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Effects of β-cyclodextrin on selected properties of electrospun thermoplastic polyurethane nanofibres

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ABSTRACT

Cyclodextrins are one of the most promising materials for the development of products with advanced properties due to inclusion complex formation ability with a wide variety of substances. More specifically, incorporation of cyclodextrins into electrospun nanofibrous materials is considered as potential candidates for functional textile applications. This study examines the electrospinning of thermoplastic polyurethane (TPU) nanofibres including β-cyclodextrin and investigates the effects of β-cyclodextrin (β-CD) on resultant fibre properties. TPU/CD nanofibres were characterized by scanning electron microscopy, FTIR, TGA and DSC analysis. Additionally phenolphthalein absorption tests were applied. It was observed that the incorporation of β-CD increased the mean fibre diameter and heterogeneity of nanofibrous membranes. The effects of β-CD on the thermal properties of TPU membranes were shown. It was proven that β-CD within TPU nanostructure could be able to form inclusion complexes. TPU/CD nanofibres are believed to have good potentials for functional textile applications.

1. Introduction

Electrospun nanofibres have been gaining a great interest due to the ease of production of multifunctional nanofibrous materials. During electrospinning a continuous filament is drawn from a polymer solution or a polymer melt through a flat tip needle by high electrostatic forces to deposit on a conducting metal collector. The detailed principles of the electrospinning process and the effects of process parameters on the resultant fibre properties have been extensively researched by many researchers and can be found elsewhere (Deitzel, Kleinmeyer, Harris, & Beck Tan, 2001; Doshi & Reneker, 1995; Frenot & Chronakis, 2003; Greiner & Wendorff, 2007; Huang, Zhang, Kotaki, & Ramakrishna, 2003; Pham, Sharma, & Mikos, 2006; Ramakrishna, Fujihara, Teo, Lim, & Ma, 2005; Subbiah, Bhat, Tock, Parameswaran, & Ramkumar, 2005; Teo & Ramakrishna, 2006; Yanılmaz, Kalaoğlu, & Karakaş, 2012). One of the most important properties of electrospun nanofibres are high surface area to volume ratios and a high degree of porosity with a nano-scaled inter-fibrous pore size (Ramakrishna et al., 2005). Furthermore, functionality of the resultant fibres can easily be raised by the addition of any substances into the spinning solution or melt. By this way, innovative functional materials can be produced having a potential use in a wide range of applications such as tissue engineering, drug delivery, wound healing, filtration, protective clothing, electromagnetic shielding, and energy applications (Cui, Zhou, & Chang, 2010; Huang et al., 2003; Khil, Cha, Kim, Kim, & Bhattarai, 2003; Sill & von Recum, 2008; Thavasi, Singh, & Ramakrishna, 2008; Yoo, Kim, & Park, 2009; Zahedi, Rezaeian, Ranaei-Siadat, Jafari, & Supaphol, 2010, Zhang, Lim, Ramakrishna, & Huang, 2005).

Electrospun nanofibrous membranes have been produced from a wide variety of polymers and their blends. Among them, thermoplastic polyurethanes (TPU) are a widely used class of polymer, which have a good biocompatibility and high mechanical properties, thus electrospun TPU membranes are of interest in terms of biomedical applications (Chen et al., 2010; Pedicini & Farris, 2003). Their unique combination of biocompatibility, non-toxicity, toughness and functionality has led to the widespread use of thermoplastic polyurethanes (TPUs) in implantable devices (vascular grafts, pacemaker leads, blood bags, bladders and artificial heart valves) and medical applications (Gupta, 2009; Huynh et al., 2010; Jiaxing, 2007; Sokolowski, Metcalfe, Hayashi, Yahiya, & Raymond, 2007; Zdrahala & Zdrahala, 1999). Besides, many commercially available TPU can easily be electrospun into nanofibres (Pedicini & Farris, 2003). Electrospinning of pure thermoplastic polyurethanes have been researched extensively by many researchers in terms of resultant fibre morphology. On the other hand, it is known that the incorporation of any material into an electrospinning solution or melt affects the resultant fibre morphology and properties, as well as electrospinning conditions, since the composition of the spinning solutions is directly related to the resultant fibre morphology. Thus the effects of additives on the behaviour of the spin solution

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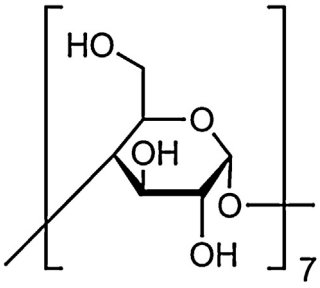

Fig. 1. Chemical structure of β-cyclodextrin (www.sigmaaldrich.com).

or melt need to be taken into account and resultant fibre properties should be investigated. In this contribution, the effects of incorporation of β-cyclodextrin on the properties of electrospun thermoplastic polyurethane (TPU) nanofibres were investigated, which will be the starting point of the development of functional TPU nanofibrous membranes that may have possible uses in medical textiles area.

Cyclodextrins are cyclic oligosaccharides which can be produced by the enzymatic degradation of starch (Del Valle, 2004). They consists of 6 (α), 7 (β), or 8 (γ) or more glucopyranose units linked by α(1→4)-glycosidic linkages, forming a torus-shaped ring structure with a hydrophobic cavity and a hydrophilic exterior (Ritter & Tabatabai, 2004; Roy, Bajpai, & Bajpai, 2011). The main interest in cyclodextrins lies in their ability to form non-covalent inclusion complexes with several compounds (Del Valle, 2004). Therefore, cyclodextrins are employed as drug carriers (Hirayama & Uekama, 1999; Uekama, Hirayama, & Irie, 1998), additives in food (Astray, Gonzalez-Barreiro, Mejuto, Rial-Otero, & Simal-Gandara, 2009; Szente & Szejtli, 2004), auxiliaries in textile processes (Buschmann, Denter, Knittel, & Schollmeyer, 1998; Voncina & Vivod, 2013), perfumes and cosmetics elements (Buschmann & Schollmeyer, 2002), enzyme models (Rizzarelli & Vecchio, 1999), separating agents (Szejtli, 2004), mass transfer promoters (Tilloy, Bricout, & Monflier, 2002), environmental protection agents or sensors for organic molecules (Becuwe, Landy, Delattre, Cazier, & Fourmentin, 2008). Among the parent cyclodextrins, β-cyclodextrin (β-CD) is the most accessible and widely used type due to its lower price, availability, approval status and the diameter of its cavity (Szejtli, 1997). Chemical structure of β-CD is shown in Fig. 1.

