ORIGINAL PAPER



# Insoluble poly(ethylene oxide) nanofibrous coating materials: effects of crosslinking conditions on the matrix stability

Murat Şimşek<sup>1</sup> · Soner Çakmak<sup>1</sup> · Menemşe Gümüşderelioğlu<sup>1,2</sup>

Received: 25 March 2016 / Accepted: 20 October 2016 / Published online: 3 November 2016 © Springer Science+Business Media Dordrecht 2016

Abstract In this study, the effect of crosslinking conditions was investigated to obtain insoluble poly(ethylene oxide) (PEO) nanofiber mats having an ultraviolet (UV) initiating and crosslinking agent, pentaerythritol triacrylate (PETA), with various ratios in the presence or absence of UV irradiation at 366 nm. At first, PEO nanofibers were electrospun from 400,000 and 600,000 g/mole molecular weights of PEO and they were compared in terms of diameter and fiber morphology. Whereas applied voltage in the range of 10-25 kV had no significant effect on the fiber morphology, fiber diameters varied by voltage. An increase in the flow rate from 0.25 to 1.00 mL h<sup>-1</sup> had an effect in favor of fabricating thicker fibers. The effect of distance to collector on the diameter and morphology was not distinctive. Fibers having irregular morphology and beads appeared with increasing the polymer concentration from 4 to 8 % w/v. Prior crosslinking, electrospinning process at selected conditions was applied to the PEO (600,000) including PETA and PEO-PETA nanofibers were obtained. Besides PETA concentration and UV application, drying conditions before UV irradiation were also found effective to obtain stable fibers in aqueous media. PEO nanofibers electrospun in the presence of 10 % PETA (w/w), dried for 8 days at 37 °C in an air atmosphere and then, irradiated with UV for 50 min were found most stable in aqueous media. However, crosslinking was also achieved in the absence of UV.

Menemşe Gümüşderelioğlu menemse@hacettepe.edu.tr **Keywords** Crosslinking · Nanofiber · Pentaerythritol triacrylate · Poly(ethylene oxide) · UV irradiation

# Introduction

Poly(ethylene oxide) (PEO) having a wide range of molecular weight is nontoxic, hydrophilic and biocompatible polymer and it has been used in a number of medical materials, i.e., wound dressings, drug delivery systems, semipermeable membranes, electrolytes for batteries, tissue engineering scaffolds, and many others [1-5].

Over the past decade, extensive studies have been carried out to investigate the effect of electrospinning conditions on fiber production from various polymers [6-9]. It has been also investigated the effect of some electrospinning parameters on PEO nanofibers. In a study, Chowdhury and Stylios [10] determined the effect of applied voltage, fiber-collecting distance, and flow rate on the nanofibers electrospun from PEO (MW: 300,000 g/mole) dissolved in water. Tan and coworkers [11] investigated the effect of applied voltage and solution concentration on PEO/water system. Doshi and Reneker [12] examined the effect of viscosity and surface tension on the electrospinning of aqueous PEO solutions. Fong et al. [13] performed some studies based on the effect of solution properties on PEO nanofiber morphology. Son et al. [14] investigated the influence of solvent on electrospinning of PEO nanofibers. Theron et al. [15] reported an experimental study investigating the effects of electric current, volume and surface charge density on PEO fibers.

Since PEO is highly soluble in water, it is necessary to crosslink it in order to obtain insoluble nanofibers and fibrous matrices. Various methods including gamma irradiation [16], electron beam irradiation [17] and ultraviolet (UV) irradiation [18–22] were employed to crosslink PEO in solution or in solid

<sup>&</sup>lt;sup>1</sup> Department of Nanotechnology and Nanomedicine, Hacettepe University, Ankara, Turkey

<sup>&</sup>lt;sup>2</sup> Department of Chemical Engineering, Hacettepe University, Ankara 06800, Turkey

state. Among them, UV-induced crosslinking methods seem as easy, safe, and cheapest techniques. During the past years UVinduced crosslinking studies in the presence of UV initiating and crosslinking agents such as pentaerythritol triacrylate (PETA) and others have been performed on the different forms of PEO substrates [18–22]. However, there is a limited study about crosslinking of PEO nanofibers by PETA in the presence of UV irradiation. In a study, Zhou et al. [21] investigated the effect of UV irradiation time on crosslinking of electrospun PEO nanofibers including PETA in the presence of cellulose nanocrystals. To date there has been no comprehensive work to investigate the effect of crosslinking conditions on PEO nanofibers and also crosslinking in the absence of UV irradiation.

