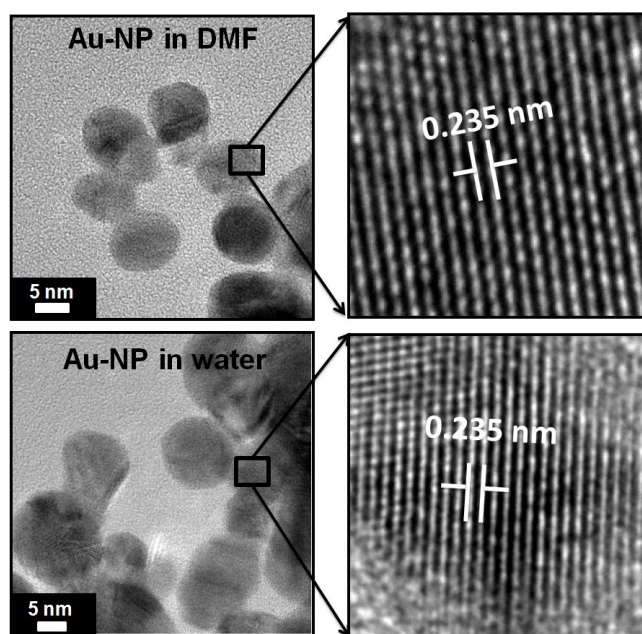


Figure 81. The representative TEM and HR-TEM images of Au-NP obtained at DMF (2 wt% NP loading) and water (1 wt% NP loading) based system of HP β CD solutions. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

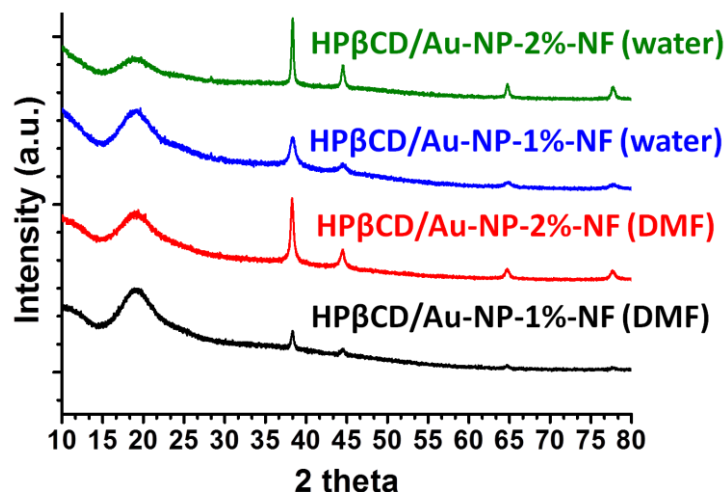


Figure 82. The XRD spectra of electrospun HP β CD/Au-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%). (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

The solid-state UV-vis absorption spectra of the electrospun HP β CD/Au-NP-NF mats are displayed in Figure 83. For all HP β CD/Au-NP-NF samples, the spectra show an absorption band at the range of 520-535 nm due to the characteristic SPR band for Au-NP [281, 282]. The maximum absorption value for HP β CD/Au-NP-1%-NF (DMF) appeared at around 525 nm and it slightly shifted to the 530 nm for the HP β CD/Au-NP-2%-NF (DMF) because of the increasing in the particle size. For the HP β CD/Au-NP-1%-NF (water), the absorption peak exhibits at around 520 nm with a slight blue-shift compared to DMF based system due to the smaller particle size of 1 wt% (6.0 ± 1.2 nm) [145, 283]. On the other hand, the significant difference was detected between the particle size of 1 wt% (6.0 ± 1.2 nm) and 2 wt% (25.01 ± 11.0 nm) Au-NP loaded HP β CD/Au-NP-NF (water) samples, so the prominently red-shift was observed to the 545 nm for the HP β CD/Au-NP-2%-NF (water) because of the some local particle aggregation.

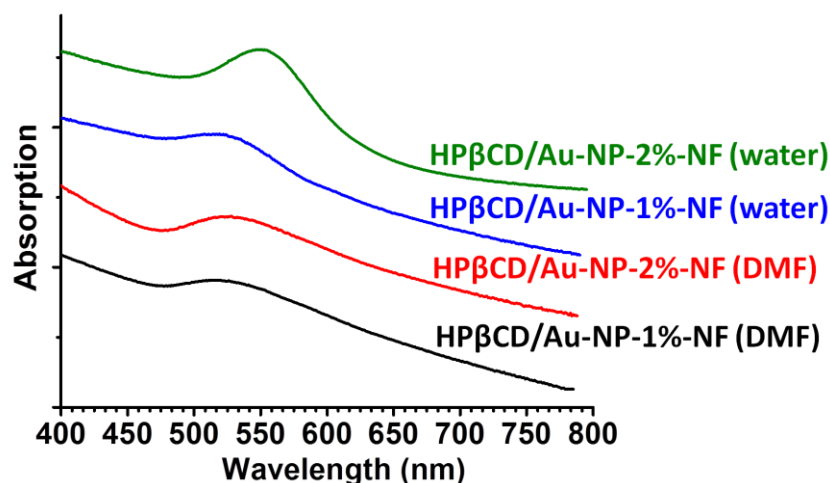


Figure 83. The solid UV-vis spectra of electrospun HPβCD/Au-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%). (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

As Ag-NP study, here we also used NaOH to improve and set-up the reduction of Au^{+3} to Au^0 . It is also reported in the literature that, at higher pH values, the Au-O^- amount increases on the Au-NP compared to the Au-OH groups [272, 284] that supplies the interaction with the OH groups of HPβCD molecules. So, Au-NP are covered by the HPβCD and their further growing and coagulations are prevented by the stabilizing effect of HPβCD molecules [272, 285]. Our FTIR measurements have proved the interaction between HPβCD molecules and NP (Figure 84). For HPβCD/Au-NP-NF, the -OH stretching mode of HPβCD molecules (3427 cm^{-1}) shifted to the lower absorption band. While the HPβCD/Au-NP-NF obtained from DMF indicated almost 17 cm^{-1} shift, the shift reached at about 25 cm^{-1} for the HPβCD/Au-NP-NF produced from water system (Figure 84). The negative shift attributed to the prevention of the HPβCD' molecular vibration because of the hydroxyl group interactions with Au. Moreover, it demonstrated the reduction and stabilizing of Au-NP by the surrounding of HPβCD molecules [272, 286].

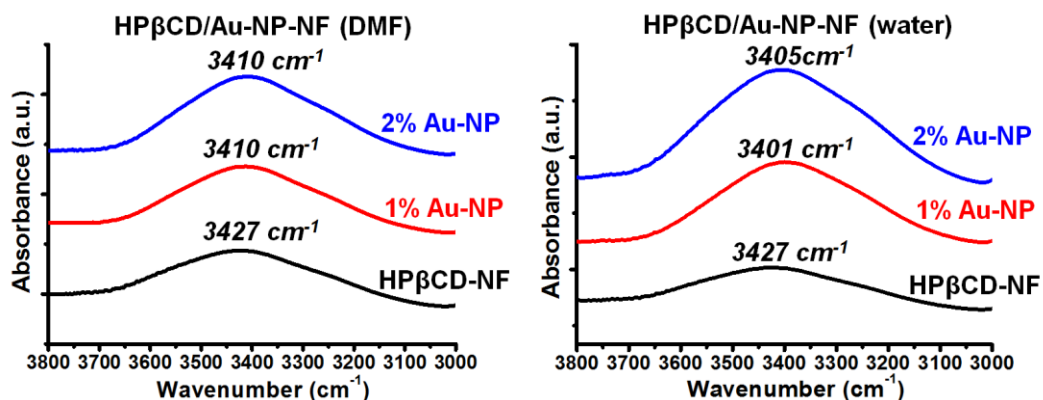


Figure 84. The FTIR spectra of HP β CD nanofibers and HP β CD/Au-NP-NF obtained in water and DMF. The zoom out region between 3800-3000 cm^{-1} at the $-\text{OH}$ stretching mode range of HP β CD molecule. (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

The structural characterizations of NP in HP β CD nanofibers matrix were also carried out by XPS study (Figure 85). It is likely that most of the Au-NP were buried in the nanofibers matrix, however, some Au-NP were present on the fiber surface as proven by the XPS. The XPS spectrum of the HP β CD/Au-NP-NF has main two doublet peaks at 88.4 eV and 84.6 eV belong to the elemental gold (Au^0) of the binding energies of Au $4f_{5/2}$ and Au $4f_{7/2}$, respectively (Figure 85). The second doublet observed at the 89.5 eV and 85.6 eV binding energies are due to Au^{+1} ionic type of gold [272, 287]. While the Au^0 atoms locate inner part of the Au-NP, the Au^{+1} ions locate outer surface to provide the interaction with the reducing agent [271, 288].

