



Electrospinning of cyclodextrin functionalized poly(methyl methacrylate) (PMMA) nanofibers

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ABSTRACT

Cyclodextrin functionalized PMMA nanofibers (PMMA/CD) were successfully produced by electrospinning technique with the goal to develop functional nanowebs. Bead-free uniform electrospun PMMA/CD nanofibers were obtained from a homogeneous solution of CDs and PMMA in dimethylformamide (DMF) using three different types of CDs, α -CD, β -CD and γ -CD. The electrospinning conditions were optimized in order to form bead-free PMMA/CD nanofibers by varying the concentrations of PMMA and CDs in the solutions. The concentration of CDs was varied from 5% up to 50% w/w, with respect to the PMMA matrix. We find that the presence of the CDs in the PMMA solutions facilitates the electrospinning of bead-free nanofibers from the lower polymer concentrations and this behavior is attributed to the high conductivity and viscosity of the PMMA/CD solutions. The X-ray diffraction (XRD) spectra of PMMA/CD nanowebs did not show any significant diffraction peaks indicating that the CD molecules are homogeneously distributed within the PMMA matrix and does not form any phase separated crystalline aggregates. Furthermore, attenuated total reflection Fourier transform infrared (ATR-FTIR) studies elucidate that some CD molecules are located on the surface of the nanowebs. This suggests that these CD functionalized nanowebs may have the potential to be used as molecular filters and/or nanofilters for waste treatment purposes.

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1. Introduction

Electrospinning is a very versatile and cost effective process for producing multi-functional nanofibers from various polymers, polymer blends and composites, etc. [1,2]. Nanofibers/nanowebs produced by electrospinning technique have several remarkable characteristics such as a very big ratio of surface area to volume, pore size within nano range, unique physical characteristics and flexibility for chemical/physical modification and functionalization. It has been shown that the unique properties and multi-functionality of the nanowebs make them very interesting for applications in various areas including biotechnology, textiles and membranes/filters, etc. [1–8].

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of α (1,4)-linked glucopyranose units having a toroid-shaped molecular structure (Fig. 1). The most common natural CDs have 6, 7, or 8 glucopyranose units in the cycle and are named as α -, β - and γ -CD, respectively. The hydrophobic nature of the CD cavity facilitates the ability of CD molecule to act as a host for various small molecules

[9,10] as well as macromolecules [11–13] to form inclusion complexes.

The functionalization of nanofibers with cyclodextrins would be extremely interesting since such nanowebs containing CDs will have a unique characteristic which can potentially improve and broaden the application areas of cyclodextrins and nanofibers. For instance, nanofibers/nanowebs have potential to be used for filtration of tiny particles as well as serving as barriers for liquid/vapor penetration since they have large surface area along with nano-porous structure [5–8]. Cyclodextrins can form inclusion complex with hazardous chemicals and polluting substances [14–18], hence, the functionalization of nanofibers with cyclodextrins will be very appealing due to the combination of their unique functionality and these nanowebs can be potentially used as molecular filters and/or nanofilters for the filtration/purification/separation purposes.

Up to date, very few studies on incorporating cyclodextrins in electrospun fibers exist in the literature [19–24]. β -CD has been used to crosslink poly(acrylic acid) nanofibers in order to produce water-insoluble polyelectrolyte nanowebs [19]. Poly(*N*-vinylpyrrolidone) (PVP) nanofibers were electrospun with β -CD [20] and in later study the composite PVP nanofibers containing gold nanoparticles were prepared in which β -CD was used as a stabilizing and reducing

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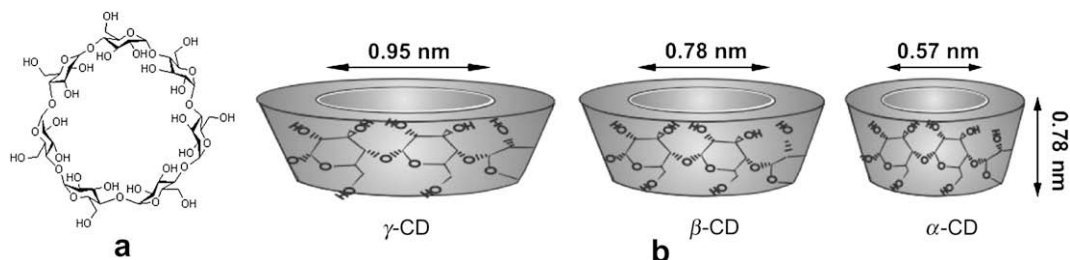