Incorporation of cyclodextrins within nanofibrous structures is of great advantage due to the combination of the absorption/release capabilities of cyclodextrins via inclusion complexes and a high surface area with a high porous structure of electrospun nanofibres. A series of papers were published including several polymers with cyclodextrins or cyclodextrin inclusion complexes for the functionalization of electrospun nanofibres. Li and Hsieh (2005) have used β-CD for the crosslinking of polyacrylic acid nanofibres. Ramaseshan et al. (2006) investigated the production of protective textile material by functionalization of PVC nanofibres using a catalyst synthesized from β-CD and o-iodosobenzoic acid for the detoxification of nerve agents. Uyar, Kingshott, and Besenbacher (2008) have reported the electrospinning of cyclodextrin pseudopolyrotaxane nanofibres using PEO as a carrier polymer. Bai, Yang, Li, Wang, et al. (2008) and Bai, Yang, Li, Zhang et al. (2008) have produced β-CD/poly(N-vinylpyrrolidone) composite nanofibres.

Studies for poly(methyl methacrylate) (PMMA) nanofibres have shown that the addition of cyclodextrins assisted the electrospinning of bead-free uniform nanofibres (Uyar, Balan, Toppare et al. 2009). It was reported that cyclodextrin-included PMMA nanofibres can entrap organic waste vapours (Uyar, Havelund, Nur, et al. 2010) and phenolphthalein (Kaur, Kotaki, Ma, Gopal, & Ramakrishna, 2006). Achieving the stability and sustained release of menthol by incorporation of cyclodextrin–menthol inclusion complexes within PMMA nanofibres has also been investigated (Uyar, Nur, Hacaloglu et al. 2009).

Uyar and Besenbacher (2009) investigated that bead-free nanofibres could be obtained by the incorporation of cyclodextrins into polyethylene oxide (PEO) nanofibres even at low polymer concentrations due to the higher conductivity and viscosity of polymer solutions.

A series of papers (Uyar, Havelund, Hacaloglu, et al. 2009; Uyar, Havelund, Hacaloğlu, et al, 2010; Uyar, Havelund, Nur, et al. 2009; Uyar, Hacaloglu, & Besenbacher, 2009) have appeared on the characterization and performances of cyclodextrin functionalized polystyrene (PS) nanofibres. It was concluded that the incorporation of cyclodextrins into a PS spinning solution led to bead-free fibres, while the surface was rougher compared to pure PS nanofibres. Phenolphthalein absorbance capability of PS/CD nanofibres and menthol stability of PS/(CD–menthol inclusion complex) nanofibres has also been reported.

Electrospinning of β-CD/polyvinyl alcohol (PVA) nanofibres was investigated by Zhang, Chen, and Diao (2011). They conducted that the number of beads decreased and the mean fibre diameters increased with the increase in β-CD concentration attributed to the increase in viscosity of polymer solutions. Teng, Li, Zhang, & Taha (2011) reported that PVA/CD/SiO_2 composite nanofibrous membranes produced by sol–gel/electrospinning method are highly efficient for indigo dye absorption. In the other study of PVA made by Kayaci & Uyar (2012a), in which CD–vanillin inclusion complexes were incorporated into fibre structure, it has been illustrated that the stabilization and slow release of vanillin was obtained.

Recently, cyclodextrin functionalized polymethacrylic acid (De Sousa et al., 2010), zein (Kayaci & Uyar, 2012b), polyacrylonitrile (Jadhav & Kim, 2013; Wang, Bai, Li, & Zhang, 2012), polylactic acid (Kayaci, Umu, Tekinay, & Uyar, 2013) and carbonaceous (Chen et al., 2011) nanofibres have also appeared in literature. The electrospinning of cyclodextrins without a carrier polymer has also been studied by several authors (Chen et al., 2013; Celebioglu & Uyar, 2010, 2011, 2012, 2013; Manasco, Saquing, Tang, & Khan, 2012; Zhang, Chen, Zha, & Diao, 2012).

In the scope of this study, it is aimed to investigate the effects of β-CD on the resultant fibre properties of electrospun TPU in terms of fibre morphology, membrane properties and thermal properties of the fibres. Incorporation of β-CD into TPU nanofibres during electrospinning was discussed for the first time in this study to the best of the authors' knowledge. This study is the prime motivation behind being a starting point of the development of TPU based functional textile structures functionalized by cyclodextrins for potential applications in medical textiles industry.

2. Experimental

2.1. Materials

Thermoplastic polyurethane (Pellethane 2103-80AE, based on 4,4′-methylene bisphenylene isocyanate, polytetramethylene oxide and 1,4 butanediol) was received from Velox (Lubrizol Advanced Materials). N,N dimethylformamide (anhydrous, 99.8%) was purchased from Sigma Aldrich. β-cyclodextrin was purchased from Wacker Chemie AG.

2.2. Electrospinning

8% and 10% TPU stock solutions were prepared by dissolving TPU granulates in N,N dimethylformamide at room temperature. β-CD was added into the spinning solution followed by a further stirring.

To examine the effects of the amounts of β-CD, 10%, 20% and 30% β-CD (w/w polymer) concentrations were used and are encoded throughout the article as CD10, CD20 and CD30, respectively.

Electrospinning of the polymer solutions was carried out by a set-up consisting of a syringe (10 ml) and needle (2.5 cm long, 22 gauges, flat tip), a ground electrode, and a high voltage supply (Simco, MP Series CM5 30 P, Charging Generator Output 30 kV DC). Polymer solutions were electrospun at a voltage of 13 kV, and a tip-to-collector distance of 20 cm with a feeding rate of 1 ml/h. A grounded stationary rectangular metal collector covered by a piece of aluminium foil was used for the nanofibre deposition.

2.3. Characterization

Viscosity of the polymer solutions was measured by using a Brookfield DV-III Rheometer with the spindle type SC4-21 and 27 at 30 rpm. Surface tension measurements were carried out by a Krüss Easy Dyne Analyser by Plate Method. Conductivity measurements were carried out using a J.P. Selecta Conductivity meter, CD-2004.

The morphology of the electrospun PVA nanofibres was characterized using scanning electron microscopy (SEM, FEI Quanta250 FEG). Each sample was coated with a thin film of gold using an EMITECH K550X ion sputtering device. Fibre diameters were determined by using Image J software. Fibre diameters were measured by using SEM images by drawing straight lines perpendicular to the fibre axis. The pixel values of the lines were converted to diameter values. Forty measurements were carried out from the different parts of each sample.

The thickness of the nanofibrous membranes was measured by a Mitutoyo digital micrometer at 0.001 mm accuracy. Each sample was measured along the diameter of nanofibrous membranes following the arrow. Thicker and thinner regions were shown as paler and darker, respectively.

Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a PerkinElmer FT-IR spectrometer. Thermal behaviour of TPU and TPU/CD samples was investigated by thermogravimetric analysis (TGA) (PERKIN ELMER TGA-4000) by heating samples from room temperature to 600 °C under continuous nitrogen purge at the rate of 20 ml/min, and by differential scanning calorimetry (DSC) (TA Instrument, Q10 DSC instrument) by heating samples from room temperature to 350 °C at the rate of 10 °C/min, under continuous nitrogen purge at the rate of 50 ml/min.

2.4. Phenolphthalein absorbance tests

Phenolphthalein (PhP) is an indicator and has often been used for proving the existence of cyclodextrins due to its high affinity for the CD cavity (Kumbasar, Atav, Yurdakul, & Voncina, 2009; Uyar,Havelund, Nur, et al. 2009). Thus, in order to test the complex

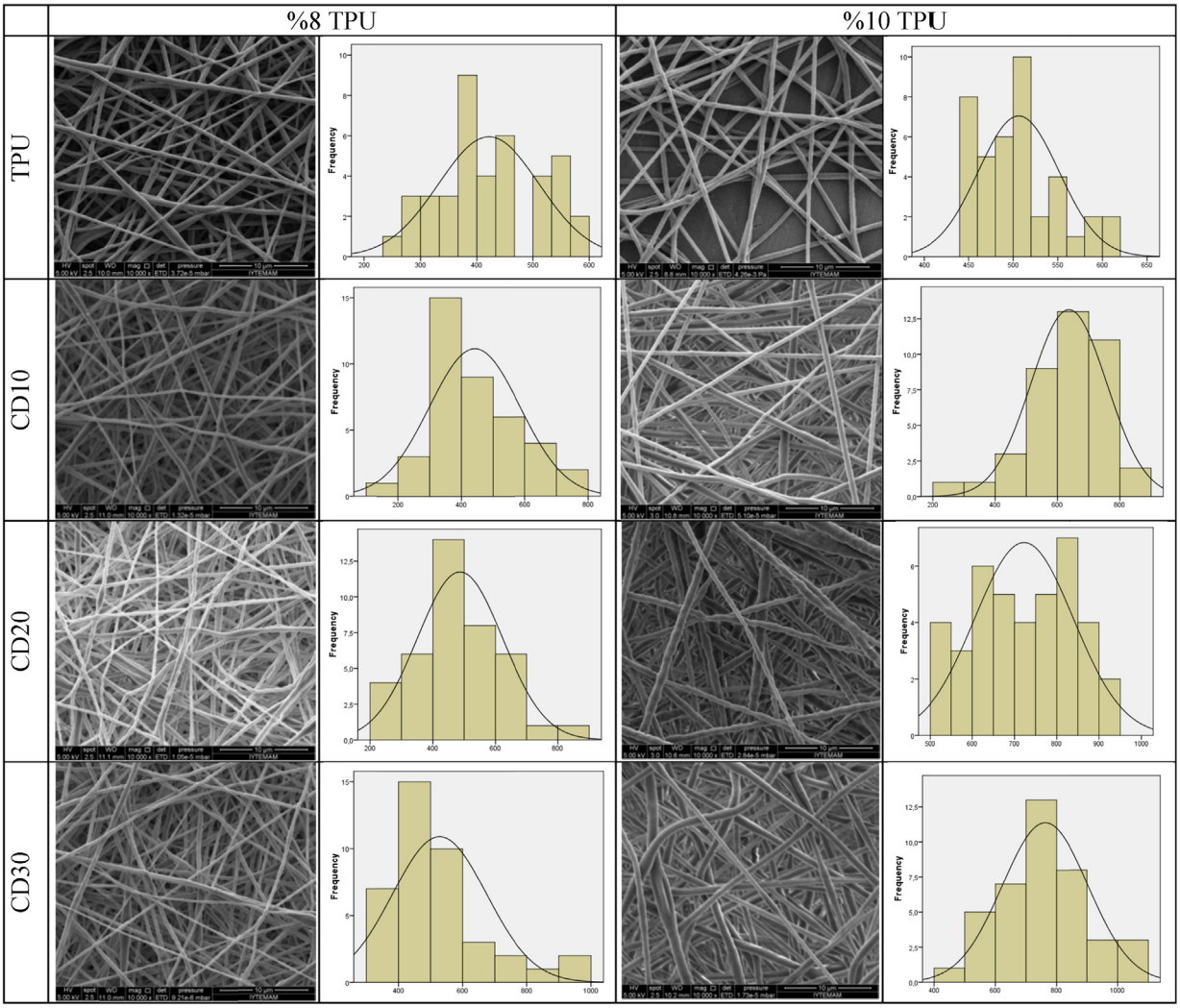

Fig. 2. SEM images of TPU and TPU/CD nanofibres and fibre diameter distribution histograms.

formation performance of the TPU and TPU/CD electrospun nanofibres, the phenolphthalein method was used as a model application. Uptake was determined by measuring the reductions in absorbance using UV–vis spectrophotometer (Perkin Elmer UV/VIS spectrometer) at maximum absorbance wave length (561 nm). PhP solution was prepared in absolute ethanol and pH of solution was adjusted to basic (above pH 11). 20 mg of fibres were immersed into UV-Vis cuvettes filled with PhP solution. The cuvettes were covered with a parafilm lid to prevent the evaporation of ethanol. Absorbance measurements were carried out 1, 4 and 24 h after the immersion of fibres.

3. Results and discussion

Fig. 2 illustrates the scanning electron micrographs of TPU and TPU/CD nanofibres, and fibre diameter distribution histograms for each membrane. Since the solution parameters are of great importance in terms of resultant fibre morphology, surface tension, viscosity and conductivity measurements of each solution were tested as displayed in Table 1. The surface tension of polymer solutions was not affected significantly by the addition of β-CD. The viscosity of the polymer solutions were slightly decreased

Table 1
Properties of TPU, TPU/CD solutions and mean diameter of nanofibres.