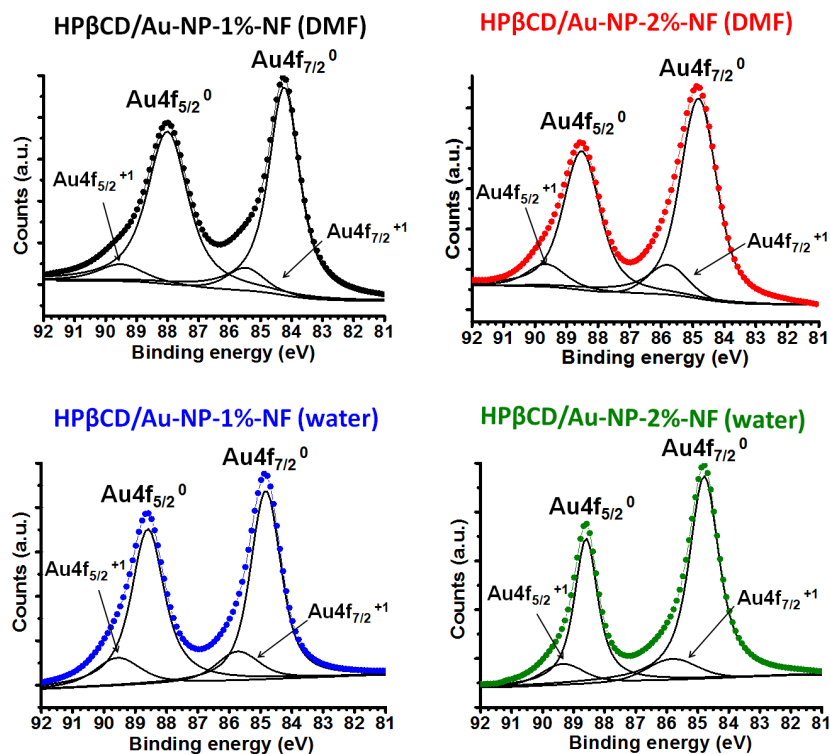


Figure 85. The high resolution XPS of electrospun HPβCD/Au-NP-NF produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%). (Copyright © 2013, Royal Society of Chemistry. Reprinted with permission from Ref.[136])

10.3. Electrospinning and characterization of the Pd-NP including HPβCD nanofibers

The Pd-NP including HPβCD nanofibers were obtained from two solvent type (water and DMF) and at two Ag-NP loading concentrations (1 wt% and 2 wt%). Figure 86 demonstrates the photograph and schematic view of HPβCD/Pd-NP solution and nanofibers. The almost black color of the solution indicates the Pd-NP formation. The SEM images of uniform and bead-free nanofibers are depicted in Figure 87. For HPβCD/Pd-NP nanofibers obtained in DMF containing 1 wt% and 2 wt% Pd-NP have AFD of 155 ± 45 nm and 145 ± 40 nm, respectively. In the case of water system, the AFD values of HPβCD/Pd-NP-NF are 585 ± 440 nm and 345 ± 195 nm for 1 wt% and 2 wt% Pd-NP, respectively. It was observed that, DMF based nanofibers indicate thinner fiber diameters compared to water based nanofibers. This situation can be originated from the lower concentration of HPβCD systems used for DMF system

that leads to thinner diameter for these nanofibers. Furthermore, along with the increasing of Pd-NP loading from 1% to 2 wt%, the AFD of nanofibers decrease for both solvent systems. The reason can be the higher conductivity of 2 wt% Pd-NP including CD solutions that results in higher stretching and thinner fiber formation during the electrospinning.

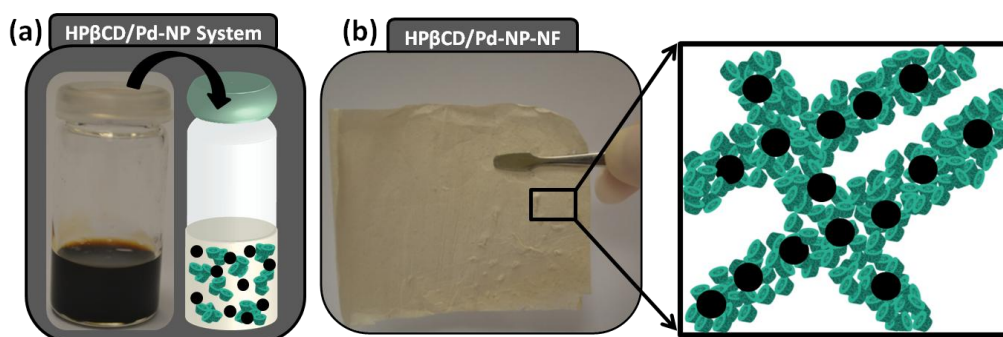


Figure 86. The photograph and the schematic observation of the Pd-NP including (a) solution and (b) nanofibers.

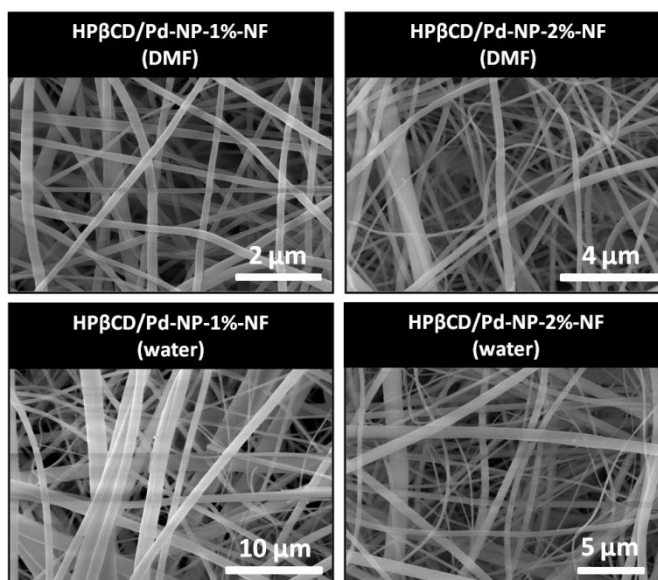


Figure 87. The representative SEM images of electrospun composite nanofibers that were produced in DMF and water at the 1 wt% and 2 wt% Pd-NP concentrations.

The morphology of the Pd-NP in the nanofibers was investigated by TEM technique. Figure 88 shows the TEM images of Pd-NP including HPβCD nanofibers obtained in DMF and water. As it is seen from TEM images, the Pd-NP disperse homogenously along the nanofiber structures with narrow size distributions. The

APS of Pd-NP were calculated from TEM images. For HP β CD/Pd-NP-1% and HP β CD/Pd-NP-2% nanofibers obtained in DMF, the APS of the Pd-NP were determined as 3.7 ± 1.0 nm and 4.0 ± 1.1 nm, respectively. On the other hand, the APS of Pd-NP were calculated as 4.7 ± 1.1 nm for HP β CD/Pd-NP-1% and 4.9 ± 1.2 nm for HP β CD/Pd-NP-2% nanofibers for water based system. It can be concluded that, the APS of the Pd-NP are not so different from each other for two different solvent types. However, there is increasing inclination at the APS of Pd-NP from 1 wt% to 2 wt% loading for both of solvent systems. Since the Pd atom potential is higher for 2 wt% loading in solutions which join the nucleation during the Pd-NP formation and results in bigger NP [277].

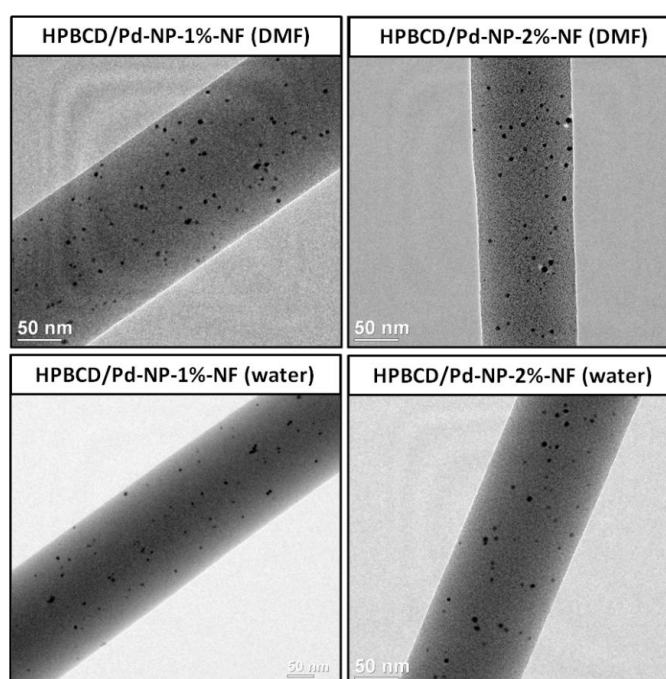


Figure 88. The representative TEM images of electrospun composite nanofibers that were produced in DMF and water at the 1% and 2% Pd-NP concentrations.

HR-TEM was performed to determine the crystalline nature of the Pd-NP. For HR-TEM, 1wt% Pd-NP loaded samples of DMF were used and the image is given in Figure 89(a). As it is seen, Pd-NP has polycrystalline structure and d -spacing was 0.224 nm from the lattice fringes which corresponded to the lattice spacing of the (111) planes of Pd [289, 290]. The crystalline structure of Pd-NP was also investigated through the SAED pattern obtained in TEM (Figure 89(b)). The

pattern including the (111), (200), (200), (220), and (311) planes reveals the polycrystallinity of Pd-NP and conform with the literature result [291]. The XPS characterization was carried out to investigate the structural characterizations of Pd-NP through the HP β CD nanofibers (Figure 90). The existences of Pd-NP, which are located on the surface of the nanofibers, were also proved by this technique. For all samples, there are doublet peaks at 335.98 and 341.38 eV which correspond to the binding energies of Pd 3d_{5/2} and Pd 3d_{3/2}, respectively and indicate the presence of elemental Pd in the nanofibers (Figure 90) [292].

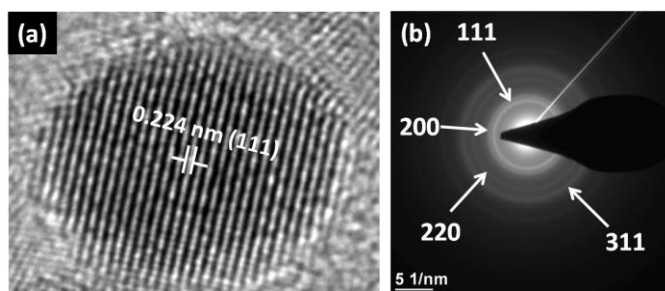


Figure 89. (a) HRTEM image and (b) SAED pattern of Pd-NP.