Fig. 1. (a) Chemical structure of β -CD and (b) approximate dimensions of α -, β -, γ -CDs.

reagent in the synthesis of gold nanoparticles [21]. Moreover, a catalyst for the detoxification of nerve agents was synthesized from β -CD and *o*-iodosobenzoic acid and this modified β -CD was incorporated into polyvinyl chloride (PVC) nanofibers in order to develop a functional nanofibrous membranes for protection from chemical warfare stimulant [22]. Poly(methyl methacrylate) (PMMA) nanofibers were electrospun with phenylcarbonylated β -CD for the attempt to capture organic molecules for waste treatment [23]. Very recently, we have produced cyclodextrin pseudo-polyrotaxane nanofibers by electrospinning of cyclodextrin inclusion complex with poly(ethylene glycol) (PEG) [24].

Here we have used the electrospinning technique to develop bead-free uniform CD functionalized PMMA nanofibers. Three types of CDs; α -CD, β -CD and γ -CD were incorporated individually in the PMMA nanofibers and the weight load of CDs in the polymer matrix was varied from 5% up to 50% (w/w). We found that the addition of CD in the PMMA solution made it easier to electrospin bead-free PMMA nanofibers from low concentration polymer solutions. We will in the present paper mainly deal with the optimization of electrospinning conditions in order to produce uniform PMMA/CD nanofibers with different CD content. We find that some CD molecules are located on the surface of the PMMA nanofibers and that these nanowebs are expected to readily capture organic waste vapors from the environment. However, the detailed study of the molecular filtration capability of these PMMA/CD nanowebs will be the subject of a forthcoming publication.

2. Experimental

2.1. Materials

The as-purchased amorphous poly(methyl methacrylate) (PMMA) ($M_w \sim 350,000$, Aldrich), *N,N*-Dimethylformamide (DMF) (Fluka, 98%) and cyclodextrins (CD) (gift from Wacker Chemie AG, Germany) were used without any purification.

2.2. Electrospinning

The homogeneous solutions were prepared by dissolving PMMA and CDs in DMF. The PMMA concentration was varied from 7.5% (w/v) up to 15% and the weight % of CDs (α -, β - and γ -) was varied from 5% (w/w) up to 50% with respect to PMMA. The homogeneous PMMA/CD solutions were placed in a 1 ml syringe fitted with a metallic needle of 0.4 mm of inner diameter. The syringe is fixed horizontally on the syringe pump (Model: KDS 101, KD Scientific) and the electrode of the high voltage power supply (Spellman High Voltage Electronics Corporation, MP Series) was clamped to the metal needle tip. The feed rate of polymer solution was varied from 1 to 4 ml/h, the applied voltage was varied from 10 to 20 kV and the tip-to-collector distance was varied from 10 cm to 20 cm. The most uniform, reproducible and bead-free nanofiber results were obtained when feed rate was 1 ml/h, the applied voltage was 15 kV and tip-to-collector distance was set at 10 cm. Therefore, these

parameters were kept constant for the electrospinning of all the polymer solutions studied. A grounded stationary rectangular metal collector (15 cm \times 20 cm) covered by a piece of aluminum foil was used as target for the nanofiber deposition. The complete electrospinning apparatus was enclosed in glass box and the electrospinning was carried out at room temperature in a horizontal position.

2.3. Measurements and characterizations

The viscosity of the solutions was measured at 24 °C using the Brookfield DV-III Ultra Rheometer which is equipped with a cone/plate accessory of spindle type CPE-41. The viscosity measurements were repeated three times to check the reproducibility and the consistency of the viscosity reading. The conductivity of the solutions was measured with Multiparameter meter InoLab® Multi 720 (WTW) at room temperature. The morphologies of the poly(methyl methacrylate) (PMMA) and cyclodextrin functionalized PMMA (PMMA/CD) nanofibers were investigated by high resolution scanning electron microscopy (SEM) (FEI, Nova 600 NanoSEM). The average fiber diameter (AFD) was determined from the SEM images and around 50 fibers were analyzed. The surface of PMMA/CD nanowebs (thickness > 100 μ m) was analyzed by attenuated total reflection Fourier transform infrared (ATR-FTIR). All spectra were recorded with Bio-Rad FTS-65A FTIR spectrometer equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The ATR setup used for the studies contained a germanium crystal at a nominal incidence angle of 65°. Spectra were collected over a range 4000–700 cm^{-1} with a resolution of 2 cm^{-1} and each spectrum was obtained by co-addition of 512 scans. X-ray diffraction (XRD) studies were performed to investigate whether or not there is crystalline aggregation of CDs in the PMMA nanofibers. XRD data were recorded using a Stoe Stadi P diffractometer with Cu $K\alpha$ radiation at 2θ range of 5°–30°.