In this paper, crosslinking of PEO nanofibers were carried out in the presence or absence of UV irradiation and subsequent characterization studies were done to determine optimum crosslinking conditions, i.e., crosslinker ratio, drying environment and drying period to prepare insoluble PEO-PETA nanofibers.

# Materials and methods

### Electrospinning and crosslinking of PEO nanofibers

High molecular weight PEOs with viscosity average molecular weight ( $M_v$ ) of 400,000 (PEO-400) and 600,000 g/mole (PEO-600) and PETA were purchased from Sigma-Aldrich (Germany). PEO powder at a certain amount (w/v) was added to distilled water to obtain homogeneous PEO solutions with various concentrations of PEO-400 and PEO-600 (Table 1). Then, mixtures were stirred under magnetic stirring overnight at room temperature. The resultant spinning solution for each concentration was transferred to a 2.5 mL syringe with a 21-gauge needle. Then, a high voltage (Gamma High Voltage Research, Ormond Beach, FL, USA) was applied to

the solution placed in a syringe pump (NE 300, New Era Pump Systems, USA). Fibers were collected on an aluminum foil fixed onto a stationary collector. PEO nanofibers were spun under electrospinning conditions given in Table 1.

The crosslinking studies were carried out by using higher molecular weight PEO i.e., PEO-600. For the production of insoluble PEO-PETA nanofibers having various ratios of PETA (1.0; 2.5; 5.0; 7.5; and 10.0 %), certain amount of PETA was added to the 4 % *w/v* of PEO-600 solution and each mixture was stirred additionally in a closed, shading area for 1 h. Then, electrospinning process was performed at room conditions under dark. The nanofibers (PEO-PETA) were spun at the applied voltage of 18 kV, the flow rate of 0.4 mL  $h^{-1}$ , and the collecting distance of 23 cm.

The PEO-PETA nanofiber matrices were cut into pieces with  $1 \times 1$  cm<sup>2</sup> and were divided into three parts. First part was crosslinked by a UV light source emitted a light intensity of 19,000  $\mu$ W cm<sup>-2</sup> at a wavelength of 366 nm (GLT Gaseund Labortechnik, Germany) immediately after electrospinning. The 2nd part of PEO-PETA nanofibers was dried at 37 °C in air for certain drying periods (1, 3, 6, or 8 days) and then, UV irradiation was applied immediately. For the 3rd part of nanofibers, drying was done at room temperature in vacuum for longer periods up to a few weeks and then, UV was applied. UV crosslinking process for all nanofiber mats was realized at a distance of 4 cm for 50 min at room conditions under dark. To parallel groups of all parts UV irradiation was not applied for comparing with the irradiated mats. All samples were immersed into distilled water to determine whether they would dissolve or not.

# Characterization

The morphology of PEO nanofibers was examined by a scanning electron microscope (SEM, Zeiss Evo 50, USA). Samples were coated with gold layer for 2 min before SEM

Mv (g/mole)	Concentration (%, w/v)	Flow Rate $(mL h^{-1})$	Voltage (kV)	Distance (cm)
400,000	6	0.30	10; 12; 14; 16; 18; 20; 25 10; 12; 14; 16; 18; 20; 25	15
		0.50	-, , , -, -, -, -	
		1.00		
600,000	4	0.50	10; 12; 14; 16; 18; 20; 25	15
	5		10; 12; 14; 16; 18; 20; 25	10
				15
				20
				25
				30
	7			15

Table 1Electrospinningconditions for PEO nanofibers

imaging. Fiber diameters were calculated from SEM images by ImageJ software (NIH, Bethesda, MD, USA). The diameters were given as average  $\pm$  standard deviation.

