



Short communication

Preparation of poly(ϵ -caprolactone)/poly(trimethylene carbonate) blend nanofibers by electrospinningJie Han^a, Christopher J. Branford-White^b, Li-Min Zhu^{a,*}^a College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, 2999 North Renmin Road, Shanghai 201620, PR China^b Institute for Health Research and Policy, London Metropolitan University, 166-220 Holloway Road, London N7 8DB, UK

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ABSTRACT

Poly(ϵ -caprolactone) (PCL)/poly(trimethylene carbonate) (PTMC) blend nanofibers have been prepared for the first time using an electrospinning process. The mixed dichloromethane (DCM) and *N,N*-dimethylformamide (DMF) (75/25, v/v) was found to be the most suitable solvent for electrospinning. Various blends of PCL/PTMC solutions were investigated for the formation of nano-scale fibers and it was found that the average diameter of the fibers was reduced and the morphology became finer when PTMC content was increased. FT-IR and DSC analysis indicated that the molecular interactions between PCL and PTMC were weak and they were phase-separated in the fibers. Due to the biocompatible properties of PCL and PTMC, the spun nanofibers developed here could have applications in the biomedical field.

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1. Introduction

Recently, electrospinning has aroused much interest as an attractive technique for producing polymer fibers with diameter ranging from several micrometers to nanometer dimensions (Ignatova, Manolova, & Rashkov, 2007). Due to the unique properties of electrospun fibers, such as large surface area to volume ratio, small pore size and superior performance of mechanical properties, they have been considered as possible candidates for many applications such as separation filters (Aussawasathien, Teerawattananon, & Vongachariya, 2008), carbonaceous materials (Ji & Zhang, 2009), biosensors (Patel, Li, Yuan, & Wei, 2006) and biomedical devices including tissue engineering scaffolds (Mo, Xu, Kotaki, & Ramakrishna, 2004), wound dressing materials (Powell, Supp, & Boyce, 2008), and drug delivery platforms for delivering various bioactive agents (Kim, Lee, & Park, 2007; Luu, Kim, Hsiao, Chu, & Hadjiargyrou, 2003; Maretschek, Greiner, & Kissel, 2008; Suwantong, Opanasopit, Ruktanonchai, & Supaphol, 2007; Xu et al., 2009a; Zeng et al., 2005).

Electrospinning also provides a promising and direct way to produce novel functional biomaterials. By selecting a combination of components and adjusting the ratio of the constituents, physical and biological properties of the result electrospun fibers, such as hydrophilicity, mechanical modulus and strength, biodegradability, biocompatibility, and specific cell interactions can be tailored

with the desired effects (Liang, Hsiao, & Chu, 2007). Numerous studies have been devoted to the study of electrospinning blend polymers, especially those composed of biocompatible and biodegradable materials. Chen, Mo, and Qing (2007) and Xu, Chen, Wang, and Jing (2009b) prepared electrospun collagen/chitosan and chitosan/PLA blend fibers, respectively, to mimic the native extracellular matrix for tissue engineering. Yang, Li, and Nie (2007) utilized gelatin/PVA electrospun nanofibers as a drug controlled release vehicle, and recently, electrospun fiber mats from gelatin/PLLA blends has been investigated for potential application for wound dressings (Gu, Wang, Ren, & Zhang, 2009).

Poly(ϵ -caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC) (structures see in Fig. 1) are two aliphatic polyesters. They are both biodegradable and biocompatible but have different biodegradation rates and different biomedical applications. PCL is a semi-crystalline polymer and has been widely used in tissue engineering scaffolding, that being due to the properties including: nonimmunogenicity, slow biodegradability and good drug permeability (Luong-Van et al., 2006). PTMC is an amorphous biomaterial which holds elastic properties at ambient temperature. It exhibits good mechanical resistance and high chemical and thermal stability. *In vivo* biocompatibility and toxicity assays revealed that PTMC blend had no influence on heart, liver, and kidney tissues (Qin et al., 2006). The synthetic copolymer of the two, P(ϵ CL-TMC), has been investigated as biopolymer to be used for surgery and nerve guide repairs because of its high biocompatibility and the advantage of controllable both the mechanical property and the degradation rates (Fabre et al., 2001; Jia, Liu, Song, & Shen, 2005).

* Corresponding author. Tel.: +86 21 67792659; fax: +86 21 67792655.
E-mail address: lzhu@dhru.edu.cn (L.-M. Zhu).

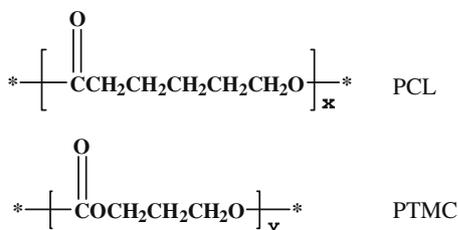


Fig. 1. Chemical structures of PCL and PTMC.

In addition, the electrospinning of neat PCL or PTMC has also been studied as biomaterials, respectively (Kenawya, Abdel-Hay, El-Newehy, & Wnek, 2009; Luong-Van et al., 2006; Song et al., 2008). Hitherto, the more promising electrospinning of PCL/PTMC complex has not as yet been reported.

The aim of this paper is to study electrospinning of PCL and PTMC blends in order to gain more details relating to the development of novel functional biomaterials. A very convenient method by using a single syringe was introduced for the preparation of blend fibers and the morphology and properties of the resultant fibers were subsequently characterized.