3. Results and discussion

3.1. Electrospinning of poly(methyl methacrylate) (PMMA) nanofibers

Initially the electrospinning of nanofibers with different PMMA concentrations was performed in order to find a protocol by means of which we can produce bead-free PMMA nanofibers. Fig. 2 shows the scanning electron microscopy (SEM) images of PMMA nanofibers electrospun from 7.5%, 10% and 15% (w/v) PMMA solution in DMF. We find that the 7.5% and 10% w/v PMMA solutions yielded beaded nanofibers due to the low viscosity of the solutions (viscosity \sim 33 cP and \sim 91 cP, respectively), but the number of beads was significantly less for 10% (w/v) PMMA solution. However, once the concentration of PMMA solution is increased to 15% (w/v) (viscosity \sim 1075 cP), uniform bead-free PMMA nanofibers were obtained with a diameter of 977 ± 88 nm. This shows that a high

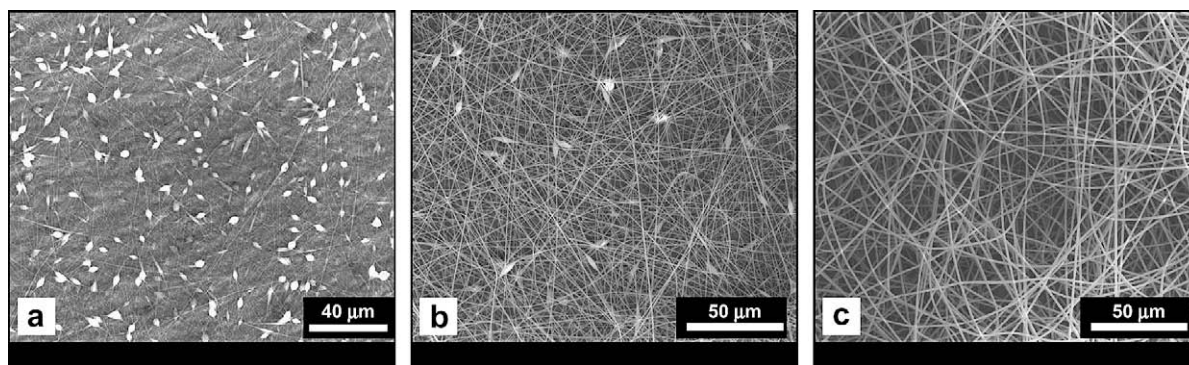


Fig. 2. SEM images of electrospun PMMA nanofibers obtained from (a) 7.5%, (b) 10% and (c) 15% (w/v) PMMA.

concentration/viscosity is required to produce uniform bead-free PMMA nanofibers.

3.2. Electrospinning of cyclodextrin functionalized PMMA nanofibers (PMMA/CD)

Table 1 summarizes the solution properties (viscosity and conductivity) and the morphological results for the PMMA and PMMA/CD nanofibers. Figs. 3 and 4 show the SEM images of electrospun cyclodextrin functionalized PMMA nanofibers (PMMA/CD) obtained from a homogeneous solution of PMMA with the addition of 5% up to 50% β -CD (w/w, with respect to PMMA). Interestingly, PMMA/CD systems yielded bead-free nanofibers even when for PMMA concentrations well below 15% (w/v). In the case of 7.5% PMMA solution, the addition of 25% (w/w) β -CD reduced the number of beads (Fig. 3a) and the addition of 50% (w/w) β -CD yielded uniform nanofibers along with very few numbers of elongated beaded structures (Fig. 3b). Similar behavior was observed when 5% (w/w) β -CD was added to 10% (w/v) PMMA resulting in much fewer beads with more elongated structure (Fig. 4a) compared to those for pure PMMA nanofibers (Fig. 2b). The bead formation was completely eliminated and uniform nanofibers were obtained when 10% (w/v) PMMA solutions containing 10, 25, 40 and 50% (w/w) β -CD were electrospun (Fig. 4b–d). These findings reveal that the addition of CD has quite a positive effect on the electrospinning of bead-free PMMA nanofibers from low concentrations.