	Surface Tension (m/Nm)	Conductivity (μS/cm)	Viscosity (cp)	Mean fibre diameter (nm)	Standard deviation of mean fibre diameter
8% TPU	37.7	1.09	658	421.44	89.501
8% TPU/CD10	38.0	1.31	626	442.20	143.040
8% TPU/CD20	37.9	1.67	649	486.62	135.890
8% TPU/CD30	37.9	1.72	675	527.94	146.270
10% TPU	39.1	1.07	2155	506.12	45.293
10% TPU/CD10	38.3	1.34	2111	636.53	121.475
10% TPU/CD20	38.9	1.56	2133	722.48	116.724
10% TPU/CD30	39.4	1.86	2244	762.92	140.189

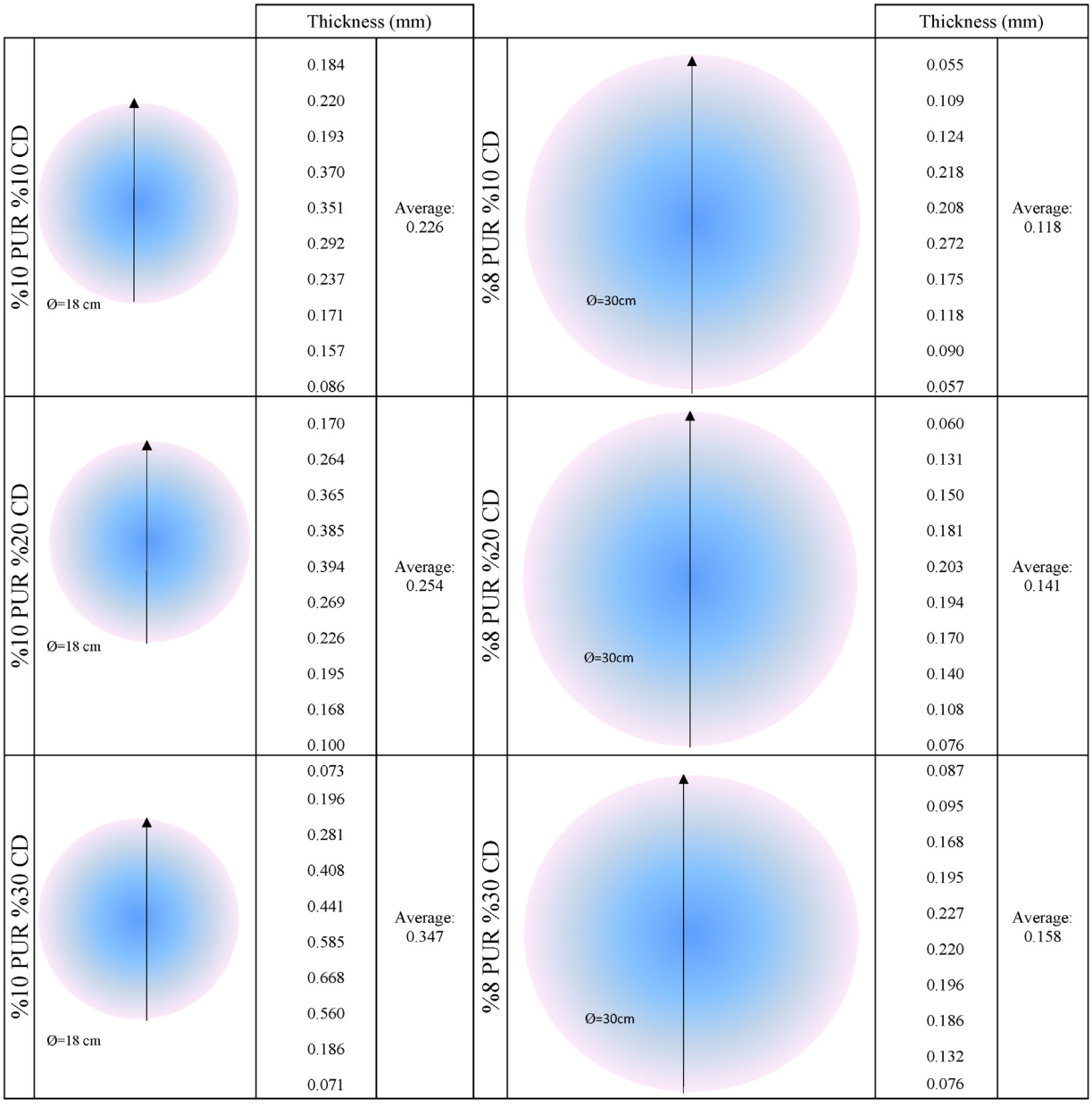

Fig. 3. Average diameter and thickness of TPU/CD nanofibrous membranes.

with the addition of 10% β-CD, however with the increase in β-CD concentration, the viscosity of the solutions increased and became higher compared to pure TPU solutions. The electrical conductivity of the solutions increased with the increase in β-CD concentration. Resultant fibre diameters increased with the increase in polymer concentration due to higher viscosity. Besides, the mean fibre diameters were noted to increase with the addition of β-CD for both 8% and 10% TPU concentrations and this increase was more pronounced at higher β-CD concentrations. Fibre diameter distribution histograms show that the variation range in fibre diameters increases with increasing the addition of β-CD. Also the standard deviations of mean fibre diameters in Table 1 highlight these variations. This means that the addition of β-CD leads to the production of more heterogeneous nanofibrous structures.

The effects of β-CD concentration on the thickness of nanofibrous membranes were also investigated, considering a change in thickness might affect the amount of any incorporated molecules within the unit area of a membrane. Fig. 3 illustrates the mean diameter and thickness of each membrane. It was visually observed that the diameter of 8% TPU/CD nanofibrous membranes (~30 cm) was higher than those of 10% TPU/CD (~18 cm), due to the lower viscoelastic force of 8% TPU solution. Thus 8% TPU/CD nanofibrous membranes have greater thickness. An increase in β-CD concentration had no effect on the collected membrane diameter. On the other hand, it was observed that the increase in β-CD concentration led to an increase in membrane thickness, which is thought to be due to the increase in fibre diameters.

Fourier transform infrared spectroscopy (FTIR) analysis of β-CD, pure TPU nanofibres and TPU/CD30 nanofibres (10% TPU concentration) are illustrated in Fig. 4 for the whole spectrum and for 700–1400 cm^{-1}, respectively. The typical bands for β-CD are observed at 3300 cm^{-1} assigned to —OH stretching vibration, 1077 cm^{-1} and 1022 cm^{-1} corresponding to coupled C—C/C—O stretching vibration, and 1152 cm^{-1} assigned to the antisymmetric stretching vibration of the C—O—C glycosidic bridge (Uyar, Balan,Toppare, et al. 2009; Uyar & Besenbacher, 2009; Zhang et al., 2011). FTIR spectra of TPU/CD30 nanofibres are similar to those of pure TPU nanofibres. However, the bands at 1078 cm^{-1} and 1154 cm^{-1} which were assigned to coupled C—C/C—O stretching vibration and antisymmetric stretching vibration of the C—O—C glycosidic bridge of β-CD, respectively, were observed. Besides, it was observed that —OH stretching vibration peak became broader with the incorporation of β-CD within TPU nanofibres. These categorically prove the existence of β-CD molecules on TPU nanofibres.