Dynamic swelling experiments were carried out to determine the most appropriate crosslinking condition. Irradiated and non-irradiated PEO fibers at a given ratio of PETA were soaked in excess phosphate buffered saline (PBS, pH: 7.4, 37 °C) at the end of each drying period until 120 h. Fiber mats were removed from the medium with certain time intervals, the surface adhered liquid drops were wiped with blotting paper and then, weight of each mat was measured. The measurements were taken until the weight of swollen fibers reached constant values. Triplicate data were obtained for each measurement. Equation (1) was used to calculate the mass swelling ratio based on dry weight.

$$\mathbf{Q} = \left[ (\mathbf{W}_{\mathrm{s}} - \mathbf{W}_{\mathrm{d}}) / \mathbf{W}_{\mathrm{d}} \right] \times 100 \tag{1}$$

where  $W_s$  is the weight of swollen sample and  $W_d$  is the weight of dried sample.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Thermo Scientific Nicolet IS10, USA) was performed to investigate the chemical structures of nanofibers due to the crosslinking process.

The phase identification and crystallinity of the samples were investigated by X-Ray diffraction (XRD; Rigaku Ultima-IV, USA).

Thermogravimetric (TGA, SII EXSTAR 600 TG/DTA 6300, Perkin Elmer, USA) and differential scanning calorimetric (DSC, Perkin Elmer Diamond, USA) analyses of nanofibers were performed at linear heating rate of 10 °C min<sup>-1</sup> under nitrogen flow.

# **Results and discussion**

# The effect of electrospinning conditions

A series of experiments were carried out with PEO-400 and PEO-600 to investigate the effect of electrospinning conditions on the fiber morphology and diameter. In electrospinning process, solvent type and dielectric constant of solvent are important factors for the fabrication of continuous and bead-free fibers. In this study, distilled water having high dielectric constant, i.e., 80 [14] was chosen for preparing PEO solutions.

The relationship between applied voltage and fiber diameter/morphology was investigated for various ratios of PEO-400 and PEO-600 at a constant distance of 15 cm. Detailed parameters were given in Table 1. Figures 1(a-f) and 2(a and b) show that all nanofibers exhibit smooth and uniform morphology at voltages in the range from 10 to 25 kV. Few beads that were not affecting general morphology

were observed on the fibers obtained from 5 % w/v of PEO-600 (Fig. 2c and d). However, fiber diameters decreased gradually with increasing voltage (Tables 2 and 3) in all compositions except 8 % w/v of PEO-400. This was attributed to stretching of fibers by higher repulsive forces induced by higher electric voltage. In contrast, an increase in the voltage caused an increase in the fiber diameter for 8 % w/v of PEO-400 to some extent. This can be explained that PEO polymer chains did not stretch any more in favor of the fabrication of thinner fibers due to high viscosity even if the voltage increased. Tan et al. [11] reported that PEO fibers from 7 % w/v PEO/water solution contained a high density of beads when it was spun at a voltage of 9.0 kV. Reneker and Chun [23] demonstrated that applied voltage had no significant effect on diameters of PEO nanofibers. In contrast, Chowdhury et al. [10] suggested that higher voltages facilitated to obtain thinner fibers.

The relationship between flow rate and morphology/ diameter was also investigated by changing flow rate from 0.25 to 1.00 mL h<sup>-1</sup> for 8 % w/v of PEO-400 (Table 1). It can be seen that there is no significant difference between fiber morphologies obtained at both flow rates of 0.25 and 0.50 mL h<sup>-1</sup> (Fig. 1c-f). However, at 1.00 mL h<sup>-1</sup> flattened-ribbon like fiber morphology appeared at each voltage since the solvent had not enough time for complete evaporation due to high flow rate (Fig. 1g and h). The fiber diameter tended to increase when the flow rate increased from 0.25 to 0.50 mL h<sup>-1</sup>.