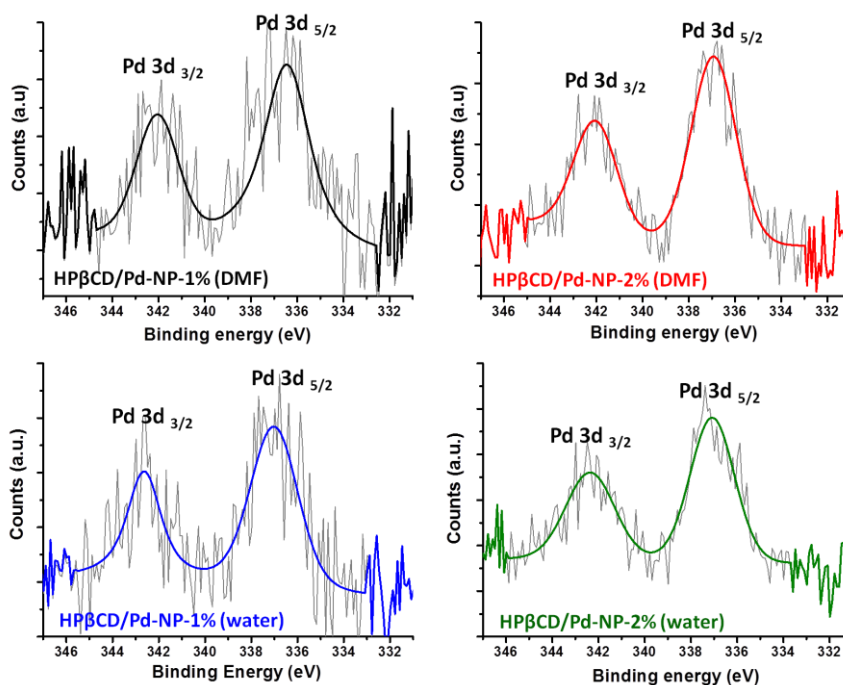


Figure 90. The high resolution XPS of electrospun HP β CD/Pd-NP nanofibers produced from two solvent systems (DMF and water) at two different NP loading (1 wt% and 2 wt%).

In recent years, metal nanoparticles have received great attention about the catalyst application and Pd-NP represents particular importance among the others, due their superior catalytic performances [293-295]. Along with the incorporation of Pd-NP in electrospun nanofibers, they are rendered into more viable and applicable form owing to portable property of nanofibrous webs. There are studies in the literature about the integration of Pd-NP with polymeric and inorganic nanofibers [296-301], as well as the application investigation of these composite nanowebs for the catalyst purposes [296, 299]. The reduction of nitro to amine groups is an important issue, especially from the wastewater treatment and organic synthesis points of view. On the other hand, this reduction phenomenon can be also considered as one of the common model to check the catalytic activity of the metal NP [107, 302]. So, in this study, the catalytic activity of Pd-NP included CD nanofibers was examined by monitoring the conversion of PNP into PAP by sodium borohydride (NaBH_4). In addition, the test was applied to pure CD nanofiber as a control sample. Figure 91 shows the UV-vis measurement results taken for the catalytic effect determination. The strong absorptions observing at all spectra at 400 nm belong to nitrophenolate ions which occur by the mixture of PNP and NaBH_4 . The existence of these ions indicates the progressing of reaction. The addition of pure CD nanofibers did not make a change at the UV-spectra of PNP, only little depression is observed at the intensity, originated from the dilution of the system (Figure 91(a)). On the other hand, for Pd-NP included nanofibers solution, there are fast depressions at the intensity of PNP absorption (400nm) even at the first 15 s, along with the formation of a new peak at 300 nm, showing the reduction of PNP to PAP. As it is mentioned in the literature, Pd-NP provide the hydrogen transfer from NaBH_4 to PNP during the reaction, so decrease the time for the full reduction of PNP that can even continue many weeks. For our measurement, after the first 15 s, the reduction reactions were monitored by taking absorptions in the 60 s time intervals. Time-dependent absorption spectra of Pd-NP including nanofibers are depicted in Figure 91(b,c). As is seen, the full fading of the green-yellow color of solutions complete prominently faster for 2 wt% Pd-NP included (Figure 91(b,c-ii)) CD nanofibers compared to 1 wt% included (Figure 91(b,c-i)) ones for both solvent types and this is due to higher amount of catalyst in the system that provide higher hydrogen transport during the

reduction and less time. When we compare Pd-NP including CD nanofibers obtained in DMF and water, we did not detect the definite differences between two solvent systems. The diameters of the nanoparticles are not so different from each other and this can be an explanation for the similarity of results for both solvent systems. Figure 91(d) indicates that the Pd-NP based samples successfully convert PNP to PAP in the presence of NaBH_4 .

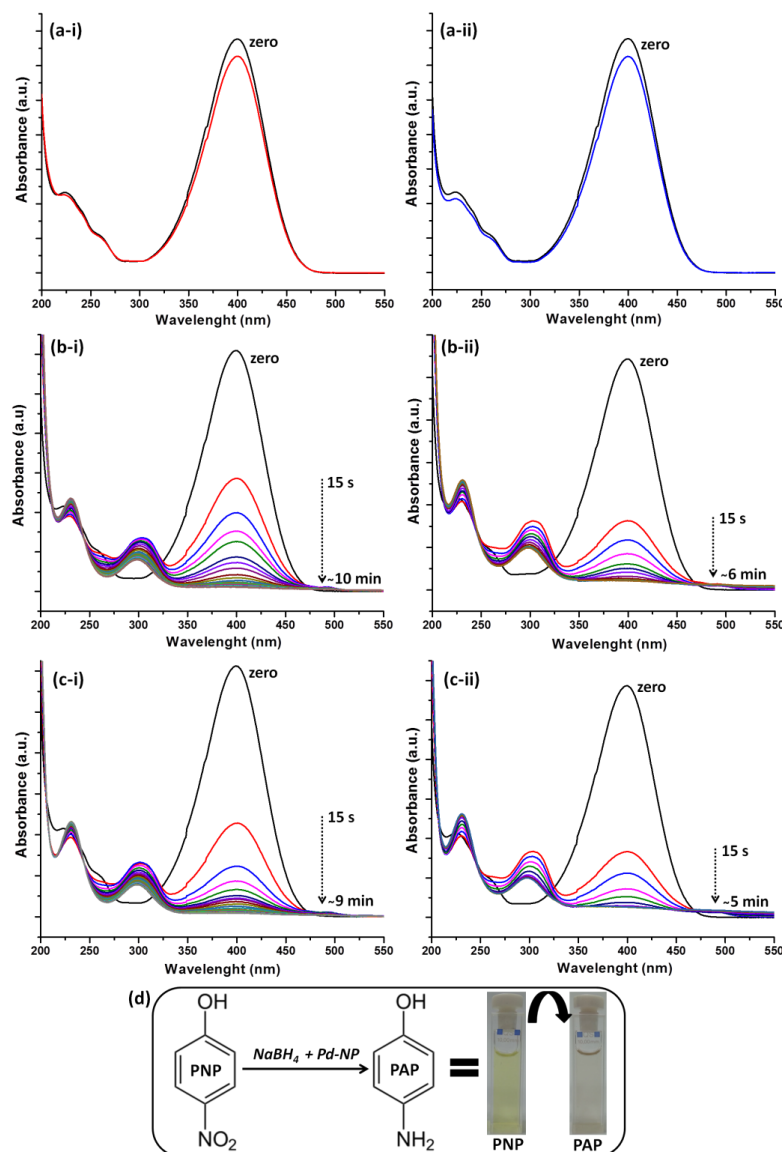


Figure 91. The UV-vis spectra taken during the catalytic activity test of (a-i) HPβCD/DMF nanofibers, (a-ii) HPβCD/water nanofibers, (b-i) HPβCD/Pd-NP-1%-DMF , (b-ii) HPβCD/Pd-NP-2%-DMF, (c-i) HPβCD/Pd-NP-1%-water and (c-ii) HPβCD/Pd-NP-2%-water nanofibers. (d) The reduction of PNP to PAP by NaBH_4 and Pd-NP system along with the decolorization visualization.

In summary, the incorporation of metal nanoparticles in electrospun HP β CD nanofibers was achieved in one-step and without additional use of toxic reducing, stabilizing agent and fiber template. The course in these studies was a green approach, since metal salts were reduced and stabilized into NP by using only HP β CD which is a natural, bio-derived, biocompatible and non-toxic cyclic oligosaccharide. HP β CD was also the only component as the fibers matrix during the electrospinning of composites nanofibers. Electrospinning of metallic NP incorporating CD nanofibers would have exclusive properties by combining the very large surface area of nanofibers with unique functionality of the metal NP and CD. For instance, the HP β CD/Au-NP-NF and their nanowebs would find a wide range of biomedical applications due to their biologically compatible characteristics as well as the specific inclusion complexation ability of the CD molecules. On the other hand, HP β CD/Ag-NP-NF would be rather proper material for the wound-healing purposes or other biomedical applications due to the antibacterial property of Ag-NP, along with the non-toxic and biocompatible nature of CD. In the case of Pd-NP incorporated CD nanofibers, we have investigated their application potential by checking the catalytic activity and we have obtained promising results. The water solubility of these nanowebs is not a restriction for using as a catalyst system, because Pd-NP incorporated CD nanofibers are easily handled and their very small amount is even enough to get a quick catalytic response, in addition these nanowebs are completely composed of non-toxic CD molecules. So Pd-NP included nanofibers would be good portable catalysis materials especially for the biological purposes. With our preceding and present studies, we have shown the facile and green route to obtain functional nanofibers incorporating metal nanoparticles. As a result, metal NP included CD nanofibers would be very attractive materials and find wide range of applications depending on the specific practices of metal NP which is improved by the incorporation of the nanofibers and CD molecules.