The addition of CD resulted in an increase in the viscosity of the PMMA solutions. It was found that the viscosity of PMMA/CD solutions was higher as the concentration of CD was increased, which may be one of the reasons why bead-free PMMA/CD

nanofibers were obtained from low polymer concentrations. Since the viscosity of the PMMA solution was increased with the addition of CD, the possibility of inclusion complexation between CD molecules and PMMA chains was considered, addition to that, our previous report showed that γ -CD and PMMA can form inclusion complex [25]. In the case of inclusion complexation, the polymer/CD solution becomes turbid or precipitation occurs due to the aggregation of threaded CD molecules on the polymer chains [11]. Furthermore, the viscosity of the polymer solution should increase significantly due to a number of interactions such as (i) those between polymer chains and cyclodextrin molecules, (ii) those between threaded neighbouring cyclodextrins on the same polymer chain and (iii) those between cyclodextrins threaded on different polymer chains [26]. However, here the PMMA/CD solutions were clear and no turbidity/precipitation was observed and the viscosity increase in PMMA/CD solutions was minor and is probably due to some interaction between the CD molecules and PMMA polymer chains. The XRD patterns of PMMA/CD nanowebbs which will be discussed in the later section did not show any clear diffraction patterns for the channel-type packing for CDs which however is the case for CDs when complexed with polymer chains [11,12,25]. This further supports that the CDs are present in PMMA fiber matrix as in an uncomplexed state. In brief, the possibility of complexation between PMMA and CD was ruled out for the PMMA/CD solutions used here for the electrospinning. It is also important to mention that the uncomplexed CD molecules in PMMA matrix is desired since the CD cavity still will be available to perform its function, that is, capture molecules from the surroundings, etc.

Unlike our previous study [25], CDs and PMMA did not form inclusion complexation mostly likely because of the solution

Table 1

Properties of PMMA and PMMA/CD solutions and the resulting electrospun fibers.

Solutions	% PMMA ^a (w/v)	CD type, % ^b (w/w)	Conductivity (μ S/cm)	Viscosity (cP)	Fiber diameter ^c (nm)	Fiber morphology
PMMA7.5	7.5	–	1.4	33.4 \pm 0.2	–	Nanofibers with beads
PMMA10	10	–	1.4	91.2 \pm 1.5	–	Nanofibers with beads
PMMA15	15	–	1.4	1075 \pm 3	977 \pm 88	Bead-free nanofibers
PMMA7.5/ β -CD25	7.5	β -, 25%	3.2	39.4 \pm 0.1	–	Nanofibers with beads
PMMA7.5/ β -CD50	7.5	β -, 50%	4.2	46.4 \pm 0.4	–	Nanofibers with very few beads
PMMA10/ β -CD5	10	β -, 5%	1.8	110.9 \pm 0.1	–	Nanofibers with beads
PMMA10/ β -CD10	10	β -, 10%	2.2	111.7 \pm 0.4	675 \pm 89	Bead-free nanofibers
PMMA10/ β -CD25	10	β -, 25%	3.4	123.5 \pm 0.1	625 \pm 70	Bead-free nanofibers
PMMA10/ β -CD40	10	β -, 40%	4.1	160.9 \pm 1.5	720 \pm 54	Bead-free nanofibers
PMMA10/ β -CD50	10	β -, 50%	4.5	172.1 \pm 1.7	816 \pm 77	Bead-free nanofibers
PMMA10/ α -CD25	10	α -, 25%	2.3	144.1 \pm 0.2	652 \pm 88	Bead-free nanofibers
PMMA10/ α -CD50	10	α -, 50%	3.3	182.3 \pm 0.3	988 \pm 170	Bead-free nanofibers
PMMA10/ γ -CD25	10	γ -, 25%	1.8	141.5 \pm 0.7	663 \pm 94	Bead-free nanofibers
PMMA10/ γ -CD50	10	γ -, 50%	2.3	195.7 \pm 0.3	1024 \pm 219	Bead-free nanofibers

^a With respect to solvent (DMF).

