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Crystallization behavior and mechanical properties of an electrospun ethanol-mediated poly(ethylene terephthalate) fibrous membrane

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ABSTRACT: A simple approach for preparing electrospun poly(ethylene terephthalate) (PET) fibrous membranes with excellent spinnability and mechanical properties is introduced in this article. To enhance the electrospinnability of PET, a small content of ethanol was incorporated into a 16 wt % PET solution. The effects of ethanol on the solution properties, mechanical properties and crystallization properties and the related morphology were systematically evaluated. The conductivity (κ) measurement indicated that ethanol could obviously improve κ of the PET solution; this correlated well with the morphology of fibers. Scanning electron microscopy images showed that the diameter of the fibers decreased with increasing solution κ. The tensile strength of the PET fibrous membrane increased 1.8 times through the blending of 2.5 vol % ethanol with the PET solution. The differential scanning calorimetry results showed that the crystallinity was improved when the ethanol content increased; this was beneficial to the enhancement of the tensile strength. The glass-transition temperature and melting temperature increased slightly, but the cold-crystallization peak shifted to a lower temperature with increasing ethanol content (<3.75 vol %); this was attributed to the increasing in the oriented degree. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42341.

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INTRODUCTION

Electrospinning is a handy and cost-effective technique for manufacturing fibers with diameters ranging from nanometers to micrometers. Electrospun fibrous membranes have gained much attention because of their distinct characteristics, such as their high porosity, nanorange pore sizes, and ease of surface functionalization. At present, energy and the environment head the list of top global problems facing society in the 21st century. So, electrospinning technology is responding to the challenges through the design and fabrication of fibrous membranes for energy and environmental applications, for example, fuel cells, electrodes of lithium-ion batteries,[1] air and liquid filtration,[2] and other fields.[3–7]

Poly(ethylene terephthalate) (PET) combines the desirable mechanical properties and outstanding processability; this makes it a promising candidate for both fiber and engineering applications. Numerous studies have shown that PET fibrous membranes can be produced by means of the electrospinning technique.[8–11]

It is well known that the disadvantages of electrospun membranes are their poor strength; many works have been done to enhance their mechanical properties. Those studies have mainly been focused on three aspects: first, the solution properties,[12] including the molecular weight and concentration; second, the electrospinning process, such as the drum linear velocity;[12] and finally, a polymer was applied to reinforce the electrospun membranes.[13] In addition, the morphology plays an important role in the mechanical properties; what is more important, uniform PET nanofibers are essential for applications. With respect to the morphology of electrospun PET fibrous membranes, many studies on the electrospinning process have been done, in particular on the solution concentration, conductivity (κ), surface tension (γ), voltage, tip-to-collector distance, and flow speed.[14–16] All of these studies have revealed that the solvent mixture of trifluoroacetic acid (TFA) and dichloromethane (DCM) is a favorable solvent for electrospun PET fibrous membranes.

For electrospun PET fibrous membranes, the reproducible production of uniform fibers is a major challenge because even small changes in the electrospinning parameters may result in morphological change.[17] In this study, to make the fibers more uniform and the spinnability better, ethanol was incorporated

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into the PET solution with TFA/DCM as the solvent mixture. Moreover, the effects of ethanol on the spinnability, morphological properties, mechanical properties, and crystallization behavior of the electrospun PET fibrous membranes were systematically evaluated.

EXPERIMENTAL

Materials

PET (Intrinsic Viscosity ≈ 0.65 dL/g, Zhejiang Guxiandao Industrial Fiber Co., Ltd.) was used for electrospinning. TFA and DCM were purchased from Zhengzhou Alfa Chemical Co., Ltd., and Tianjin Fengchuan Chemical Reagent Technologies Co., Ltd., respectively. Ethanol was obtained from Zhengzhou Yinfeng Assay Reagent Co., Ltd. They were all used as solvents without further purification.

Preparation of the PET Fibrous Membrane

PET chips were dried in a vacuum oven at 80°C for 24 h before solution preparation. The PET fibrous membranes were electrospun from a 16 wt % PET solution in a 1:1 v/v mixture of TFA and DCM. Ethanol was incorporated into the PET solution to enhance κ of solution. The contents of ethanol in the solution were 0, 1.25, 2, 2.5, 3.75, and 5 vol %, respectively. The membranes were named PET-0, PET-1.25, PET-2, PET-2.5, PET-3.75, and PET-5 accordingly. The solution was electrospun at a distance of 21 cm (the distance between the needle tip and the collector), 25 kV high voltage, and 0.6 mL/h flow rate at room temperature. The needle with an inner diameter of 0.5 mm was used as the spinneret. The electrospun PET fibrous membrane was collected on aluminum foil, all of the samples were electrospun for 4 h and were then dried overnight at 60°C in a vacuum.