The relationship between the distance and morphology/ diameter was investigated by changing the distance from 10 to 30 cm at a constant flow rate of 0.5 mL h<sup>-1</sup> and applied voltage of 15 kV for 5 % w/v of PEO-600. Nanofibers including a few beads were obtained at all distances. The effect of the distance on fiber diameters was not significantly distinctive (Table 3). Chowdhury et al. [10] reported that average diameter of PEO fibers decreased when the collection distance was increased.

It was not observed any significant morphological difference between nanofibers obtained from both PEO-400 and PEO-600 depending on increasing of PEO concentration (Figs. 1a-d and 2). However, the fibers tended to be thicker in spite of lower flow rate when PEO-400 ratio was changed from 6 to 8 % w/v (Table 2). As can be seen in Table 3, an increase in PEO-600 concentration from 4 to 5 % w/v had no effect on fiber diameters at a constant distance of 15 cm. On the other hand, fibers having irregular morphology with some droplets inside were obtained with increasing the polymer concentration up to 7 % w/v (data not shown). Tan et al. [11] investigated the effect of PEO concentration in the range from 4 and 10 % w/v on fiber formation. They fabricated fiber mats with fiber junctions and bundles from 4 % w/v PEO solution, while nanofiber formation was inhibited beyond the concentration of 10 % w/v due to cohesion.

**Fig. 1** SEM images of PEO-400 nanofibers produced at 15 cm distance to collector, 6 % *w/v*, 0.30 mL h<sup>-1</sup> (**a**) 10 kV, (**b**) 20 kV; 8 % w, 0.25 mL h<sup>-1</sup> (**c**) 10 kV, (**d**) 20 kV; 8 % *w/v*, 0.50 mL h<sup>-1</sup>(**e**) 10 kV, (**f**) 20 kV (5 KX, *upper right* images: 30 KX); 8 % *w/v*, 1.00 mL h<sup>-1</sup> (**g**) 14 kV and (**h**) 18 kV (2 KX, *upper right* images: 10 KX)



#### **Crosslinking of PEO nanofibers**

UV light is a light spectrum at wavelengths varied from 100 to 400 nm. It can be divided into four spectral regions: a) Vacuum UV (100–200 nm), b) UV-C (200–280 nm), c) UV-B (280–315 nm), and d) UV-A (315–400 nm). UV-A light can be used to crosslink polymers in the presence of photocrosslinking agents. As a crosslinker, PETA is typically used to crosslink PEO in different forms (solution or solid membrane) in the presence of UV irradiation. Doytcheva et al. [18] crosslinked the solvent casted PEO-PETA membranes via UV irradiation. In another study, Zhou et al. [21] optimized UV

irradiation time for the crosslinking of PEO-PETA nanofibers.

In the presented study, we used 366 nm UV-A light by taking into account the previous study reported in the literature [21]. The distance between UV source and samples was set as 4 cm and UV irradiation was applied for 50 min i) immediately after electrospinning or ii) after certain drying periods at 37 °C in air or iii) after drying at room temperature in vacuum. It was purposed to determine optimum parameters (i.e., crosslinker ratio, drying environment and drying period) for obtaining insoluble PEO-PETA nanofibers in the presence or absence of UV irradiation. Fig. 2 SEM images of PEO-600 nanofibers produced at 15 cm distance to collector and 0.50 mL  $h^{-1}$ . 4 % w/v (a) 10 kV, (b) 20 kV; 5 % w/v, (c) 10 kV and (d) 20 kV (5 KX, upper right images: 30 KX)



## Swelling behaviour of PEO nanofibers

In order to determine the optimum crosslinker ratio, 1.0, 2.5, 5.0, 7.5 and 10.0 % *w/w* ratios of PETA were used and the swelling behavior of PEO-PETA nanofibers was investigated. The original size of 1st part of PEO-PETA nanofibers which were irradiated immediately after spinning of PEO-PETA solutions reduced