The thermal stability of electrospun TPU and TPU/CD nanofibres was measured using thermogravimetric analysis. TG curves of TPU and TPU/CD nanofibres for 10% polymer concentration are shown in Fig. 5. It was observed that pure TPU nanofibres have a single step degradation which started at around 285 °C, and half-weight loss temperature was around 350 °C. On the other hand, initial degradation step of TPU/CD nanofibres started from 300 °C which accounts for the starting point for TPU present within nanofibres. The second step was slightly observed at around 385 °C, which can be associated with the β-CD inside the nanofibres. TPU/CD30 nanofibres showed similar tendencies to TPU/CD10 nanofibres,

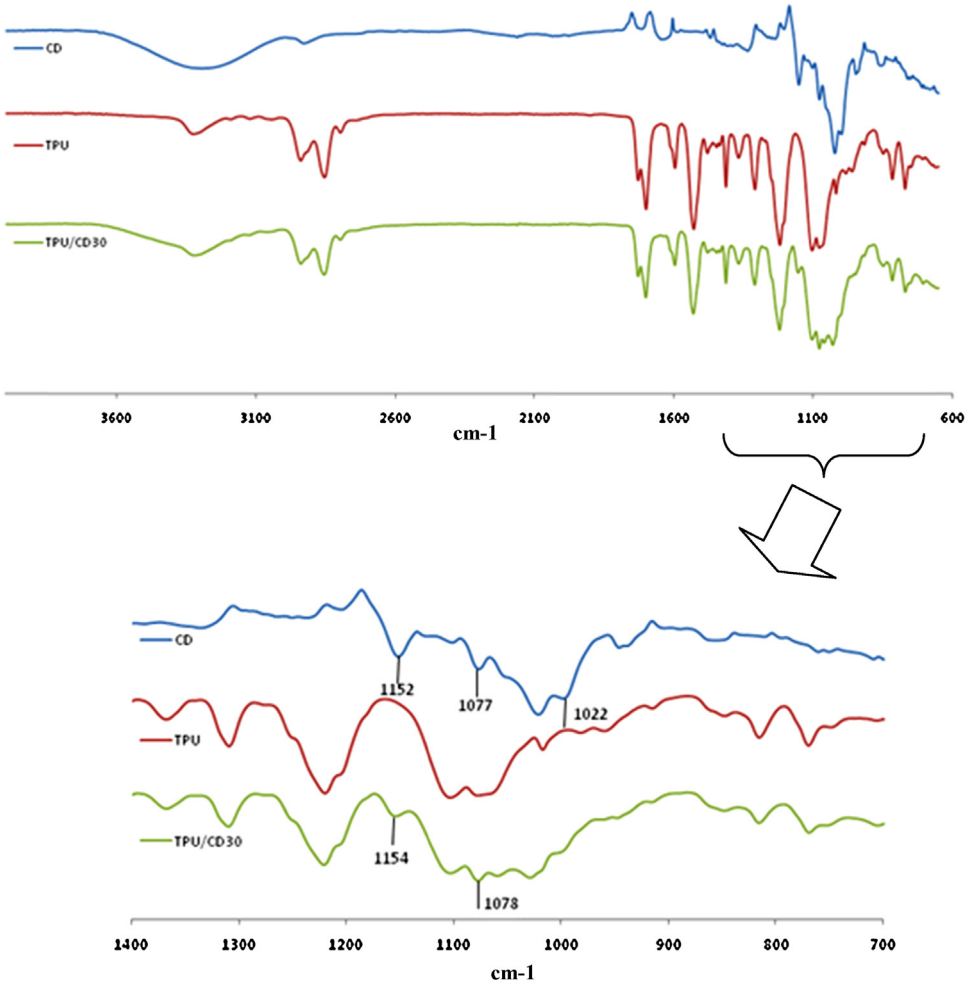

Fig. 4. FTIR spectra of β-CD, pure TPU nanofibres and TPU/CD30 nanofibres.

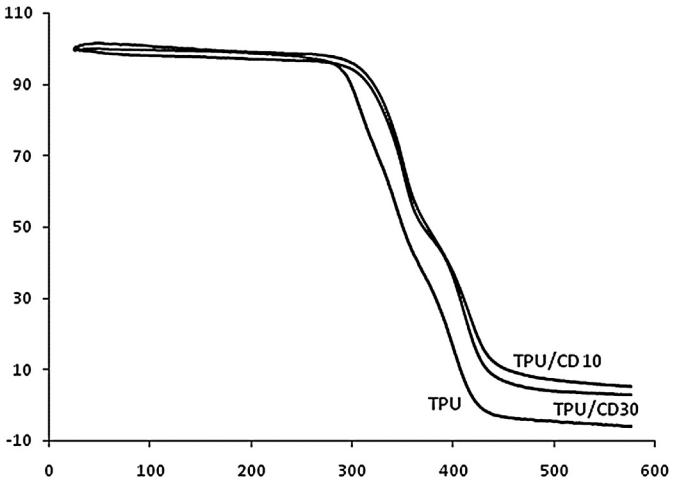

Fig. 5. TG curves of TPU and TPU/CD nanofibres (10% TPU concentration).

which concludes that the difference in concentration of β-CD is not significant in terms of the thermal properties of TPU/CD composite nanofibres. It can be concluded that the incorporation of β-CD into TPU nanofibres impeded the start of degradation. Besides, the residual weight was increased for β-CD included nanofibres.

Differential scanning calorimetry curves of pure TPU nanofibres and TPU/CD nanofibres for 10% polymer concentration are shown in Fig. 6. The DSC curve of pure TPU nanofibres shows two very small peaks at 56 °C and 95 °C and these endothermic peaks can be associated with the melting temperatures of soft and hard segments, respectively (Barick & Tripathy, 2010). It is obvious that, the incorporation of β-CD into the fibre structure led to a change in melting points and melting enthalpies. However the effects of β-CD concentration on melting points of TPU/CD nanofibres are not clear. TPU/CD10 and TPU/CD30 nanofibres have higher melting points (112 °C and 127 °C) while TPU/CD20 nanofibres have a similar melting point (96 °C) with pure TPU nanofibres. It can be claimed that β-CD increases the heat of melting of TPU nanofibres.