Characterization and Measurements

Viscosity (η), γ, and κ of the prepared solutions were determined with a rheometer (DV-II, Brookfield Co.), γ instrument (QBZY, Ningbo Unitools Measuring Instrument Co., Ltd.), and κ meter (DDS-307A, Shanghai Jingke Instrument and Equipment Co., Ltd.) at 25°C, respectively.

The morphology of the PET fibrous membrane was examined by scanning electron microscopy (SEM; Quanta 250, FEI). The fibrous membrane was spurred a thin layer of gold before examination. The mechanical properties of the PET fibrous membranes were tested with a tensile testing instrument (XQ-1A, Shanghai New Fiber instrument Co., Ltd.). The fibrous membranes were cut into rectangular strips 50 mm in length and 2.5 mm in width. All of the samples were tested under a crosshead speed of 10 mm/min. Five points were randomly selected in each sample to test the thickness with a micrometer.

The crystallization behavior of the PET fibrous membrane was investigated by a differential scanning calorimeter (DSC; 204, Netzsch, German). The samples were heated from ambient temperature to 300°C at a rate of 10°C/min under a dynamic nitrogen atmosphere (70 mL/min). The percentage crystallinity (X_c) was calculated from eq. (1):

$$X_c = \frac{\Delta H_m}{\Delta H_f^0} \times 100\% \quad (1)$$

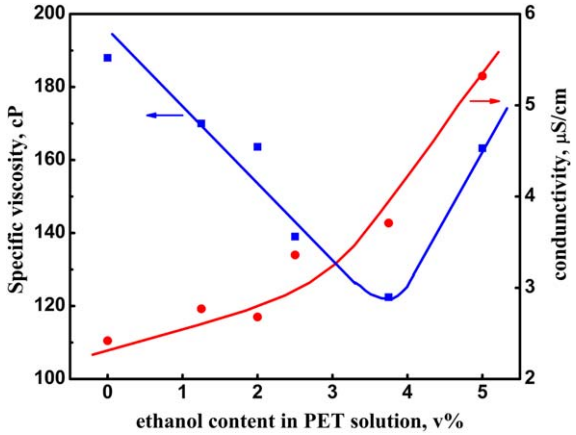

Figure 1. Dependence of η and κ of the PET solutions on the content of ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where ΔH_m is the enthalpy of fusion obtained directly from the areas of melting and ΔH_f^0 (144 J/g) is the fusion heat of the fully crystalline PET.

RESULTS AND DISCUSSION

Solution Properties and Morphology of the Electrospun Fibrous Membranes

The zero-shear viscosity (η_0) was approximated from the flow curves with the actual or extrapolated values for the apparent η at 0.1 s^{-1} and was used to calculate the specific viscosity (η_{sp}):[18]

$$\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$$

where η_s is the viscosity of solvent.

Figure 1 shows that η_{sp} and κ varied as a function of the ethanol content in PET solution. As shown in Figure 1, η of the PET solution first decreased and then increased with the addition of ethanol. The η_{sp} of the PET solution had the lowest value when blended with 3.75 vol % ethanol. At first, the PET chain conformation was changed from the stretch to the winding form through the addition of nonsolvent, a part of the entangled PET chains were destroyed, the PET chain size decreased, and η decreased because of the decreasing hydrodynamic volume. Then, a greater content ethanol made the PET chain curl and form a new entanglement between PET intermolecular and increase the intermolecular forces. This process is the competition between the re-entanglement and curling of the PET chain, and the reconfiguration of the intermolecular entanglements holds a leading post, so η of the solution increases even though the PET chain curls further. It is widely reported that a high η is favorable for effective chain entanglement and the formation of bead-free fibers.[18]

In addition to the solution η, the solution κ is another important parameter during the process. As shown in Figure 1, κ of the PET solution obviously increases with increasing ethanol. The addition of a nonsolvent to the PET solution may lead to the dissociation of the nonsolvent and nonsolvent spread on the polymer surface; it will obviously increase the net charge of the polymer solution. κ of solution directly affects the morphology