^b With respect to the polymer (PMMA).

^c The average fiber diameter was calculated for the systems which only yielded bead-free fibers.

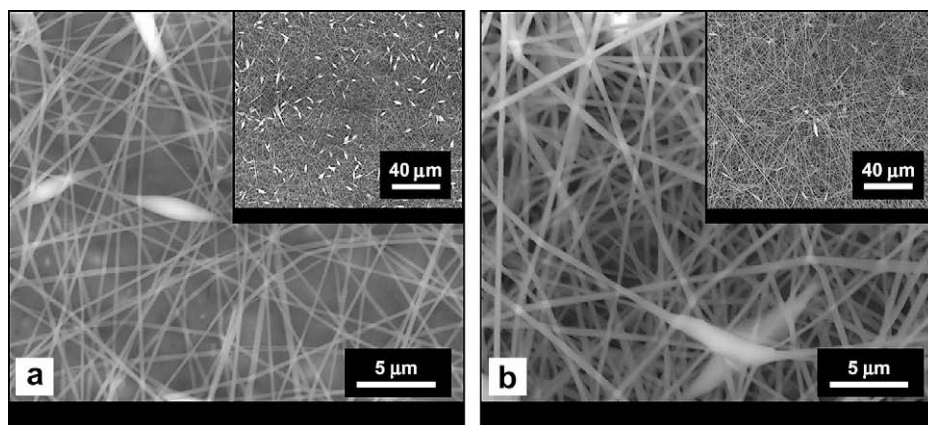


Fig. 3. SEM images of electrospun PMMA/ β -CD nanofibers obtained from solutions of (a) PMMA7.5/ β -CD25, (b) PMMA7.5/ β -CD50. The insets show lower magnification images.

preparation method, solvent system, high molecular weight of PMMA and the high concentration/viscosity of the polymer solution we used. Here, DMF was used as a solvent both for CDs and PMMA, and DMF is a very good solvent for CDs which promote de-complexation when used as a solvent. Addition to that, polymer-cyclodextrin inclusion complexation generally performed with polymers with low molecular weights and using much diluted polymer solutions [11–13,25] where CD and polymer molecules have freely able to move and form the complex.

We have found that the conductivity of PMMA/CD solutions is increased compared to that for pure PMMA solutions which implies that the addition of β -CD causes an increase in the solution conductivity. We also found that the increase in the conductivity was higher as the load of β -CD was increased (Table 1). The solution conductivity is one of the main controlling parameters in electrospinning process since the polymer solution is being stretched as a result of the repulsion of the charges present at the surface. The

increase in conductivity of the solution results in the production of bead-free fibers from lower polymer concentrations since polymer solution was subjected to higher stretching under the high electrical field [27,28]. Recently, we have reported that a slight increase in the solution conductivity resulted in significant morphological variations for the polystyrene yielding bead-free electrospun fibers [29]. Here, we observed a similar behavior where bead-free uniform PMMA/CD nanofibers produced from lower polymer concentrations contributed by the higher solution conductivities of the PMMA/CD systems.

Similar findings were observed when α -CD and γ -CD were used instead of β -CD. Electrospun bead-free PMMA/CD nanofibers were also obtained from 10% (w/v) PMMA solutions when 25% and 50% (w/w) of α -CD or γ -CD were added to the polymer solutions (Fig. 5). The viscosity and conductivity of the CD/PMMA solutions were also higher when α -CD and γ -CD were present compared to that of the pure PMMA solution. When PMMA/CD solutions containing α -CD,