CHAPTER-4: ELECTROSPINNING OF INSOLUBLE POLY-CYCLODEXTRIN NANOFIBERS

11. Electrospinning of Insoluble Poly-cyclodextrin Nanofibers for the Removal of Waste Molecules from Aqueous Environment

Electrospun nanofibers/nanowebs possess several unique properties that make them good candidate for the water filtration, separation and cleaning applications, such as; large specific surface area, highly porous structure with nano size range, high degree of interconnection and modifiable nature [1, 2, 47, 80]. The potential of nanofibrous structure for filtration purposes has been reported in literature by showing separation of tiny particles, filtration of liquid medium [47, 51, 303] and waste vapor treatment [56, 80, 155]. Even, production variability, low-cost and high out-put of this technique make possible the filtration performance to enter into competition with conventional filtration systems. Moreover, electrospun nanofibers facilitate for chemical/physical functionalization that can leads to better uptake performance during the filtration process [304-308].

Additionally, filtration and separation systems are another application fields for CD molecules owing to their capturing capability of hazardous organic molecules by inclusion complexation [113, 164, 165, 167]. CD molecules are commonly utilized in the form of powder or crosslinked polymeric granules [90, 91, 94, 113]. Unfortunately, this state can cause limitation during their usage. The combination of CD molecules into polymeric nanofibers by electrospinning can be an alternative way to benefit from them more efficiently. Even, in our previous studies, we have reported the physical blending of CD molecules with polymeric nanofibers [48, 56, 57] and investigated their potential for the removal of organic waste molecules from water-based environment [48, 57]. However, water solubility of CD restricts their use for water purification purposes, because of a probable leaching from nanofiber surface that can be occurred during filtration. Therefore, as a next step, we have chemically modified the surface of polymeric nanofiber that includes the permanent attachments of CD molecules on the fiber surface [45, 54]. In one of these studies, citric acid was used as a crosslinking agent for the formation of CD (α -CD, β -CD and

γ -CD) polymer (CDP) and after the surface modification of polyethylene terephthalate (PET) nanofibers, the molecular filtration performance of PET/CDP was investigated as well [54]. In other study, β -CD-functionalized CA nanofibers were produced by combination of electrospinning and “click” chemistry. That is, β -CD was grafted onto electrospun CA nanofibers via “click” reaction. Furthermore, the molecular filtration performance of β -CD-functionalized CA nanofibers were investigated by removing phenanthrene (as a model PAH) from the aqueous solutions [45].

Our preliminary finding suggested that CD functionalized polymeric nanofibers have potentials to be used as molecular filters for the purpose of water purification and/or waste water treatment. Unfortunately, their abilities are restricted by the amount of CD molecules that are located on the nanofiber surface. So, the nanoweb systems which are completely composed of CD molecules might be more attractive and extremely efficient compared to CD included polymeric nanofibrous web by integrating the high surface area of the electrospun nanofibers with inclusion complexation property of CD molecules. Actually, as we mentioned in *Chapter1.*, we have generated polymer-free CD nanofibers from modified CD (HP β CD, HP γ CD and M β CD) and native CD (α -CD, β -CD and γ -CD). Additionally, we have observed that these CD nanofibers are very proper and proficient for the air filtration purposes. However, the solubility of these nanowebs limits their use in liquid environment and further modifications. So, we adopted a strategy that depends on the formation of crosslinked CD polymer with no solubility in water, thus we intended to eliminate the solubility obstacle of these nanofibers that restrict their application field. The polymeric CD were already generated by using different kinds of crosslinker that binds them to each other from their OH groups hence their solubility are enhanced or hindered depending on the crosslinker amount, beside these poly-CD powders or granules were investigated in terms application for filtration and control release purposes [112-117]. However, as far as we known, there is no report in the literature about the production of poly-CD nanofibers obtained with the similar strategy. From this point of view, here, different kind of crosslinking agents (epichlorohydrin (ECH), citric acid (CA), 1,2,3,4-butaneteracarboxylic acid (BTCA), hexamethylene

diisocyanate (HMDI) and poly(ethylene glycol) diglycidyl ether (PEGDE)) were tried and the optimum conditions were determined for each of them to obtain insoluble CD nanofibers. From the durability investigation, it was detected that the ECH based poly-CD nanofibers are the most stable one among others. So, the detailed characterizations (rheology, Fourier transform infrared spectrometer (FTIR), thermogravimetric analyzer (TGA), X-ray diffractometer (XRD)) and the entrapment tests (phenolphthalein and phenanthrene) were carried out for the poly-CD nanofibers which were obtained by using ECH as a crosslinking agent.

The conversion of CD molecules into macromolecular structure has already been achieved by connecting them to each other with an appropriate crosslinker. CD polymers can be obtained from its native or derivative types; but here, there are two reasons for the use of the HP β CD derivate; firstly it has high solubility that supplies the required concentrated solution for the fiber formation, secondly β -CD is evaluated as almost the most suitable type for the capturing guest molecules by having a mean cavity size [130, 133]. Figure 92 indicates photograph of the insoluble poly-CD nanowebs obtained with ECH; the SEM image and the schematic representation of the fiber structure. We estimated a branched CD distribution exists through the uniform fiber structure due to the uncontrolled reaction of crosslinking agents and CD hydroxyl groups.

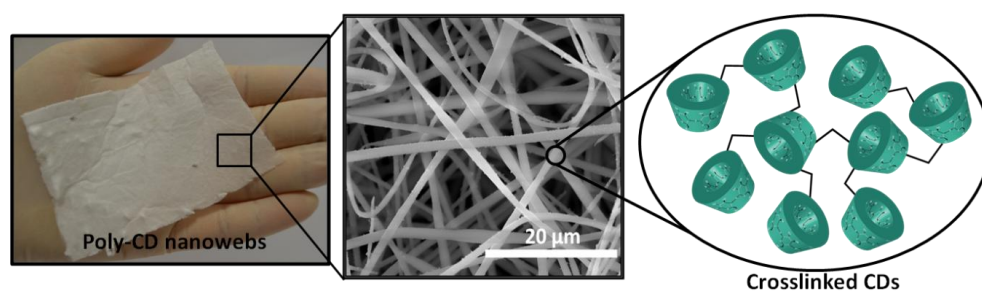


Figure 92. Photograph of the insoluble poly-CD nanowebs obtained with ECH; the SEM image and the schematic representation of the fiber structure.

Here, we have achieved the optimization conditions for five different crosslinking agents (ECH, CA, BTCA, HMDI and PEGDE) to obtain insoluble poly-CD nanofibers. In the case of ECH and PEGDE, the ether linkage is constituted between hydroxyl groups of CD in basic conditions by the opening of epoxy groups

at crosslinker structures (Figure 93) [309-313]. For CA and BTCA, the hydroxyl groups of CD react with the carboxyl groups of CA and BTCA so as to create ester groups between CD molecules during the crosslinking process [116, 117, 314-317]. On the other hand, the use of HMDI leads to urethane bond formation among the CD molecules by the crosslinking [318]. The above mentioned binding types were summarized in the different studies of literature which are focused on the production of insoluble CD polymers.

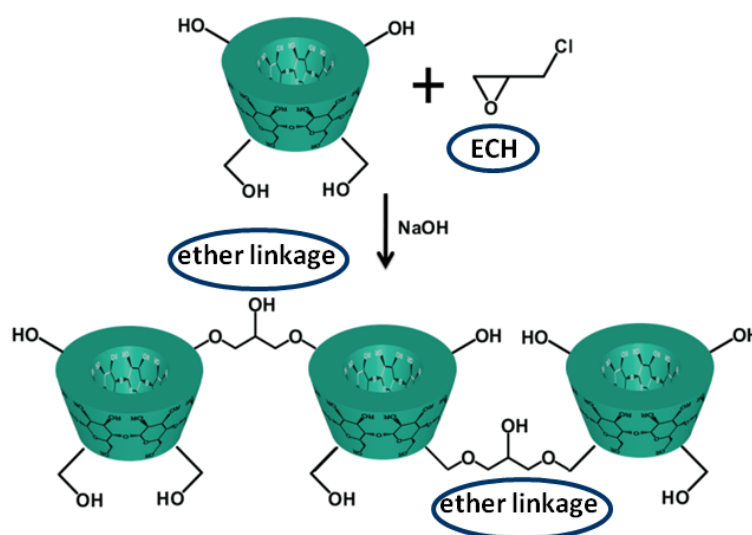


Figure 93. The schematic view of the constitution of the ether linkage between CD molecules in the case of ECH usage.

To check the durability of crosslinked poly-CD nanofibers, we have immersed all of them in water for 24 hour. Figure 94 indicates the SEM images of poly-CD nanowebs before and after durability test. As is seen, all poly-CD nanowebs have bead-free and uniform morphology (Figure 94(a-i), (b-i), (c-i), (d-i), (e-i)) and the fibers morphology is still protected after they were kept in water for 24 hour (Figure 94(a-ii), (b-ii), (c-ii), (d-ii), (e-ii)) proving the insolubility of the obtained nanowebs. When we soaked nanowebs in water, we noticed that, the nanofibers produced with PEGDE and HMDI swell like gel. The reason might be the long chain part in their structure compared to others that leads to bigger spaces between CD molecules when they are linked each other. Depending on this, the structure become more flexible and loose that cause higher water absorption and swelling during the immersing in water. After the solubility test, we have also recognized the durability

of nanowebs against treatments and usage. It was observed that, the poly-CD nanowebs produced by using ECH is the most durable and stable ones among other nanowebs with less deformation in its webs structure. So ECH based poly-CD nanowebs were selected as the most proper one to investigate the filtration performance of poly-CD nanowebs by entrapping unwanted molecules from the liquid environment.