2. Experimental

2.1. Materials

PCL (Mw ~ 100,000) and PTMC (Mw ~ 100,000) were provided by Minghe Functional Polymer Co., Ltd. (Qingdao, China). Dichloromethane (DCM) and *N,N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All other chemicals and reagents were of analytical quality and used without further purification.

2.2. Electrospinning

Different blend ratios of PCL and PTMC (9:1, 7:3 and 5:5, w/w) were dissolved in a mixture of DCM/DMF (75:25, v/v) to prepare the electrospinning solutions at a concentration of 8 wt.%. Prior to electrospinning, the mixtures were stirred for 2 h and then degassed with an ultrasonicator (59 Hz, 350 w, Shanghai Jinghong Instrument Co., Ltd. Shanghai, China) for 30 min to obtain the homogeneous co-dissolved spinning dopes. They were then carefully placed into a 5 mL syringe which included a metallic needle with an internal diameter of 0.5 mm. Electrospinning was carried out under a fixed electric field of 14 kV/18 cm. The feeding rate of the solutions was controlled at 0.8 mL/h by means of a single syringe pump (Cole-Parmer®, USA). All experiments were carried out at room temperature and a relative humidity of 40%. The resulting fibers were further dried for 24 h at ambient temperature in a vacuum drying oven (320 Pa, Shanghai Laboratory Instrument Work Co. Ltd., Shanghai, China) to remove the residual organic solvent and moisture.

2.3. Characterization of electrospun fibers

2.3.1. Morphology

The surface morphology of electrospun fibers was assessed using a JSM-5600LV scanning electron microscope (Japan Electron Optics Laboratory Co. Ltd.). Prior to the examination, the samples were gold sputter-coated under argon atmosphere to render them electrically conductive and pictures were taken at an excitation voltage of 10 kV.

2.3.2. FT-IR spectroscopy

The molecular interactions of the blend electrospun fibers were assayed on a Fourier-transform infrared (FT-IR) spectrometer (Nicolet-Nexus 670, Nicolet Instrument Corporation, Madison, USA). The test sample was dissolved in chloroform and the solution was laid on a KBr disk. FT-IR spectrum of the samples was recorded after removal of chloroform by evaporation.

2.3.3. Differential scanning calorimetry analysis

The differential scanning calorimetry (DSC) analyses were carried out using an MDSC 2910 differential scanning calorimeter (TA Instruments Co., USA). Test samples were heated from –60 to 250 °C at a heating rate of 10 °C/min. The nitrogen gas flow rate was set as 40 mL/min.

3. Results and discussion

3.1. Morphology

One of the most important qualities related with electrospinning is the fiber morphology (Huang, Zhang, Kotaki, & Ramakrishna, 2003). From our initial experiments, it was found that without PTMC or the content of PTMC more than 50%, continuous fiber-structures could not be formed; while when the ratios of PCL and PTMC in the range of 9:1–5:5, nano-scale fibers could be obtained successfully. So, the ratios of 9:1, 7:3 and 5:5 were selected as the typical to be further investigated in this study. The surface morphologies of the electrospun fibers were demonstrated in Fig. 2. It can be observed that they possess common features of being round-shaped, randomly arrayed and highly porous. PCL and PTMC were well blended in the fibers. It should be noted that the fiber morphology was significantly affected by PCL/PTMC blend ratios. The 9/1 blend fibers exhibited some stump-like structures (in white circles, Fig. 2a), thus reflecting the fragility of the polymer fibers at this blending ratio. When the content of PTMC was raised to 30% (PCL/PTMC 7:3), fewer stump-like structures were noted and the fibers appeared more continuous and smoother (Fig. 2b). The most consistent fiber morphology was obtained when PCL and PTMC were equally blended (PCL/PTMC 5:5) (Fig. 2c). Moreover, it was demonstrated in Fig. 3 that with PCL/PTMC blend ratios of 9:1, 7:3 and 5:5, the diameter of the resultant fibers was 302 ± 109 , 266 ± 101 and 203 ± 77 nm, respectively. Fiber diameter and diameter distribution were seen to decrease with the increasing content of PTMC. These results could be related to the overall property of the polymer solution. That included viscosity, surface tension and conductivity. Increasing the content of PTMC could assist in achieving thinner and more uniform nanofibers in this study, probably due to the increased suitability of the polymer solution used for electrospinning.

Selecting an appropriate solvent system is crucial for successful electrospinning (Chen et al., 2007). DCM is a good solvent for both PCL and PTMC, but is not appropriate for electrospinning, as when DCM alone was used as the solvent, the resultant fibers exhibit larger diameters and with many beads. However it is known that DMF is a good electrospinning solvent due to its high dielectric constant (Fong, 2007). Here, DMF was added into the solution of PCL/PTMC in DCM to improve the fiber formation. During this study, several mixtures with different DCM/DMF ratios were explored as the solvents for preparing of the spin dopes. The solvent mixture with the DCM/DMF ratio of 75/25 was identified as the optimal system based upon the morphology of the nanofibers and the stability of the electrospinning. Similar observations have also been reported by Liao, Zhang, Gao, Zhu, and Fong (2008) who used a mixture of chloroform/DMF as the electrospinning solvent for PLGA.

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