**Table 2**Diameters of fibers obtained from PEO-400 at differentelectrospinning conditions

Concentration (%, w/v)	Flow Rate $(mL h^{-1})$	Voltage (kV)	Distance (cm)	Diameter (nm)
6	0.30	10	15	$311 \pm 33$
		12		$299\pm29$
		14		$295\pm28$
		16		$280\pm27$
		18		$273\pm23$
		20		$264\pm29$
8	0.25	10	15	$320\pm42$
		12		$325\pm35$
		14		$346\pm40$
		16		$341\pm33$
		18		$318\pm35$
		20		$318\pm36$
	0.50	10		$358\pm47$
		12		$362\pm52$
		14		$405\pm43$
		16		$412\pm51$
		18		$394\pm36$
		20		$379\pm38$

rapidly when they were soaked into PBS (pH: 7.4, 37 °C). The parallel group of 1st part which was not irradiated, exhibited similar swelling behavior to the irradiated ones. For this reason, fiber mats at each PETA ratio were additionally dried for 1, 3, 6 or 8 days at 37 °C in air or at room temperature in vacuum for longer periods and irradiated at the end of the each drying period. Then, the irradiated and nonirradiated mats were soaked into PBS for 120 h to investigate the effect of PETA ratio, drying period, drying environment and also UV irradiation on the physical and swelling behavior of fiber mats.

At the second stage, experiments were carried out for the 2nd part of PEO-PETA nanofibers. Irradiated and nonirradiated fiber mats at 1.0; 2.5 and 5.0 % of PETA (w/w) ratios which were dried for 1 or 3 days rolled up and their size became smaller than their original size as soon as they immersed into PBS. However, this behavior improved to some extent at the end of the 6th or 8th day of drying period. Both groups disintegrated by exhibiting very low stability or their weights could not be measured due to an increase in the level of gelation after 24 h or 48 h soaking in PBS. However, the extent of the gelation of nonirradiated fiber mats was much dominated.

For 7.5 % of PETA (w/w) ratio, the irradiated (PEO-PETA7.5/UV) fibers and the nonirradiated ones (PEO-PETA7.5) at the end of the 1st day of drying period exhibited such a behavior similar to those having 1.0–5.0 % of PETA in the swelling medium. However, physical instability of both groups began to improve beginning from 3 days of drying period and became better at the end of the 8 days of drying period. In addition, fiber mats exhibited better mechanical stability throughout the swelling period. Swelling graphs of both groups are shown in Fig. 3a and b. Minimum swelling degree for both groups was obtained at the end of the drying

 Table 3
 Diameters of fibers obtained from PEO-600 at different electrospinning conditions

Concentration (%, w/v)	Flow Rate $(mL h^{-1})$	Voltage (kV)	Distance (cm)	Diameter (nm)
4	0.5	10	15	$246\pm30$
		12		$238\pm27$
		14		$228\pm24$
		18		$213\pm26$
		20		$181\pm32$
		25		$174\pm21$
5	0.5	15	10	$210\pm31$
		10	15	$246\pm31$
		12		$227\pm32$
		13		$218\pm31$
		14		$221\pm23$
		15		$211\pm24$
		18		$203\pm29$
		20		$187\pm25$
		25		$179\pm27$
		15	20	$242\pm30$
			25	$245\pm31$
			30	$240\pm34$

period of 8 days. Equilibrium swelling ratio of PEO-PETA7.5/ UV fibers was 950 %, as it was 1376 % for PEO-PETA7.5 fibers.

For 10.0 % of PETA (*w/w*) ratio, both of irradiated PEO-PETA (PEO-PETA10/UV) and nonirradiated (PEO-PETA10) fiber mats exhibited similar swelling behavior to PEO-PETA7.5/UV or PEO-PETA7.5 until the 6th day of drying period. At the end of the 8th day, PEO-PETA10/UV and PEO-PETA10 fiber mats retained their physical form and remained flat during swelling. Equilibrium swelling ratio of PEO-PETA10/UV fibers was 772 %, whereas it was 1097 % for nonirradiated ones at the end of the 8 days swelling period (Fig. 3c and d). The irradiated and nonirradiated forms of the 3rd part of PEO-PETA fibers that were dried at room temperature in vacuum exhibited physically stable behavior after 3 or 4 weeks drying period.