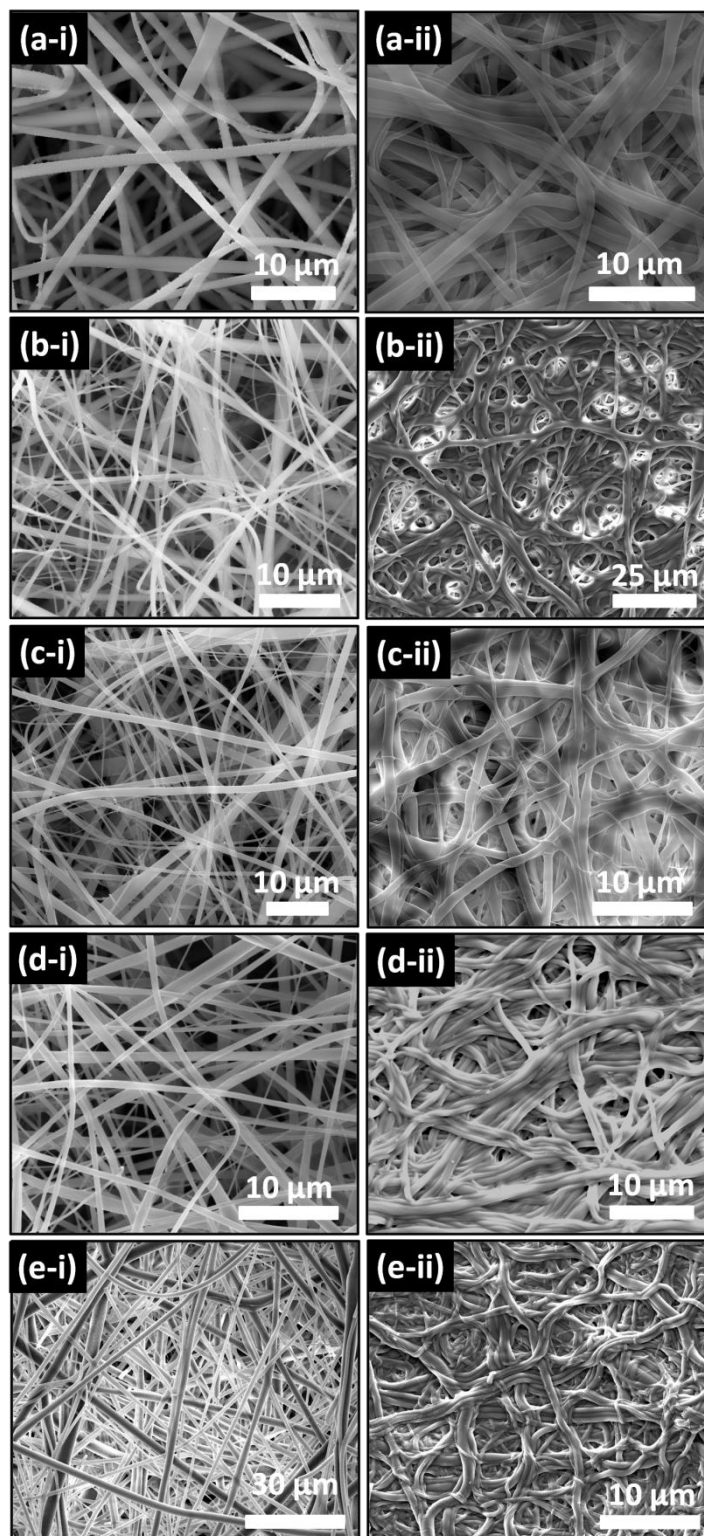


Figure 94. The SEM images of poly-CD nanofibers, produced with (a) ECH, (b) CA, (c) BTCA, (d) HMDI and (e) PEGDE, (i) before and (ii) after immersing in water for 24 h.

In addition to water immersing test we have also investigated the stability of ECH based poly-CD nanowebs against other solvent types. Figure 95 shows the SEM images of nanofibers that soaked in acetonitrile, ethanol, methanol, chloroform, DMF and DMSO. As it seen from the SEM images, the fiber morphology is still protected after 24 hours holding in organic solvents and this feature is favorable for the further modification of poly-CD nanowebs that can be performed in the above mentioned solvents.

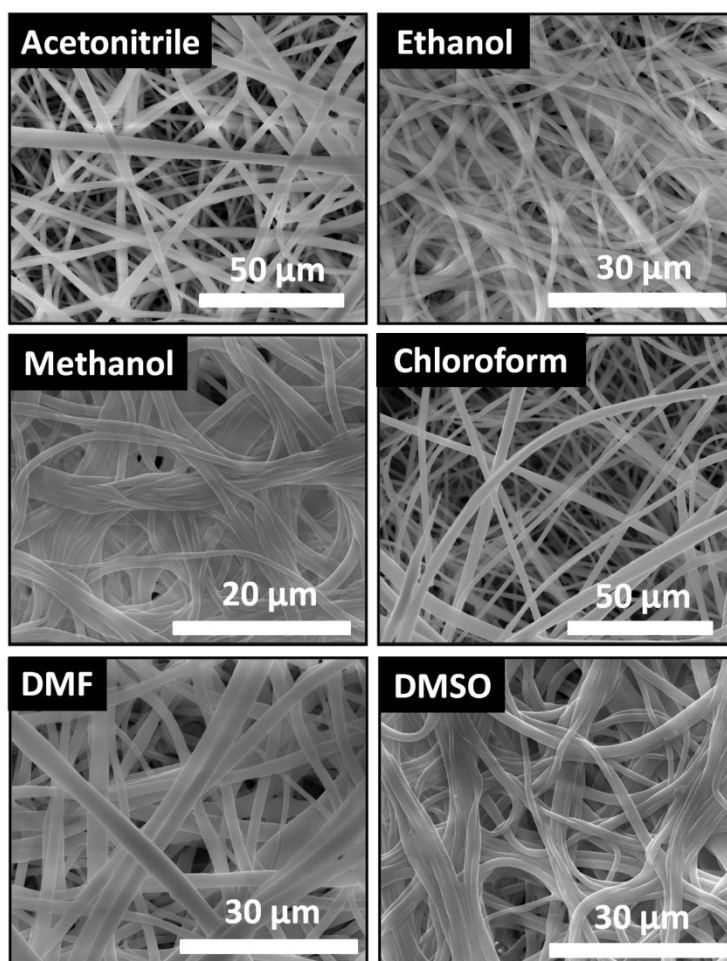


Figure 95. The SEM images of ECH based poly-CD nanofibers after soaking these nanowebs in acetonitrile, ethanol, methanol, chloroform, DMF and DMSO for 24 hours.

11.1. Rheological characterization of the poly-CD solutions

The rheological changes in the CD solution during the polymer formation were evaluated by performing time sweep viscosity and modulus test at process temperature 50 °C. To obtain more reliable evidence for CD polymer occurring, we also performed the viscosity test for ECH free HP β CD solution. Figure 96(a) indicates the time sweep viscosity measurement for ECH included and ECH free CD solutions. We observed that, the ECH loaded solution viscosity increased markedly after 30 min. due to the increase of crosslinking density during the polymerization of CD monomers. On the other hand, for ECH free solution, there was only a small increment that continued with a stable value till the end of measurement. As it is mentioned before, we also investigated the oscillatory time sweep profiles for poly-CD solutions (Figure 96(b)). In the whole experiment period, the storage modulus is higher than loss modulus indicating the viscoelastic networks formation and solid-like behavior of the system [175, 319]. Additionally, the both modulus show rising regime in the progressing time, related to the increasing amount of crosslinked part [319, 320]. Moreover, the viscosity measurement of ultimate polymer solution was carried out depending on the increasing shear stress before the electrospinning process (Figure 96(c)). The shear sweep test results show the Newtonian behavior of ultimate solutions due to the stable viscosity value against increasing shear stress. In the first step of measurement, the sharp decline is observed at the viscosity value of ECH included sample but as the higher stress value, viscosity behaves in a fixed regime. As it is seen in Figure 96(c), the ECH loaded solution has higher viscosity according to ECH free one owing to presence of crosslinked sections in the solution.