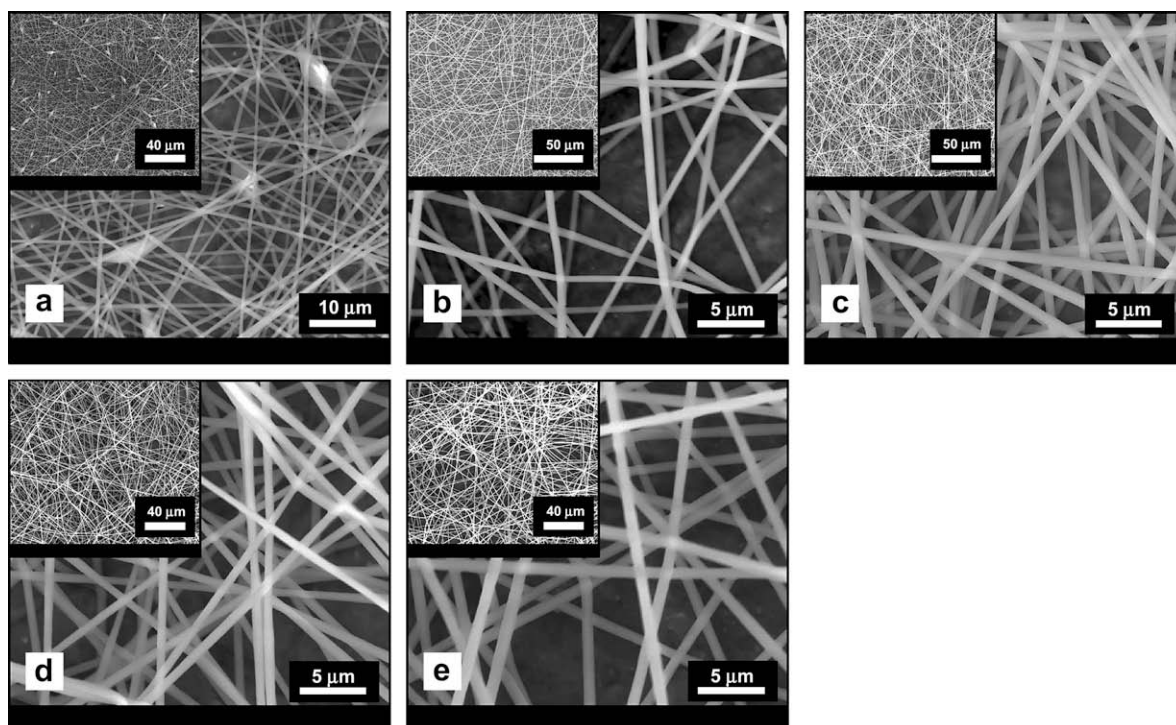


Fig. 4. SEM images of electrospun PMMA/ β -CD nanofibers obtained from solutions of (a) PMMA10/ β -CD5, (b) PMMA10/ β -CD10, (c) PMMA10/ β -CD25, (d) PMMA10/ β -CD40 and (e) PMMA10/ β -CD50. The insets show lower magnification images.