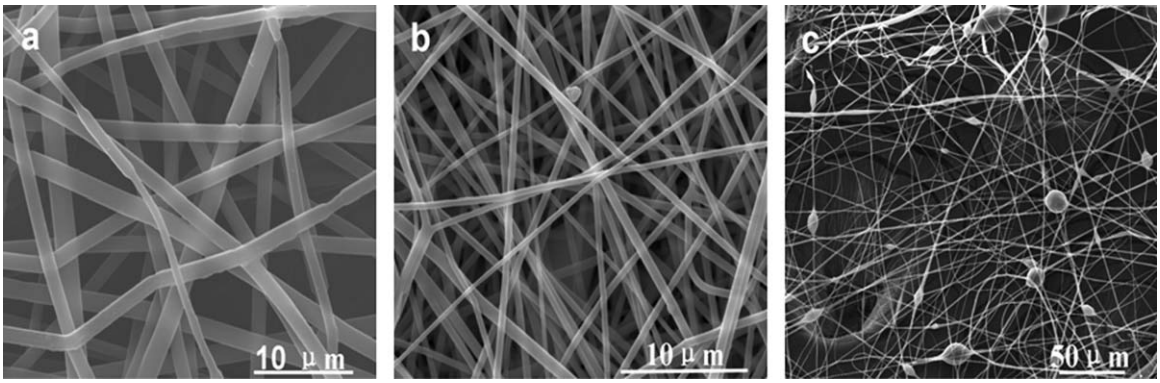

Figure 2. SEM images of the electrospun PET fibrous membranes (16 wt %): (a) PET-0, (b) PET-2.5, and (c) PET-3.75.

of fibers. A high κ is beneficial to spinnability, for forming uniform and thinner fibers,[17] because more charges are present on the surface of the polymer solution jet, which is subjected to stronger stretching because of the repulsion of charges under the same electrical field.[19–21] So, the high content ethanol will be benefit for electrospinning. However, in this study, the PET solution changed from clear to opaque when the ethanol content was beyond 3.75 vol %. Consequently, the spinnability of the PET solution was enhanced when the content of ethanol in the PET solution was 2.5 vol %.

SEM observation was performed to investigate the morphological changes at different ethanol concentrations. The SEM images depicted in Figure 2 show that uniform fibers were obtained at 2.5 vol % ethanol, but the bead fibers yielded an increase in ethanol concentration to 3.75 vol %. For simplicity, in this experiment, only samples with 2.5 and 3.75 vol % and the virgin one were selected to clarify the effect of ethanol on the morphology. As shown in Figure 2(a), the pristine PET fibrous membranes exhibited bamboolike fibers. However, uniform and thinner fibers were observed in the PET-2.5 sample [Figure 2(b)], and the bead appeared in the fibers [Figure 2(c)] when the ethanol content increased to 3.75 vol %. This result identifies that the high κ and proper η contributed to the formation of uniform fibers.

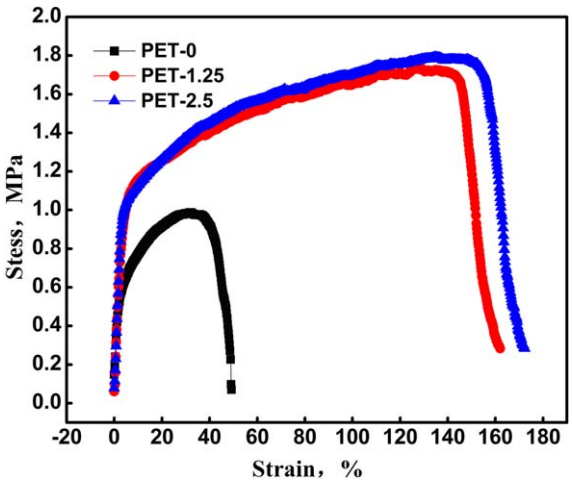

Figure 3. Representative stress–strain curves of the electrospun PET fibrous membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Properties of the PET Fibrous Membranes