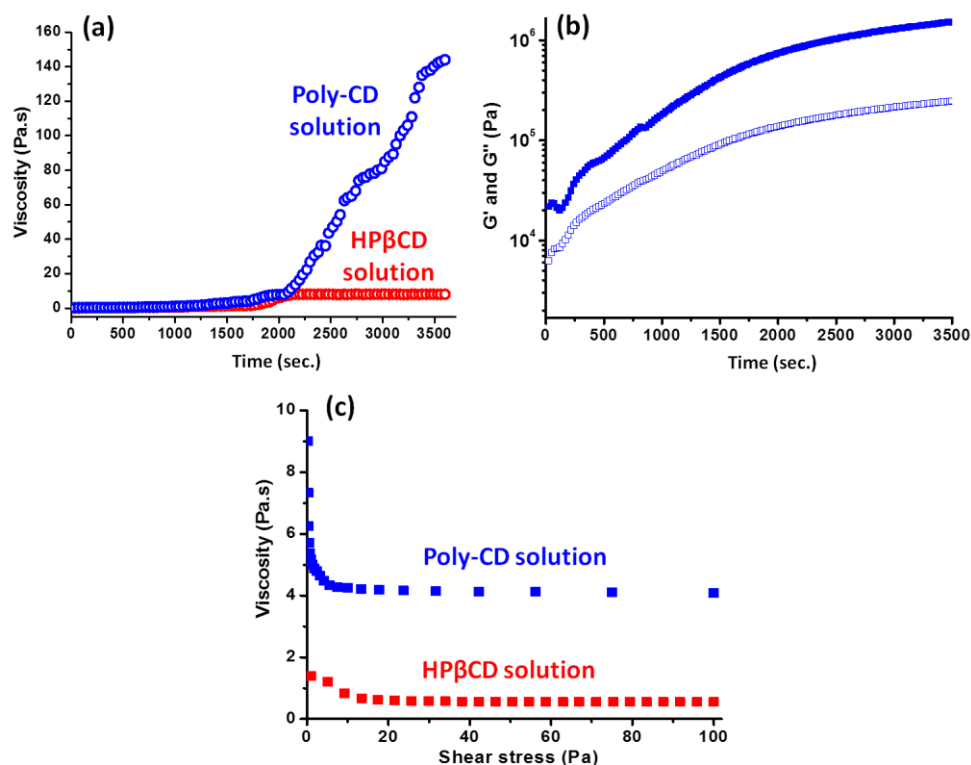


Figure 96. Time sweep (a) viscosity and (b) modulus measurement results taken at process temperature 50 °C. (c) Viscosity measurement of ultimate poly-CD and HPβCD solutions before the electrospinning.

11.2. Structural characterization of poly-CD nanofibers

FTIR, TGA and XRD techniques were used for the structural characterization of poly-CD nanofibers (Figure 97). The infrared spectra of HPβCD possess prominent absorption bands at about 1155, 1082 and 1035 cm⁻¹ owing to C–H and C–O stretching vibration [321]. The similar base configuration was also protected for HPβCD polymers however in wider and weaker manner according to its monomer type along with the formation of new ether bonds (Figure 97(a)) [322-324]. On the other hand, TGA enabled us to evaluate the results in terms of thermal behavior differences. As it is known, the CD show main degradation at about 300 and 350 °C [133], after all, we observed that while HPβCD nanofibers started to degrade at lower temperature, the poly-CD nanofibers started its degradation at higher temperature compared to powder CD (Figure 97(b)). This early degradation of HPβCD nanofibers can be based on the higher surface area and higher contact points through the sample. On the other hand, the crosslinked structure existing in the poly-CD

nanofibers enhance the degradation temperature of sample due to more energy requirement for their decomposition. Finally, the XRD patterns demonstrate the amorphous nature of HP β CD powder, nanofiber and poly-CD nanofiber with the similar scattering pattern (Figure 97(c)). The absence of distinctive diffraction peaks proved the lack of definite orientation between CD molecules for both fiber and polymer structures.

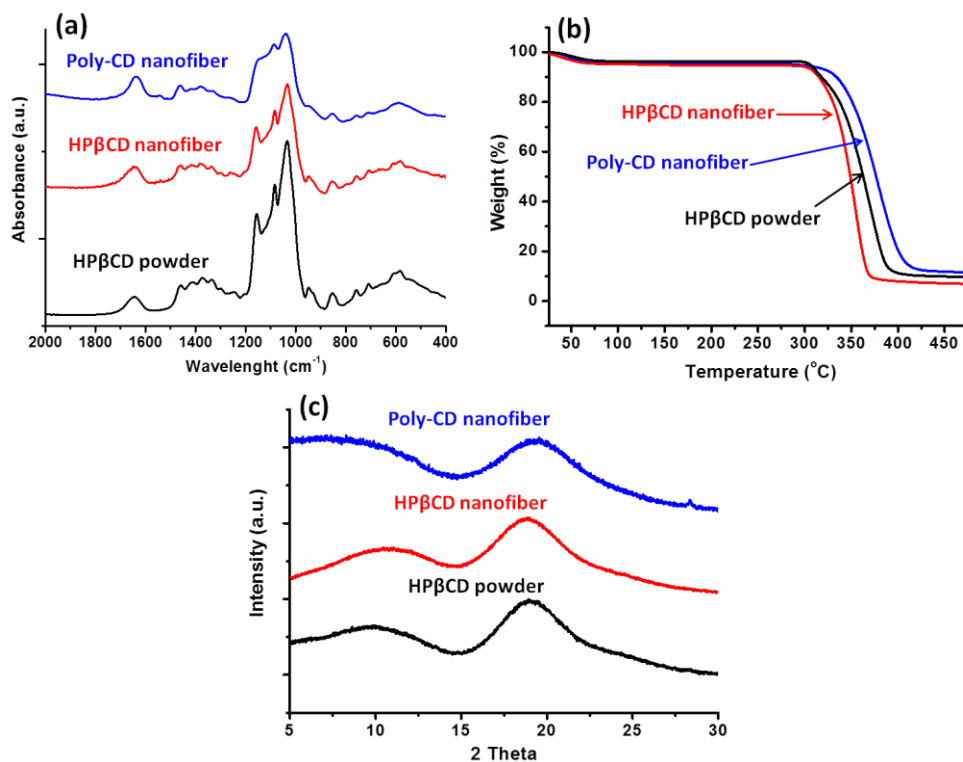


Figure 97. (a) FTIR, (b) TGA and (c) XRD spectra of poly-CD nanofibers, HP β CD nanofibers and HP β CD powders.

11.3. Filtration performance of poly-CD nanofibers

The molecular filtration potential of poly-CD nanofibers were investigated by using two kind of organic molecules; phenolphthalein and phenanthrene. The encapsulation tests of each molecule were carried out by using different methods; UV-vis-NIR spectroscopy, and HPLC for phenolphthalein and phenanthrene, respectively. For phenolphthalein entrapment test, we compared the nanofibers performance with the granule type poly-CD granules that we produced at the same time with nanofiber by using the same procedure. On the other hand, we have

investigated re-usability of poly-CD nanofibers during the entrapment of phenanthrene by performing the second cycle test.

As it is known, phenolphthalein is a model system due to its inclusion complex (IC) ability with CD and easy detection by UV-vis measurements [48, 57]. In our previous study, we even compared the filtration capability of three native CD types for phenolphthalein molecules (α , β , and γ -CD) [48]. In this study, for the filtration test, we located the poly-CD nanofibers and its granules types at the bottom of two separate quartz vials filled with pink phenolphthalein solution and recorded the decline in the absorbance as a function of progressive time intervals. We observed that, there is a distinctive depression at the absorbance of phenolphthalein solutions and they turn into colorless owing to removal of phenolphthalein molecules by making IC with CD molecules. Figure 98 shows the UV-vis spectra and the rate of phenolphthalein absorption as a function of time. While the fully removal of phenolphthalein molecules by nanofibers was completed in 120 minutes, it took 10 hours for the poly-CD granules. Moreover, when the removal rates are compared, nanofibers show quicker decreasing at the beginning of the measurements. It achieved almost half of the sorption just in the first 25 minutes and reached its saturation point at the 90 minute. The differences between these two samples can be originated from the higher surface area of nanofibers according to granule types.

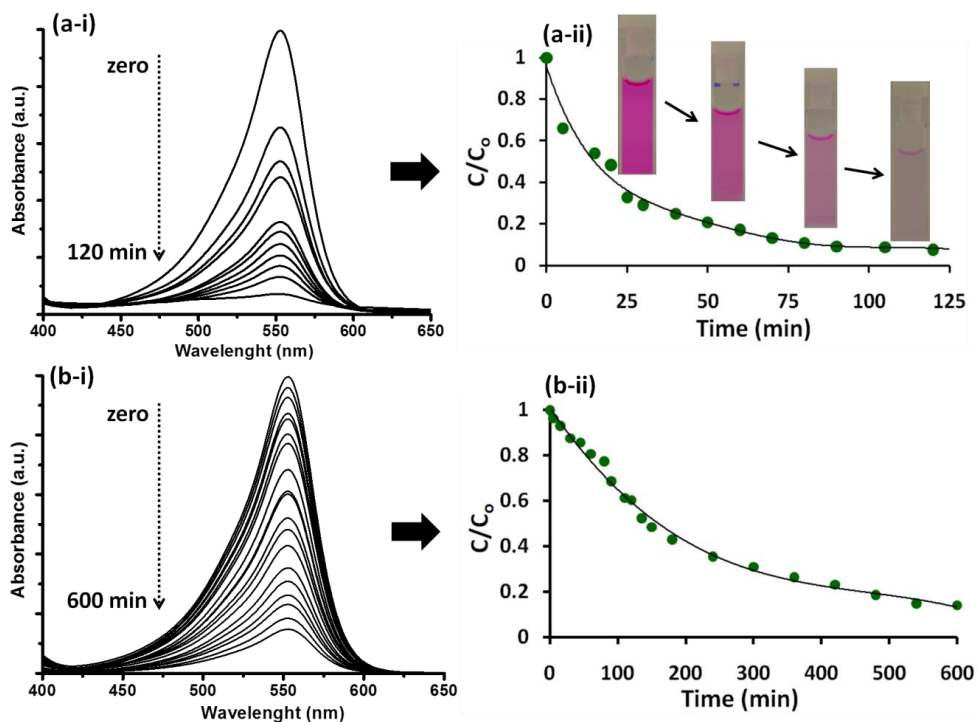


Figure 98. (i) The UV-vis spectra and (ii) the rate (C/C_0) of phenolphthalein removing in the progressing time intervals belong to (a) poly-CD nanofibers (b) poly-CD granules.