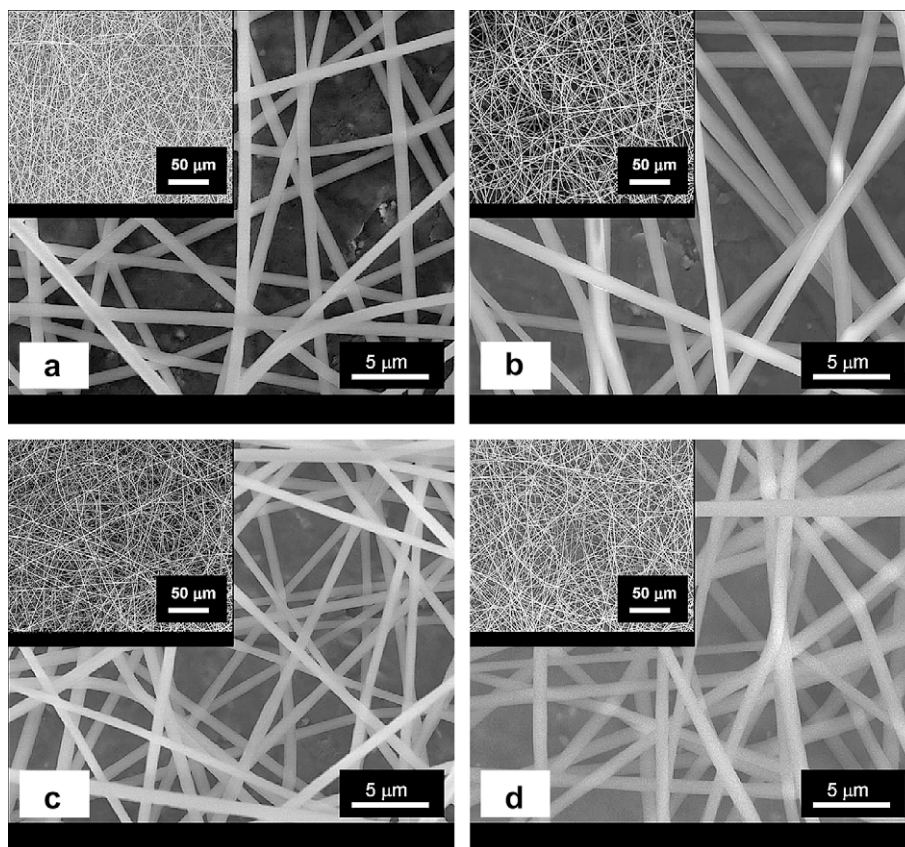


Fig. 5. SEM images of electrospun PMMA/CD nanofibers obtained from solutions of (a) PMMA10/ α -CD25, (b) PMMA10/ α -CD50, (c) PMMA10/ γ -CD25 and (d) PMMA10/ γ -CD50. The insets show lower magnification images.

β -CD and γ -CD were compared, the viscosities of γ -CD-PMMA and α -CD/PMMA solutions were slightly high and the solution conductivity was lower than that for β -CD/PMMA, which resulted in somewhat thicker fibers. Additionally, the PMMA/CD solutions containing the same type of CD with a higher CD content yielded thicker fibers as well. The increase in fiber diameter is mostly due to the greater resistance of the more viscous solutions to be stretched in the electrospinning process.

3.3. Characterization of cyclodextrin functionalized PMMA nanofibers

To confirm the presence of CDs on the surface, the PMMA/CD nanowebs were analyzed by a surface sensitive technique, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The ATR-FTIR spectra of PMMA and PMMA10/ β -CD50 nanowebs are depicted in Fig. 6 as example. The absorption bands observed for PMMA/CD nanowebs at around 1030, 1055 and 1080 cm^{-1} (corresponding to the coupled C–C/C–O stretching vibrations of CD) confirm that CD molecules are present on the surface of the nanowebs. This strongly indicates that these CDs could be used for inclusion complexation and that the PMMA/CD nanowebs may be used as molecular filters and/or nanofilters for the removal of organic molecules from the environment. In fact, our on-going studies reveal that PMMA/CD nanowebs are very effective to capture organic waste vapors (e.g.: styrene, aniline and toluene) from surroundings. The detailed surface characterization of PMMA/CD nanowebs by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and their performance as molecular filters for capturing organic waste vapors from the environment will be the subject of a future publication.

CDs are crystalline and have crystal structures referred as “cage” or “channel” types [30,31]. The commercially as-received CDs have cage structures with an arrangement where the cavity of each molecule is blocked by neighboring molecules. For the channel structure, the CD molecules are aligned and stacked on top of each other forming long cylindrical channels. The channel arrangement of CD molecules is the confirmation for the inclusion complexation when formed with polymers [11,12,25].

The X-ray diffraction (XRD) of cage-type and channel-type packing structures of α -, β - and γ -CD have strong diffraction peaks in the range of $2\theta = 5\text{--}30^\circ$ [32–34]. The as-received α -CD has three salient characteristic peaks associated with its cage-type crystal structure occurring at $2\theta \cong 12.0^\circ$, 14.5° and 21.5° . The α -CD with

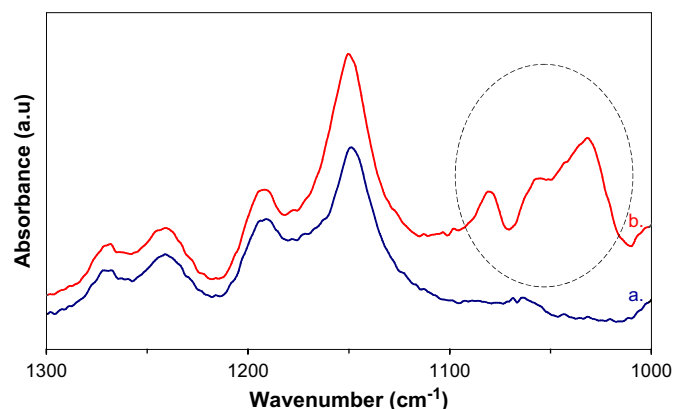


Fig. 6. ATR-FTIR spectra of (a) PMMA (b) PMMA10/ β -CD50 nanowebs.