In order to test the performance of β-CD, whether they can form inclusion complexes or blocked within TPU fibres, the phenolphthalein absorbency test was applied. Phenolphthalein has high affinity for the β-CD cavity and can be used as a model for testing β-CD inclusion complexation performance. TPU/CD nanofibres were immersed into phenolphthalein solution and the change in the colour of the solutions was tested by UV–vis spectrometry. The cumulative decrease of phenolphthalein absorbance (%) over time at 561 nm is shown in Fig. 7. It was indicated that the absorbance of phenolphthalein solution decreased significantly with the increase

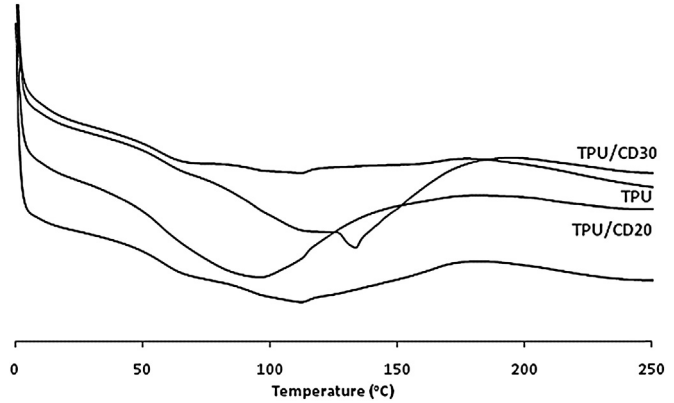

Fig. 6. DSC thermograms of TPU and TPU/CD nanofibres.

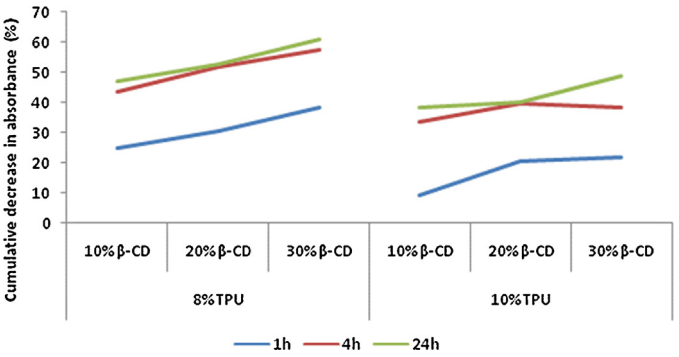

Fig. 7. Cumulative decrease in phenolphthalein absorbance (%) over time at 561 nm.

of the β-CD concentration and time. On the other hand, 8% TPU/CD nanofibres were observed to absorb a higher amount of phenolphthalein, which is thought to be due to their larger surface area since they have finer fibres compared to 10% TPU/CD nanofibres. These results confirm that β-CD within TPU nanofibres can form inclusion complexes.

4. Conclusions

The effects of the incorporation of β-CD on the properties of electrospun TPU nanofibres were investigated in this study. It was observed that TPU/CD nanofibres had higher fibre diameters compared to pure TPU nanofibres and fibre diameters increased with the increase in β-CD concentration. Correspondingly, membrane thickness was increased due to the increase in fibre diameters. Also it was shown that addition of β-CD led to the formation of more heterogeneous nanofibrous structures in terms of fibre diameter distribution.

The existence of β-CD on TPU/CD nanofibres was confirmed by FTIR analysis. TGA analysis showed that β-CD impeded the start of degradation of TPU nanofibres. The change in melting point of TPU nanofibres by the addition of β-CD was proven by DSC analysis.

Inclusion complex formation capability of TPU/CD nanofibres was proven by the phenolphthalein test method. 8% TPU/CD nanofibres absorbed a higher amount of phenolphthalein due to their larger surface area since they have finer fibres compared to 10% TPU/CD nanofibres. This indicates that TPU nanostructure did not prevent the inclusion complex formation of β-CD and TPU/CD nanofibrous membranes are believed to have good potentials for functional applications such as controlled release systems and biotechnological applications.

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References

Akcakoca Kumbasar, E. P., Atav, R., Yurdakul, A., & Voncina, B. (2009). Using of the cyclodextrin and phenolphthalein interaction for the determination of the amount of fixed β-cyclodextrin on cotton. In *Proceedings of AUTEX 2009 World Textile Congress* 26–28 May, Izmir, Turkey, (pp. 88–94).

Astray, G., Gonzalez-Barreiro, C., Mejuto, J. C., Rial-Otero, R., & Simal-Gandara, J. (2009). A review on the use of cyclodextrins in foods. *Food Hydrocolloids*, *23*(7), 1631–1640.

Bai, J., Yang, Q., Li, M., Wang, S., Zhang, C., & Li, Y. (2008). Preparation of composite nanofibers containing gold nanoparticles by using poly(N-vinylpyrrolidone) and β-cyclodextrin. *Materials Chemistry and Physics*, *111*(2–3), 205–208.

Bai, J., Yang, Q., Li, M., Zhang, C., & Yiaoxian, L. (2008). Synthesis of poly(N-vinylpyrrolidone)/β-cyclodextrin composite nanofibers using electrospinning techniques. *Journal of Materials Processing Technology*, *208*(1–3), 251–254.

Barick, A. K., & Tripathy, D. K. (2010). Thermal and dynamic mechanical characterization of thermoplastic polyurethane/organoclay nanocomposites prepared by melt compounding. *Materials Science and Engineering: A*, *527*(3), 812–823.

Becuwe, M., Landy, D., Delattre, F., Cazier, F., & Fourmentin, S. (2008). Fluorescent indolizine-b-cyclodextrin derivatives for the detection of volatile organic compounds. *Sensors*, *8*(6), 3689–3705.

Buschmann, H.-J., & Schollmeyer, E. (2002). Applications of cyclodextrins in cosmetic products: A review. *Journal of Cosmetic Science*, *53*, 185–191.

Buschmann, H.-J., Denter, U., Knittel, D., & Schollmeyer, E. (1998). The use of cyclodextrins in textile processes – An overview. *Journal of the Textile Institute*, *89*(3), 554–561.

Celebioglu, A., & Uyar, T. (2010). Cyclodextrin nanofibers by electrospinning. *Chemical Communications*, *46*, 6903–6905.

Celebioglu, A., & Uyar, T. (2011). Electrospinning of polymer-free nanofibers from cyclodextrin inclusion complexes. *Langmuir*, *27*(10), 6218–6226.

Celebioglu, A., & Uyar, T. (2012). Electrospinning of nanofibers from non-polymeric systems: Polymer-free nanofibers from cyclodextrin derivatives. *Nanoscale*, *4*, 621–631.

Celebioglu, A., & Uyar, T. (2013). Green and one-step synthesis of gold nanoparticles incorporated into electrospun cyclodextrin nanofibers. *RSC Advances*, *3*, 10197–10201.

Chen, R., Huang, C., Ke, Q., He, C., Wang, H., & Mo, X. (2010). Preparation and characterization of coaxial electrospun thermoplastic polyurethane/collagen compound nanofibers for tissue engineering applications. *Colloids and Surfaces B: Biointerfaces*, *79*(2), 315–325.

Chen, P., Liang, H.-W., Lv, X.-H., Zhu, H.-Z., Yao, H.-B., & Yu, S.-H. (2011). Carbonaceous nanofiber membrane functionalized by beta-cyclodextrins for molecular filtration. *ACS Nano*, *5*(7), 5928–5935.