Swelling studies showed that the most appropriate crosslinking was achieved for PEO nanofibers including 10.0 % (w/w) of PETA which were irradiated after the 8 day of drying process at 37 °C. It was also observed that PEO-PETA nanofibers were crosslinked directly by PETA in the absence of UV irradiation at the same conditions, but crosslinking between PEO and PETA was much effective in the presence of UV irradiation.



Fig. 3 Swelling behavior of (a) PEO-PETA7.5/UV, (b) PEO-PETA7.5, (c) PEO-PETA10/UV, and (d) PEO-PETA10 in PBS depending on drying period at 37 °C (

**Fig. 4** SEM images and diameter distributions of (**a**) PEO-PETA7.5, (**b**) PEO-PETA7.5/UV, (**c**) PEO-PETA10 and (**d**) PEO-PETA10/UV at the end of the 8 days drying period (5 KX, *upper left* images 30 KX)





Fig. 5 SEM surface morphology images of (a) PEO, (b) PEO-PETA10 and (c) PEO-PETA10/UV (100 KX)

**Fig. 6** ATR-FTIR spectra of (**a**) powder PEO, PEO-PETA10, and PEO-PETA10/UV at the end of the 8 days drying period; (**b**) PEO-PETA10/UV depending on drying period



In a possible crosslinking mechanism [21], PETA and PEO radicals are formed when PETA is excited with UV light by taking a hydrogen atom from PEO. PETA radicals can dimerize, attach to PEO radical or initiate its polymerization. The main crosslinking reaction takes place by recombination of carbon bonds of PEO. In the literature, crosslinking studies by using PETA were performed under constant flow of argon/nitrogen or in a dynamic vacuum to avoid quenching by oxygen [21, 22]. In our study, the crosslinking of PEO nanofibers was successfully carried out in the presence of UV light at room conditions. Previously, it was stated that PEO particles having high molecular weight could be crosslinked by radicalic reaction using PETA as a crosslinker and organic peroxide as an initiator in isooctane medium [19]. In our study, it was also discovered that the fibers from PEO/water solution



Fig. 7 XRD patterns of PEO, PEO-PETA10 and PEO-PETA10/UV

were crosslinked directly by PETA in air conditions in the absence of UV light. Doytcheva et al. [20] stated that single side irradiated PEO films (from solvent casting) rolled up rapidly in water, whereas they retained its form and remained flat after the irradiation of both sides. This was attributed to heterogeneous crosslinking density throughout the thickness of films. In our study, the PEO-PETA fiber-based matrices in the swelling medium also showed the similar behavior due to heterogeneous crosslinking density throughout the fiber mats after drying for 1 day or 3 days. However, contrary to Doytcheva both sides irradiation of PEO fibers did not cause any improvement in their physical form. The mechanical and physical improvement observed with the extension of drying period exhibited that crosslinking process between PEO and PETA sustained throughout this period and effective crosslinking was achieved in the presence or absence of UV irradiation at the end of drying period.

#### SEM analysis

Figure 4 shows SEM images of PEO-PETA7.5, PEO-PETA7.5/UV, PEO-PETA10, and PEO-PETA10/UV nanofibers. Fiber diameters were  $194 \pm 43$  nm for PEO-PETA7.5 and  $224 \pm 41$  nm for PEO-PETA7.5/UV, respectively. PEO-PETA10 and PEO-PETA10/UV had diameters of 230  $\pm 42$  nm and  $239 \pm 34$  nm, respectively. It could be interpreted that UV irradiation and increasing PETA ratio facilitated the formation of thicker fibers. SEM images of PEO, PEO-PETA10 and PEO-PETA10/UV nanofibers at higher magnifications (Fig. 5) clearly revealed that their surface morphologies resemble to each other.