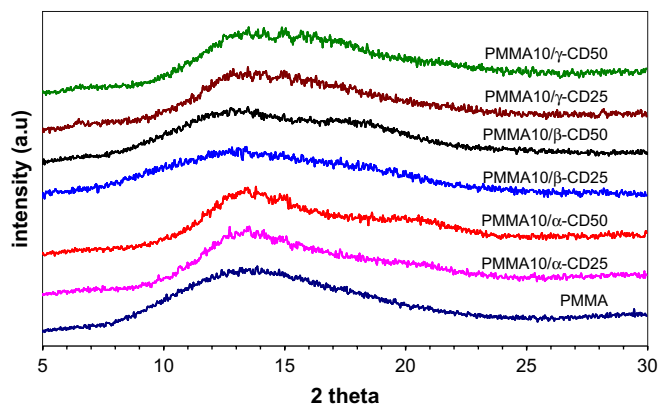


Fig. 7. 2-D XRD diffraction patterns of PMMA and PMMA/CD nanoweb.

the channel-type packing structure has two salient peaks centered at $2\theta \cong 13^\circ$ and 20° . As-received β -CD cage crystals have prominent characteristic diffraction peaks at $2\theta \cong 10.5^\circ$, 12.5° , 19.5° and 21° . The typical channel-type β -CD has two major peaks at $2\theta \cong 11.5^\circ$ and 18° . The characteristic peaks for cage γ -CD occur at approximately $2\theta \cong 12.3^\circ$, 16° and 21.8° . Channel-type γ -CD has one major peak at $2\theta \cong 7.5^\circ$ with minor reflections at $2\theta \cong 14^\circ$, 15° , 16° , 16.8° and 22° .

The XRD studies were performed for the PMMA/CD nanoweb to investigate if any CD crystalline aggregates present in the fiber matrix. Fig. 7 shows the 2-D XRD spectra of PMMA and PMMA/CD nanoweb. PMMA is an amorphous polymer showing a broad halo XRD diffraction pattern. The XRD diffraction patterns of the PMMA/CD nanoweb are very similar to those for the PMMA nanoweb which also depicts a broad halo pattern without any strong diffraction peaks. No distinct peaks for the channel-type CD crystals were observed indicating that CD and PMMA did not form inclusion complexes. These findings are consistent with the viscosity data and the physical appearance of the solutions as discussed previously. During electrospinning, it is also possible that CD molecules could phase separate from PMMA matrix and form cage-type crystal aggregates. However, the XRD results mainly showed broad halo diffraction features for PMMA/CD nanoweb containing CDs below 50% (w/w), although some very weak peaks were observed for PMMA/CD nanoweb with 50% (w/w) CDs indicating that only at very high CD content a small amount of crystalline aggregations were present. However, the lack of any major significant XRD diffraction peak for PMMA/CD nanoweb indicates that the majority of the CD molecules were distributed homogeneously in the PMMA matrix without forming any crystal aggregates. This is also a good indication revealing that the cavities of CD molecules are not blocked by each other and are supposedly available for inclusion complexation.

4. Conclusion

Electrospinning of cyclodextrin functionalized PMMA nanofibers (PMMA/CD) was carried out with the goal to develop functional nanoweb. The bead-free uniform electrospun PMMA/CD nanofibers were obtained by incorporating three types of CDs; α -CD, β -CD and γ -CD into PMMA matrix. The concentration of CDs

was varied from 5% up to 50% (w/w, with respect to polymer) in PMMA matrix. It was revealed that the addition of CDs to the polymer solutions assisted the electrospinning of bead-free nanofibers from low polymer concentration. A 10% (w/v) PMMA solution without CD yielded beaded fibers whereas the solutions with same PMMA concentration containing CDs were electrospun into bead-free uniform nanofibers, a finding which was attributed to the higher conductivity and viscosity of the PMMA/CD solutions. The X-ray diffraction (XRD) data suggested that CD molecules were mostly homogeneously distributed within the PMMA nanofibers without forming phase separated crystalline aggregates. Furthermore, attenuated total reflection Fourier transform infrared (ATR-FTIR) studies revealed that some CD molecules were located on the surface of the nanoweb. This indicates that these CD functionalized nanoweb may be utilized as molecular filters and/or nanofilters for the removal of organic wastes.

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