Chen, M., Nielsen, S. R., Uyar, T., Zhang, S., Zafar, A., Dong, M., et al. (2013). Electrospun UV-responsive supramolecular nanofibres from a cyclodextrin–azobenzene inclusion complex. *Journal of Materials Chemistry C*, *1*, 850–855.

Cui, W., Zhou, Y., & Chang, J. (2010). Electrospun nanofibrous materials for tissue engineering and drug delivery. *Science and Technology of Advanced Materials*, *11*(1), 014108.

De Sousa, F. B., Guerreiro, J. D. T., Ma, M., Anderson, D. G., Drum, C. L., Sinisterra, R. D., et al. (2010). Photo-response behavior of electrospun nanofibers based on spiropyran–cyclodextrin modified polymer. *Journal of Materials Chemistry*, *20*, 9910–9917.

Deitzel, J. M., Kleinmeyer, J., Harris, D., & Beck Tan, N. C. (2001). The effect of processing variables on the morphology of electrospun nanofibres and textiles. *Polymer*, *42*(1), 261–272.

Del Valle, E. M. M. (2004). Cyclodextrins and their uses: A review. *Process Biochemistry*, *39*(9), 1033–1046.

Doshi, J., & Reneker, D. H. (1995). Electrospinning process and applications of electrospun fibers. *Journal of Electrostatics*, *35*(2–3), 151–160.

Frenot, A., & Chronakis, I. S. (2003). Polymer nanofibres assembled by electrospinning. *Science*, *8*(1), 64–75.

Greiner, A., & Wendorff, J. H. (2007). Electrospinning: A fascinating method for the preparation of ultrathin fibers. *Angewandte Chemie International Edition*, *46*(30), 5670–5703.

Gupta, B. S. (2009). Textile materials and structures for wound care products. In S. Rajendran (Ed.), *Advanced textiles for wound care* (pp. 48–92). Cambridge: Woodhead Publishing Limited.

Hirayama, F., & Uekama, K. (1999). Cyclodextrin-based controlled drug release system. *Advanced Drug Delivery Reviews*, *36*(1), 125–141.

Huang, Z.-M., Zhang, Y.-Z., Kotaki, M., & Ramakrishna, S. (2003). A review on polymer nanofibres by electrospinning and their applications in nanocomposites. *Composites Science and Technology*, *63*(15), 2223–2253.

Huynh, T. T. N. Y., Padois, K., Sonvico, F., Rossi, A., Zani, F., Pirot, F., et al. (2010). Characterization of a polyurethane-based controlled release system for local delivery of chlorhexidine diacetate. *European Journal of Pharmaceutics and Biopharmaceutics*, *74*(2), 255–264.

Jadhav, A. H., & Kim, H. (2013). Preparation and application of supramolecular assembled β-cyclodextrin/polyacrylonitrile composite nanofibers as a highly efficient adsorbent for dye removal. *Advanced Materials Research*, *622–623*, 827–832.

Jiaxing, Y. Q. (2007). Smart wound-care materials. In L. V. Lagenhove (Ed.), *Smart textiles for medicine and healthcare* (pp. 27–50). Cambridge, England: Woodhead Publishing Limited.

Kaur, S., Kotaki, M., Ma, Z., Gopal, R., & Ramakrishna, S. (2006). Oligosaccharide functionalized nanofibrous membranes. *International Journal of Nanoscience*, *5*(1), 1–11.

Kayaci, F., & Uyar, T. (2012a). Encapsulation of vanillin/cyclodextrin inclusion complex in electrospun polyvinyl alcohol (PVA) nanowebs: Prolonged shelf-life and high temperature stability of vanillin. *Food Chemistry*, *133*(3), 641–649.

Kayaci, F., & Uyar, T. (2012b). Electrospun zein nanofibers incorporating cyclodextrins. *Carbohydrate Polymers*, *90*(1), 558–568.

Kayaci, F., Umu, O. C. O., Tekinay, T., & Uyar, T. (2013). Antibacterial electrospun poly(lactic acid) (PLA) nanofibrous webs incorporating triclosan/cyclodextrin inclusion complexes. *Journal of Agricultural and Food Chemistry*, *61*(16), 3901–3908.

Khil, M.-S., Cha, D.-I., Kim, H.-Y., Kim, I.-S., & Bhattarai, N. (2003). Electrospun nanofibrous polyurethane membrane as wound dressing. *Journal of Biomedical Materials Research Part B: Applied Biomaterials*, *67B*(2), 675–679.

Li, L., & Hsieh, Y.-L. (2005). Ultra-fine polyelectrolyte fibers from electrospinning of poly(acrylic acid). *Polymer*, *46*(14), 5133–5139.

Manasco, J. L., Saquing, C. D., Tang, C., & Khan, S. A. (2012). Cyclodextrin fibers via polymer-free electrospinning. *RSC Advances*, *2*, 3778–3784.

Pedicini, A., & Farris, R. J. (2003). Mechanical behavior of electrospun polyurethane. *Polymer*, *44*(22), 6857–6862.

Pham, Q. P., Sharma, U., & Mikos, A. G. (2006). Electrospinning of polymeric nanofibres for tissue engineering applications: A review. *Tissue Engineering*, *12*(5), 1197–1211.

Ramakrishna, S., Fujihara, K., Teo, W.-E., Lim, T.-C., & Ma, Z. (2005). *An introduction to electrospinning and nanofibers*. Singapore: World Scientific Publishing Co. Pte. Ltd.

Ramaseshan, R., Sundarrajan, S., Liu, Y. J., Barhate, R. S., Lala, N. L., & Ramakrishna, S. (2006). Functionalized polymer nanofibre membranes for protection from chemical warfare stimulants. *Nanotechnology*, *17*(12), 2947–2953.

Retrieved from www.sigmaaldrich.com, β-cyclodextrin, produced by Wacker Chemie, A. G., Burghausen, Germany, W26 Aldrich4028.

Ritter, H., & Tabatabai, M. (2004). *Cyclodextrins. Encyclopedia of polymer science and technology* (Vol. 9) John Wiley & Sons, Inc.

Rizzarelli, E., & Vecchio, G. (1999). Metal complexes of functionalized cyclodextrins as enzyme models and chiral receptors. *Coordination Chemistry Reviews*, *188*(1), 343–364.

Roy, A., Bajpai, J., & Bajpai, A. K. (2011). Carbohydrate polymers as versatile materials in controlled release technologies. In C. E. Jones (Ed.), *Encyclopedia of polymer research* (pp. 1195–1225). New York: Nova Science Publishers.