#### **ATR-FTIR** analysis

To elucidate the effect of UV irradiation on crosslinking reaction, PEO-PETA10 and PEO-PETA10/UV were analyzed by ATR-FTIR. Figure 6 a shows peaks belonging to the powder PEO, PEO-PETA10, and PEO-PETA10/UV fibers. Pure PEO has a characteristic peak at 2882  $\text{cm}^{-1}$  (C-H stretching). Compared to PEO, PEO-PETA10 and PEO-PETA10/UV fibers have additional characteristic peaks (C=O stretching at  $1730 \text{ cm}^{-1}$ , C=C stretching at 1634 cm<sup>-1</sup>). In the process of crosslinking, when PETA takes a proton from PEO, double C=O bond of PETA is cleaved and PETA and PEO radicals are formed. PEO radical attacked to C=C bond of PETA and initiated the polymerization of PETA. A decrease in peak intensity at C-H stretching of PEO and C=O stretching of PETA indicates that these bands involved in the crosslinking reaction. Compared to PEO-PETA10, PEO-PETA10/UV has lower peak intensities. We concluded again that the crosslinking reaction was much effective in the presence of UV irradiation. The effect of drying period on the crosslinking process could

be followed by observing decreased peak intensities of PEO-PETA10/UV (Fig. 6b) by time. There was a clear evidence in Fig. 6b indicating that the crosslinking process sustained throughout 8 days of drying period.

# **XRD** analysis

Figure 7 displays XRD patterns of PEO, PEO-PETA10 and PEO-PETA10/UV nanofiber samples. Two typical diffraction peaks at  $2\theta = \sim 19.2^{\circ}$  and  $\sim 23.4^{\circ}$  for PEO nanofibrous mats are attributed to (120) and (112) crystal plane, respectively [24]. It is obvious that the characteristic diffraction peaks of crystalline PEO reduced with the crosslinking process with or without UV. This result indicates that the organization of PEO molecular chains into ordered structures was prevented during the crosslinking process, suggesting the existence of crosslinked reaction between PEO and PETA.

#### Thermal analyses

Figure 8 shows TGA and DSC curves of PEO, PEO-PETA10 and PEO-PETA10/UV samples. Thermal degradation of the



Fig. 8 a TGA and (b) DSC thermograms of PEO, PEO-PETA and PEO-PETA10/UV

samples was in the range of 350–450 °C. However, PEO-PETA10/UV exhibited slower degradation after 400 °C and its degradation ratio was about 96.2 at 500 °C. There was no significant difference among melting temperatures of the PEO, PEO-PETA10 and PEO-PETA10/UV samples. Crystallinity of PEO-PETA10/UV tended to reduce in the presence of UV, which is compatible with the results of the study by Zhou et al. [21].

# Conclusion

In this study, crosslinked PEO nanofibers were produced at moderate conditions for the purpose of obtaining stable PEO coatings especially for medical applications. At first the effect of electrospinning conditions i.e., applied voltage, flow rate, distance to collector, and polymer concentration and molecular weight on the morphology and diameters of the electrospun PEO nanofibers was investigated and compared. Among these parameters, the flow rate and the concentration of PEO solution predominantly affected the formation of the nanofibers having flattened-ribbon like or irregular morphology. The fiber diameter usually depended on applied voltage and flow rate. In order to obtain insoluble PEO nanofibrous mats for various applications electrospinning process was carried out in the presence of UV-initiating/crosslinking agent PETA and UV irradiation which is user-friendly method was applied. It was concluded that, stability of PEO nanofibers strongly depended on the concentration of PETA and the conditions of drying process applied before UV irradiation. Additionally, it was indicated that, PEO-PETA nanofibers became insoluble in the absence of UV irradition at the end of certain drying periods. However, drying of nanofibrous mats at 37 °C in an air atmosphere for 8 days and then, application of UV irradiation is necessary to achieve effective crosslinking. The insoluble PEO nanofibers produced at the presented conditions can be evaluated for the coating of implant materials and encapsulation of biochemical agents for tissue engineering and pharmaceutical applications.