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widespread pollutants which are highly toxic, carcinogenic, and their toxicity increases with increasing molecular weight [325]. Moreover, several studies show that PAHs pollutions cause serious health problems for human and living organisms [325, 326]. For these reasons, varieties of adsorbents such as nanofibers, silica gel, porous nanoparticles etc., have been developed for the removal of PAHs [54, 327, 328]. PAHs are important organic pollutants because of their mutagenic and carcinogenic potentials. However, the low-water solubility of these components limits the remediation process of contaminated water and soil [325, 326]. As it is known, CD are capable of encapsulating organic compounds due to their hydrophobic cavity and there are many studies reported complexation between CD and PAHs molecules [329-333]. Phenanthrene is the most commonly known example through other hydrocarbons, so in this study, it was chosen as a model PAH to examine the molecular filtration potential of poly-CD nanofibers. The HPLC method was

carried out to detect filtration performance of nanowebs and Figure 99 depicts the decrease of phenanthrene concentration (%) against progressing time intervals. The stock solutions were prepared at the maximum solubility (1.8 $\mu\text{g/mL}$) of phenanthrene molecules in water/ACN (50 mL/10 μL) system and nanofibers were being kept into this organic compound aqueous solution during the test. As it is seen, even, in the first 50 min, poly-CD nanowebs removed 50% of phenanthrene from the solution, and this ratio reached to 93% at the end of first cycle. Moreover, the used samples were washed with ACN and then it was again immersed into the phenanthrene solution to investigate the re-usability of poly-CD nanofibers. We observed that our samples are re-usable since the 70% of phenanthrene was extracted from the same concentrated solution of this hydrocarbon at the second cycle by the inclusion complexation (Figure 99).

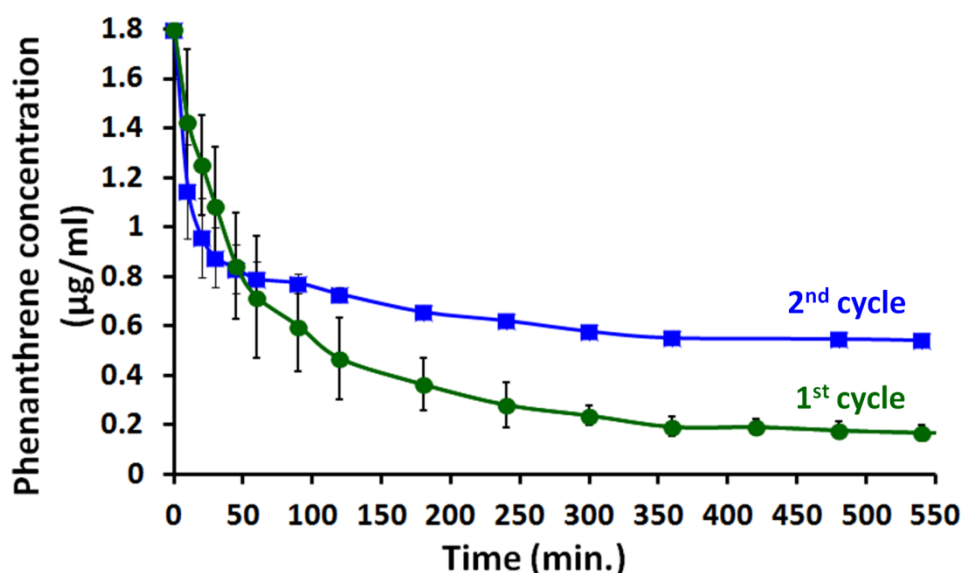


Figure 99. The time dependent decrease of phenanthrene concentration in aqueous solution for 1st and 2nd cycles.

It is known that, hydrophobic interactions are the relation type between CD cavity and organic molecules during the inclusion complexation. Besides, repulsive interactions between the hydrophobic guest and the aqueous environment, and more favorable interactions between hydrophobic guest and apolar CD cavity are the driving forces for the removing of organic compounds from the aqueous environment [91]. In the case of poly-CD

nanofibers, only CD molecules become more applicable compared to their powder form by the location on a stable carrier matrix. However, it does not cause any change at the entrapment and removing mechanism of phenolphthalein and phenanthrene molecules by CD. Here, it was also observed that, poly-CD nanofibers still kept their fiber structure after the filtration tests (Figure 100).

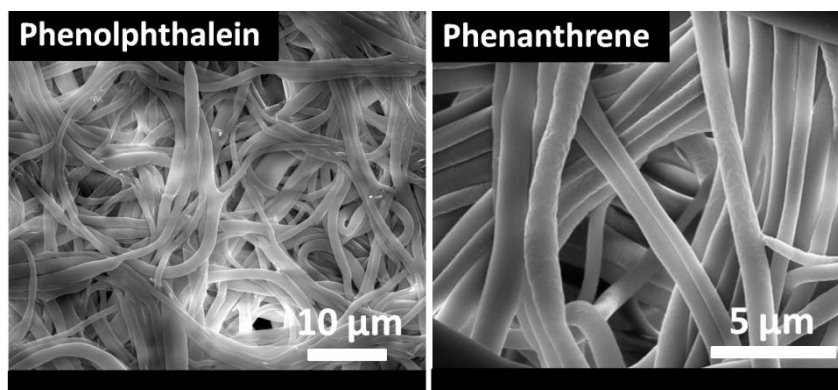


Figure 100. The SEM images of poly-CD nanofibers after phenolphthalein and phenanthrene removing test.

In this study, we have achieved the very early production of poly-CD nanofibers which are not soluble in water and organic solvents. Firstly, we have tried different kinds of crosslinking agent (ECH, CA, BTCA, HMDI and PEGDE) and we have successfully obtained insoluble poly-CD nanofibers by optimizing conditions for all of them. It was detected that ECH based poly-CD nanofibers show the highest durability among others in water. So the detailed structural characterizations of nanowebs, which are produced by using ECH, were experienced, beside the application potential of these poly-CD nanofibers was investigated by removing phenolphthalein and phenanthrene from liquid environment. The poly-CD nanowebs are completely composed of CD molecules and not soluble even in strong solvents owing to its polymeric structure. This approach enables us to obtain magnificent materials having insoluble nature along with the integration of nanofibers high surface area and porous structure with IC property of CD. Here, we have demonstrated and represented a filter membrane possessing bioavailability and biodegradability properties outshine in terms of providing the post-used requirements by giving no additional load to the environment. However, we assume that, the

application potential of these nanowebs is not limited with the encapsulation and removing of hazardous or unwanted compounds from the required environment. Poly-CD nanowebs, obtained with different crosslinking agents, can be also served as promising release and capturing systems for various functional additives (drugs, antibacterials, essential oils, dyes, nanoparticles etc.) with the permanent, reusable and biocompatible nature. Moreover, due to the modification availability of CD molecules, the surface of the poly-CD nanowebs can be functionalized by various compounds having unique properties and response. Hence, the ultimate poly-CD nanofibrous webs can be also good candidate for the development of new applications such as biotechnology or advanced functional systems such as sensors, molecular switches or other diagnostic systems.

CONCLUSIONS AND FUTURE PROSPECTS

In this dissertation, the pioneer studies regarding to electrospinning of polymer-free cyclodextrin (CD) nanofibers were reported. As our initial effort, we have successfully obtained nanofibers from three different CD derivatives; hydroxypropyl- β -cyclodextrin (H β CD), hydroxypropyl- γ -cyclodextrin (H γ CD) and methyl- β -cyclodextrin (M β CD) in three different solvent systems; water, dimethylformamide (DMF) and dimethylacetamide (DMAc) without using a carrier polymeric matrix. Here, the required characterizations were performed to investigate the possible impulsions for the fiber formation from these non-polymeric systems and it was concluded that, the self-assembly and aggregation properties of CD enable the electrospinning of these molecules into nanofibers from their concentrated solutions by acting as the chain entanglement and overlapping concept of polymer solutions. It was also observed that, the morphologies and the thickness of the electrospun fibers were highly dependent on the CD derivatives and the type of solvent system used. Afterwards, HP β CD and HP γ CD nanofibers, which were successfully produced in DMF and water solvent system, were chosen for the evaluation of the molecular entrapment performance of CD nanofibers by exposing them to volatile organic compounds (VOCs) vapor. The comparative results indicated that, CD nanofibers can entrap higher amount of VOCs from the surroundings compared to their powder forms due to the higher surface area of nanofibers and the higher accessibility and availability of CD cavity to entrap VOCs. Moreover, it was observed that, CD and VOCs type are the other factors that affect the entrapment efficiency. To conclude, modified CD nanofibers would be very attractive material for air filtration purposes owing to highly porous structure and inclusion complexation capability of CD. After the optimization studies of modified CD, we have focused on the electrospinning of native CD (α -CD, β -CD and γ -CD). However, the limited solubility of these CD was a remarkable obstacle against the study, when compared with the quite high solubility of modified CD. Then, we have tried various kinds of organic solvents and their blend system to solve the native CD at the required level of concentration for the uniform fiber formation. Finally, we have achieved the electrospinning of α -CD and β -CD in 10% NaOH aqueous

solution; γ -CD in dimethyl sulfoxide (DMSO)/water (50/50, v/v) blend system. Here also, the detailed characterizations were carried out to demonstrate the importance of aggregation formation and intermolecular interactions between CD molecules in their highly concentrated solutions. Furthermore, γ -CD nanofibers, having the highest production efficiency among other native CD (α -CD and β -CD), were employed for the entrapment of the VOCs from the surrounding. It was found that, while γ -CD nanofibers were quite successful for entrapping VOCs by inclusion complexation, γ -CD in powder form did not show any entrapment capability, so γ -CD nanofibers are also very promising filtering material for the removal of organic waste vapors from the environment due to their very high surface area along with their inclusion complexation capability.