Tensile testing was used to evaluate the effect of the ethanol on the mechanical properties of the PET fibrous membranes. Typical stress–strain curves of the electrospun PET fibrous membranes are presented in Figure 3, and their tensile properties are summarized in Table I. We noted that the slight increase in the modulus and yield stress with increasing ethanol (<3.75 vol %) and the transition from more brittle behavior for the PET-0 fibrous membranes to more extensible and plastic behavior for the ethanol-mediated PET fibrous membranes. The pristine PET fibrous membranes displayed the lowest tensile strength (0.98 MPa). The tensile strength of the PET fibrous membranes obtained from blending with 2.5 vol % ethanol reached 1.79 MPa. In contrast to the literature (Li *et al.*[13] prepared a neat PET membrane with 0.96 MPa, and Afra[14] manufactured PET membranes obtained from a 12.5% PET solution, and its tensile strength reached 1.68 MPa when the drum linear velocity was 22.5 m/min), we focused on the enhancement of the mechanical properties by increasing κ of the solution. The strength increase from ethanol mediation could be explained as follows. Ethanol was a nonsolvent for PET, so the addition of ethanol to the polymer solution have led to the dissociation of ethanol, and the ethanol randomly spread on the polymeric surface. The stronger drawing force induced by an electric field resulted in the better orientation of the polymer chain.[22] In addition, κ increased with increasing ethanol, and this resulted in the production of bead-free uniform and thinner fibers because the polymer solution was subjected to more stretching under a high electrical field.[17] (Figure 2) The finer fibers corresponded to a high tensile strength; this was attributed to a size effect, which was due to the electrospinning process and the macromolecular orientations in the fibers.[23,24] Therefore, the difference in the tensile properties between the fibers arose from both the size effect and the addition of ethanol.

From the results of tensile testing, the Young's modulus and tensile strength showed an increase with increasing ethanol to 2.5 vol %; this was followed by a decrease at higher contents. All of these results indicate that minute additions of ethanol

Table I. Mechanical Properties of the Resulting PET Fibrous Membranes

	Tensile strength (MPa)		Elongation (%)		Young's modulus (MPa)		Yield stress (MPa)	
	Average of five samples	Standard deviation	Average of five samples	Standard deviation	Average of five samples	Standard deviation	Average of five samples	Standard deviation
PET-0	0.98	0.32	49.2	5.44	7.56	3.12	0.66	0.11
PET-1.25	1.72	0.25	162.1	4.87	13.85	2.11	1.04	0.04
PET-2	1.73	0.16	167.8	5.12	13.27	2.32	1.06	0.06
PET-2.5	1.79	0.08	172.4	5.05	13.32	1.98	1.16	0.03
PET-3.75	1.48	0.57	134.2	5.96	11.66	2.58	0.99	0.08
PET-5	1.34	0.46	128.6	6.24	10.98	3.15	0.93	0.13

during the electrospun PET fibrous membranes significantly enhanced the mechanical properties. So, it is a significant and simple way to enhance the mechanical properties.

Crystallization Behavior

It is well known that a higher orientation degree is one of the most popular explanations for a higher tensile strength.[25,26] The addition of ethanol enhanced κ of the PET solution; this resulted an increase in the chain orientation because stronger stretching was subjected to a high electrical field. In addition, the orientation degree affected the glass-transition temperature (T_g), melting temperature (T_m) and cold-crystallization peak (T_{cc}). Therefore, the crystallization behavior of the PET pellets and electrospun PET fibrous membranes as a function of ethanol was analyzed by DSC, and the trends of T_g, T_m, and T_{cc} were used to provide the analysis of the orientation variations of the membranes with increasing ethanol. The DSC curves are shown in Figure 4, and the thermal data are summarized in Table II. The DSC trace of the as-received opaque PET pellets involved an endothermic melting peak at 259.2°C, and X_c was 35%. The electrospun fibrous membranes exhibited quite different thermal behaviors than those of the raw PET pellets. As shown in Figure 4, all of the electrospun PET fibrous membranes involved a clear T_g and T_{cc}; this demonstrated that the samples contained mostly amorphous phase.