Sill., T. J., & von Recum, H. A. (2008). Electrospinning: Applications in drug delivery and tissue engineering. *Biomaterials*, *29*(13), 1989–2006.

Sokolowski, W., Metcalfe, A., Hayashi, S., Yahiya, L., & Raymond, J. (2007). Medical applications of shape memory polymers. *Biomedical Materials*, *2*(1), 23–27.

Subbiah, T., Bhat, G. S., Tock, R. W., Parameswaran, S., & Ramkumar, S. S. (2005). Electrospinning of nanofibers. *Journal of Applied Polymer Science*, *96*(2), 557–569.

Szejtli, J. (1997). Utilization of cyclodextrins in industrial products and processes. *Journal of Materials Chemistry*, *7*(4), 575–587.

Szejtli, J. (2004). Past, present, and future of cyclodextrin research. *Pure and Applied Chemistry*, *76*(10), 1825–1845.

Szente, L., & Szejtli, J. (2004). Cyclodextrins as food ingredients. *Trends in Food Science & Technology*, *15*(3–4), 137–142.

Teng, M., Li, F., Zhang, B., & Taha, A. A. (2011). Electrospun cyclodextrin-functionalized mesoporous polyvinyl alcohol/SiO_2 nanofiber membranes as a highly efficient adsorbent for indigo carmine dye. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *385*(1–3), 229–234.

Teo, W. E., & Ramakrishna, S. (2006). A review on electrospinning design and nanofibre assemblies. *Nanotechnology*, *17*(14), 89–106.

Thavasi, V., Singh, G., & Ramakrishna, S. (2008). Electrospun nanofibres in energy and environmental applications. *Energy & Environmental Science*, *1*, 205–221.

Tilloy, S., Bricout, H., & Monflier, E. (2002). Cyclodextrins as inverse phase transfer catalysts for the biphasic catalytic hydrogenation of aldehydes: A green and easy alternative to conventional mass transfer promoters. *Green Chemistry*, *4*, 188–193.

Uekama, K., Hirayama, F., & Irie, T. (1998). Cyclodextrin drug carrier systems. *Chemical Reviews*, *98*, 2045–2076.

Uyar, T., & Besenbacher, F. (2009). Electrospinning of cyclodextrin functionalized polyethylene oxide (PEO) nanofibers. *European Polymer Journal*, *45*(4), 1032–1037.

Uyar, T., Kingshott, P., & Besenbacher, F. (2008). Electrospinning of cyclodextrin–pseudopolyrotaxane nanofibers. *Angewandte Chemie International Edition*, *47*(47), 9108–9111.

Uyar, T., Havelund, R., Hacaloglu, J., Zhou, X., Besenbacher, F., & Kingshott, P. (2009). The formation and characterization of cyclodextrin functionalized polystyrene nanofibers produced by electrospinning. *Nanotechnology*, *20*(12), 125605.

Uyar, T., Havelund, R., Nur, Y., Hacaloglu, J., Besenbacher, F., & Kingshott, P. (2009). Molecular filters based on cyclodextrin functionalized electrospun fibers. *Journal of Membrane Science*, *332*(1–2), 129–137.

Uyar, T., Nur, Y., Hacaloglu, J., & Besenbacher, F. (2009). Electrospinning of functional poly(methyl methacrylate) nanofibers containing cyclodextrin–menthol inclusion complexes. *Nanotechnology*, *20*(12), 125703.

Uyar, T., Balan, A., Toppare, L., & Besenbacher, F. (2009). Electrospinning of cyclodextrin functionalized poly(methyl methacrylate) (PMMA) nanofibers. *Polymer*, *50*(2), 475–480.

Uyar, T., Hacaloglu, J., & Besenbacher, F. (2009). Electrospun polystyrene fibers containing high temperature stable volatile fragrance/flavor facilitated by cyclodextrin inclusion complexes. *Reactive & Functional Polymers*, *69*(3), 145–150.

Uyar, T., Havelund, R., Hacaloglu, J., Besenbacher, F., & Kingshott, P. (2010). Functional electrospun polystyrene nanofibers incorporating α-, β-, and (-cyclodextrins: Comparison of molecular filter performance. *ACS Nano*, *4*(9), 5121–5130.

Uyar, T., Havelund, R., Nur, Y., Balan, A., Hacaloglu, J., Toppare, L., et al. (2010). Cyclodextrin functionalized poly(methyl methacrylate) (PMMA) electrospun nanofibers for organic vapors waste treatment. *Journal of Membrane Science*, *365*(1–2), 409–417.

Voncina, B., & Vivod, V. (2013). Cyclodextrins in textile finishing. In M. Günay (Ed.), *Eco-friendly textile dyeing and finishing* (pp. 53–75). Croatia: InTech.

Wang, S., Bai, J., Li, C., & Zhang, J. (2012). Functionalization of electrospun β-cyclodextrin/polyacrylonitrile (PAN) with silver nanoparticles: Broad-spectrum antibacterial property. *Applied Surface Science*, *261*(15), 499–503.

Yanılmaz, M., Kalaoğlu, F., & Karakaş, H. (2012). Study on optimising the morphology of electrospun polyurethane nanofibers. *Tekstil ve Konfeksiyon*, *22*(3), 212–217.

Yoo, H. S., Kim, T. G., & Park, T. G. (2009). Surface-functionalized electrospun nanofibres for tissue engineering and drug delivery. *Advanced Drug Delivery Reviews*, *61*(12), 1033–1042.

Zahedi, P., Rezaeian, I., Ranaei-Siadat, S.-O., Jafari, S.-H., & Supaphol, P. (2010). A review on wound dressings with an emphasis on electrospun nanofibrous polymeric bandages. *Polymers for Advanced Technologies*, *21*(2), 77–95.

Zdrahala, R. J., & Zdrahala, I. J. (1999). Biomedical applications of polyurethanes: A review of past promises, present realities, and a vibrant future. *Journal of Biomaterials Applications*, *14*(1), 67–90.

Zhang, Y., Lim, C. T., Ramakrishna, S., & Huang, Z.-M. (2005). Recent development of polymer nanofibres for biomedical and biotechnological applications. *Journal of Materials Science: Materials in Medicine*, *16*(10), 933–946.

Zhang, W., Chen, M., & Diao, G. (2011). Electrospinning β-cyclodextrin/poly(vinyl alcohol) nanofibrous membrane for molecular capture. *Carbohydrate Polymers*, *86*(3), 1410–1416.

Zhang, W., Chen, M., Zha, B., & Diao, G. (2012). Correlation of polymer-like solution behaviors with electrospun fiber formation of hydroxypropyl-β-cyclodextrin and the adsorption study on the fiber. *Physical Chemistry Chemical Physics*, *14*, 9729–9737.