As a second main issue, we have also reported very early studies on the electrospinning of polymer-free nanofibers from the cyclodextrin inclusion complexes (CD-IC). Firstly, a well-known antibacterial agent, triclosan was chosen as a guest molecule, and then the IC suspension was prepared in the high concentrated solution of HP β CD. The uniform nanofibers were obtained from this IC suspension without using polymeric matrix. The IC formation between HP β CD and triclosan was proved by different techniques, beside it was determined that, the CD-IC nanofiber formation also depend on the presence of sufficient aggregates and intermolecular interactions. As next, we have also obtained IC nanofibers of triclosan by using HP γ CD. The complex efficiency differences between HP β CD and HP γ CD IC nanofibers were determined by using appropriate methods. Afterwards, the antibacterial tests for triclosan/CD-IC nanofibers were performed against Gram-negative (*E. coli*) and Gram-positive (*S. aureus*) bacteria. The more efficient antibacterial effect was attained for triclosan/HP β CD-IC and triclosan/HP γ CD-IC nanofibers compared to pure triclosan powder due to enhanced solubility of antibacterial agent by inclusion complexation. CD molecules are able form complexes in a wide range of molecule type, by utilizing from this potentiality; we have also produced polymer-free nanofibers from vanillin/CD-IC and essential oils (EOs)/CD-IC. Vanillin is very common agent used in food applications due to its flavor/fragrance property; however, it has volatile nature. For vanillin/CD-IC

nanofibers, three modified CD types (HP β CD, HP γ CD and M β CD) were used for the preparation of electrospinning solutions in three different solvent systems (water, DMF and DMAc). Then the water based vanillin/CD-IC nanofibers were selected for the water solubility which is an important issue in terms of food based applications. We have observed that, the inclusion complexation provide significantly higher solubility for vanillin compounds compared to its pure powder form. As well as, higher thermal stability is obtained as results of IC formation. Here, the EOs/CD-IC systems were formed by using six types of EOs (thymol, eugenol, citral, camphor, cineole and cymene) and three different CD types (HP β CD, HP γ CD and M β CD). As it is known, EOs are extraction product of plant, they represent antiseptic, anesthetic, antimicrobial, antibacterial, antioxidant, insecticide/insect repellent properties and flavor/fragrance, however they are not soluble in water and very sensitive to external factors (light, heat, oxygen etc.). So, we expect that, both vanillin/CD-IC and EOs/CD-IC nanofibers would be quite applicable in active and smart food applications along with the non-toxic, edible nature of CD and possible higher solubility and stability as a result of IC formation. The electrospun CD-IC nanofibers are also very intriguing materials due to the integration of large surface area of the nanofibers with specific functionalities of CD-IC supramolecular structures. Moreover, the nanofiber type of CD-IC reduces the use difficulties originated from their powder form and modified them into more applicable state, especially for biotechnology and food practices with the highest active agent content.

In the third part of this thesis, we mentioned the studies regarding to functionalization of CD based nanofibers with metal nanoparticles. As the first step, we have achieved one-step synthesis of Ag-NP by using polyvinyl alcohol (PVA) and PVA/HP β CD aqueous solution as reducing and stabilizing medium as well as the electrospinning matrix. Here, HP β CD was added to the PVA solutions at the increasing amount and due to the reducing and stabilizing effect of CD molecules, the definite decreasing was observed at the size of the Ag-NP with the addition of HP β CD. The homogenous distribution without the aggregation of Ag-NP was obtained through the nanofibers structures. Beside the green and size tunable metal nanoparticles synthesis, we have also observed that, the obtained composite

nanofibers exhibit both SERS and antibacterial effect. Therefore, these electrospun nanofibrous mats would be a good candidate for sensing or other biomedical uses. In the proceeded step, we have eliminated the polymeric matrix from the systems, thereby; HP β CD was used as reducing, stabilizing agent as well as fiber template during the one-step synthesis of metal nanoparticles incorporated nanofibers production. Here, three different metal nanoparticles (Ag-NP, Au-NP and Pd-NP) were synthesized by natural and bio-derived HP β CD molecules, so no additional toxic reducing or stabilizing agent were used during process. In this green approach, HP β CD was also the only component as the fibers matrix during the electrospinning. Additionally, Pd-NP are known with their efficient catalyst effect, hence we have checked the catalyst potential of Pd-NP incorporated CD nanofibers and shown that, these functional nanofibers would be a portable catalyst system along with the non-toxic nature of CD, especially for biotechnology purposes. In brief, the incorporation of CD nanofibers with metal nanoparticles can lead to production of very attractive materials by integrating very large surface area of nanofibers with unique functionality of the metal nanoparticles and CD.

In the last part of the thesis, we reported the very early production of insoluble poly-CD nanofibers via electrospinning. For this, we have firstly applied different kinds of crosslinking agents (epichlorohydrin (ECH), citric acid (CA), 1,2,3,4-butaneteracarboxylic acid (BTCA), hexamethylene diisocyanate (HMDI) and poly(ethylene glycol) diglycidyl ether (PEGDE)) and we achieved the optimization of conditions for all them to attain insoluble poly-CD nanofibers. The detailed structural analysis were performed for poly-CD nanofibers which are obtained by using ECH, since we have observed that, these nanofibers represents the highest morphological stability among others. In addition, we have showed the molecular entrapment capability of ECH based poly-CD nanofibers by removing phenolphthalein and phenanthrene from liquid environment.

To conclude, electrospinning of nanofibers from CD molecules is a quite novel and attractive research topic. In these studies, the very large surface area of electrospun nanofibers is integrated with the specific host-guest inclusion

complexation and other unique properties of CD molecules. Moreover, CDs are rendered into more applicable nanofiber form that provides convenience during their practices. CD are already being used in pharmaceuticals, functional foods, textiles, filtrations, and sustained/controlled delivery systems, therefore, having nanofiber/nanoweb structures might hopefully open up the possibilities and extend the use of CD in the fields of filtration, biotechnology, food, sensing or in other functional systems. Moreover, our findings may lead to the fabrication of new functional nanofibers from other types of CD and/or other supramolecular systems via electrospinning.

The generation of poly-CD nanofibers by using different CD types and crosslinking agents might constitute the potential future research directions of CD electrospinning. In last period of the thesis, we focalized on the elimination of the solubility constraint of CD nanofibers that restrict their application and further modifications. We suppose that, the variety and the application potential of these poly-CD nanofibers would be extended by the integration of different functional compounds and surface modifications. For instance, IC-poly-CD nanofibers can be obtained by using various drugs or food additives. Thus, these composite nanowebs can be also served as promising release and capturing systems with the permanent, reusable and biocompatible nature. Moreover, due to the modification availability of CD molecules, the surface of the poly-CD nanowebs can be functionalized chemically by various molecules having unique properties and response. Hence, the ultimate poly-CD nanofibrous webs can be also good candidate for the development of new applications such as biotechnology or advanced functional systems such as sensors, molecular switches or other diagnostic systems. In addition, the surface functionalization of poly-CD nanofibers would be performed by permanent metal nanoparticles growing and these nanowebs would be very attractive material depending on the nanoparticles properties for the long-term practices.

LIST OF PUBLICATIONS

Publications from thesis studies

- 1) **A. Celebioglu** and T. Uyar*, Cyclodextrin nanofibers by electrospinning, *Chemical Communication*, 2010, 46, 6903-6905, [DOI:10.1039/C0CC01484B](https://doi.org/10.1039/C0CC01484B) (INSIDE FRONT COVER).
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- 5) **A. Celebioglu** and T. Uyar*, Electrospinning of Polymer-free Nanofibers from Cyclodextrin Inclusion Complexes” *Langmuir*, 2011, 27, 6218–6226, [DOI:10.1021/la1050223](https://doi.org/10.1021/la1050223).
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- 8) **A. Celebioglu** and T. Uyar*, Green and One-step Synthesis of Gold Nanoparticles Incorporated in Electrospun Cyclodextrin Nanofibers, *RSC Advances*, 2013, 3, 10197-10201, [DOI: 10.1039/C3RA41175C](https://doi.org/10.1039/C3RA41175C).
- 9) **A. Celebioglu**, H. S. Sen, E. Durgun and T. Uyar* "Molecular entrapment of volatile organic compounds (VOCs) by electrospun cyclodextrin nanofibers", (submitted)

10) A. Celebioglu, F. Kayaci and T. Uyar*, "Polymer-free nanofibers from vanillin/cyclodextrin inclusion complexes: high thermal stability and enhanced solubility of vanillin" (in preparation).

11) A. Celebioglu and T. Uyar*, "Cyclodextrin as reductant, stabilizer and fiber matrix for “green” and one-step synthesis of silver nanoparticles incorporated in electrospun nanofibers"(in preparation).

12) A. Celebioglu and T. Uyar*, "Palladium nanoparticles incorporated cyclodextrin nanofibers for the catalytic reduction of p-nitrophenol"(in preparation).

13) A. Celebioglu and T. Uyar*, "Electrospinning of insoluble poly-CD nanofibers"(in preparation).

Others

14) A. Celebioglu and T. Uyar*, Electrospun porous cellulose acetate fibers from volatile solvent mixture, *Materials Letters*, 2011, 65, 2291-2294, [DOI: 10.1016/j.matlet.2011.04.039](https://doi.org/10.1016/j.matlet.2011.04.039).

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18) R. Garifullin, O. Ustahuseyin, **A. Celebioglu**, G. Cinar, T. Uyar*, and M. O. Guler*, Noncovalent Functionalization of Nanofibrous Network with Bio-inspired Heavy Metal Binding Peptide, *RSC Advances*, 2013, 3, 24215-24221, [DOI: 10.1039/C3RA43930E](https://doi.org/10.1039/C3RA43930E).

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