## References

- Ma L, Deng L, Chen J (2014) Applications of poly(ethylene oxide) in controlled release tablet systems: a review. Drug Dev Ind Pharm 40:845–851
- Shah KR, Chaudhary SA, Mehta TA (2014) Polyox (polyethylene oxide) multifunctional polymer in novel drug delivery system. Int J Pharm Sci Drug Res 6:95–101
- Nien Y-H, Shih C-Y, Yang C-Y, Lu C-J, Ye Q-X (2013) Preparation and characterization of electrospun polycaprolactone/polyethylene oxide membranes. J Polym Res 20:166–171

- Kunteppa H, Parveen A, Kumar HGH, Roy AS (2013) AC conductivity and battery application of polyethylene oxide/PANI/sodium chlorate composites. Adv Mater Lett 4:856–861
- Nayak R, Padhye R, Kyratzis IL, Truong YB, Arnold L (2012) Recent advances in nanofibre fabrication techniques. Text Res J 82:129–147
- Arslan A, Şimşek M, Aldemir SD, Kazaroğlu NM, Gümüşderelioğlu M (2014) Honey-based PET or PET/chitosan fibrous wound dressings: effect of honey on electrospinning process. J Biomater Sci Polym Ed 25:999–1012
- Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B (2002) Structure and process relationship of electrospun bioabsorbable nanofiber membranes. Polymer 43:4403–4412
- Zeng J, Xu X, Chen X, Liang Q, Bian X, Yang L, Jing X (2003) Biodegradable electrospun fibers for drug delivery. J Control Release 92:227–231
- Hekmati AH, Rashidi A, Ghazisaeidi R, Drean J-Y (2013) Effect of needle length, electrospinning distance, and solution concentration on morphological properties of polyamide-6 electrospun nanowebs. Text Res J 83:1452–1466
- Chowdhury M, Stylios GK (2012) Analysis of the effect of experimental parameters on the morphology of electrospun polyethylene oxide nanofibres and on their thermal properties. J Text Inst 103: 124–138
- Deitzel JM, Kleinmeyer J, Harris D, Tan NCB (2001) The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer 42:261–272
- Doshi J, Reneker DH (1995) Electrospinning process and applications of electrospun fibers. J Electrostat 35:151–160
- Fong H, Chun I, Reneker DH (1999) Beaded nanofibers formed during electrospinning. Polymer 40:4585–4592
- Son WK, Youk JH, Lee TS, Park WH (2004) The effects of solution properties and polyelectrolyte on electrospinning of ultrafine poly (ethylene oxide) fibers. Polymer 45:2959–2966
- Theron SA, Zussman E, Yarin AL (2004) Experimental investigation of the governing parameters in the electrospinning of polymer solutions. Polymer 45:2017–2030
- Savaş H, Güven O (2001) Investigation of active substance release from poly (ethylene oxide) hydrogels. Int J Pharm 224:151–158
- Merrill EW, Dennison KA, Sung C (1993) Partitioning and diffusion of solutes in hydrogels of poly(ethylene oxide). Biomaterials 14:1117–1126
- Doycheva M, Petrova E, Stamenova R, Tsvetanov C, Riess G (2004) UV-induced cross-linking of poly (ethylene oxide) in aqueous solution. Macromol Mater Eng 289:676–680
- Doytcheva M, Dotcheva D, Stamenova R, Tsvetanov C (2001) UVinitiated crosslinking of poly(ethylene oxide) with pentaerythritol triacrylate in solid state. Macromol Mater Eng 286:30–33
- Doytcheva M, Dotcheva D, Stamenova R, Orahovats A, Tsvetanov C, Leder J (1997) Ultraviolet-induced crosslinking of solid poly(ethylene oxide). J Appl Polym Sci 64:2299–2307
- Zhou C, Wang Q, Wu Q (2012) UV-initiated crosslinking of electrospun poly(ethylene oxide) nanofibers with pentaerythritol triacrylate: effect of irradiation time and incorporated cellulose nanocrystals. Carbohydr Polym 87:1779–1786
- Doytcheva M, Stamenova R, Zvetkov V, Tsvetanov CB (1998) U.V. irradiation-induced crosslinking of solid poly(ethylene oxide) modified with tetraalkyl ammonium salt. Polymer 39:6715–6721
- Reneker DH, Chun I (1996) Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology 7:216–233
- Zhou C, Chu R, Wu R, Wu Q (2011) Electrospun polyethylene oxide/cellulose nanocrystal composite nanofibrous mats with homogeneous and heterogeneous microstructures. Biomacromolecules 12: 2617–2625