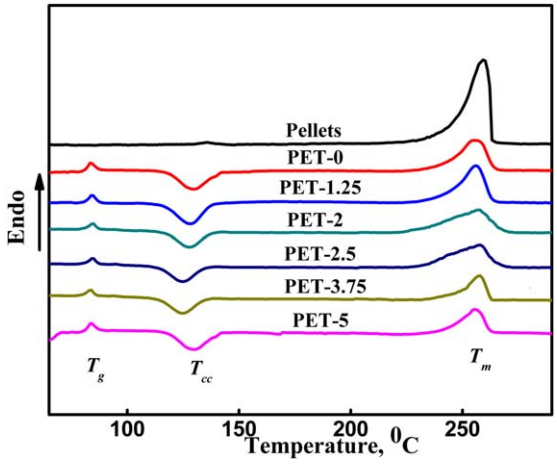

Figure 4. DSC curves of the raw PET and electrospun PET fibrous membranes with different contents of ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The T_g of the pristine PET fibrous membrane appeared at 83.3°C; this was lower than that of the PET fibrous membranes prepared from solution with ethanol (83.4–85.0°C). This indicated that the PET chains in the ethanol-mediated PET fibrous membranes exhibited a highly oriented state.[27] It also proved that the chain mobility of the amorphous PET in the PET fibrous membranes could be limited by ethanol when the content of ethanol was less than 3.75 vol %. T_g increased with increasing ethanol; this could be explained as follows. First, the polymer solution with higher κ was subjected to stronger stretching under a high electrical field; this resulted in a higher orientation of the fiber. However, when the addition of ethanol increased to 3.75 vol %, the solution became opaque, and the bead appeared. From the results of X_c, the fraction of the amorphous state increased; this means that the bead contained more amorphous state, and the orientation decreased when the ethanol content was above 3.75 vol %. Second, the solvent in the electrospun PET fibrous membranes could induce crystallization because some crystal nuclei were likely to form. This limited the chain mobility and increased T_g. The solvent-induced crystallization effect became obvious as the ethanol content increased. Finally, the PET fibrous membranes were dried overnight at 60°C; the physical aging resulted in cohesional entanglement and restricted the chain segmental motion.[28]

The cold crystallization resulted mainly from the incomplete crystallization in the spinning process. The clear T_{cc} indicated that the amorphous phase of the electrospun PET fibrous membranes increased compared with the that of the raw PET pellet. In addition, the high orientation played an important role in accelerating the cold crystallization, so a lower T_{cc} was found in highly oriented fibers.[29] Compared the trace of pristine PET fibrous membrane and ethanol-mediated fibrous membranes, we found that T_{cc} shifted to a lower temperature as the ethanol content increased

Table II. Thermal Properties of the PET Nanofibers

Sample	T_g (°C)	T_{cc} (°C)	T_m (°C)	X_c (%)
Pellets	—	—	259.2	35.3
PET-0	83.3	128.7	255.3	12.8
PET-1.25	83.8	127.5	255.8	13.2
PET-2	85.0	127.3	257.0	14.1
PET-2.5	85.0	123.9	258.1	14.9
PET-3.75	84.0	123.5	257.3	13.7
PET-5	83.4	129.2	255.4	12.9

when the content of ethanol was no more than 3.75 vol %. This suggested that the chain mobility decreased because of the increasing orientation with increasing ethanol content.[29] Moreover, the physical aging and solvent-induced crystallization resulted in the acceleration of the crystallization of the PET fibrous membranes and in T_{cc} moving to a lower temperature.[30]

Figure 4 also illustrates that the T_m shifted slightly to a higher temperature; the exotherm broadened and turned worse with increasing ethanol content (<3.75 vol %). The X_c values calculated according to eq. (1) are summarized in Table II. This shows that the electrospun PET nanofibers exhibited a lower X_c than the raw opaque PET pellets, and the T_m decreased from 260°C for the raw PET pellets to 255–258°C for the electrospun PET fibers. The previous results were ascribed to the increasing orientation.[31] In addition, we noted that the melting peak became asymmetric with increasing ethanol. The asymmetric melting peak may have contributed to the different crystal forms. This is a conjectural view, and more work is needed to demonstrate this.

As shown in Table II, PET-2.5 had the lowest T_{cc} and the highest T_g, T_m, and X_c in all samples; this indicated that the addition of 2.5 vol % ethanol increased the orientation and crystallization of the PET membranes.

According to the previous discussion, on the whole, the orientation degree exhibited a slightly increasing trend with increasing ethanol content when the content of ethanol was less than 3.75 vol %. Although the changes were not obvious, the trend was in agreement with the changes in the tensile strength.

CONCLUSIONS

In this study, ethanol-mediated PET fibrous membranes were fabricated with the electrospinning technique. The effects of ethanol on the morphology, crystallization behavior and related mechanical properties were investigated by SEM, DSC and tensile testing. This study demonstrated that the addition of 2.5 vol % ethanol to the electrospun PET fibrous membrane obviously improved the morphology and mechanical properties, enhanced the crystallization behavior and orientation at the same time. All of these resulted from the increase in the net charge concentration of the polymer solution. This study indicates that the electrospun PET fibrous membrane with strong tensile strength can be easily fabricated from the PET solution through incorporation with 2.5 vol % ethanol. This method is a simple yet effective approach for improving the spinnability of the solution and mechanical properties of the membranes.

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