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Effect of polar additives on melt electrospinning of non-polar polypropylene

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Abstract: Melt or solution electrospinning are effective and direct techniques for producing nanoscale fibers. Polypropylene (PP) cannot be easily dissolved at ambient temperature. Thus, it is commonly electrospun in the melt state. However, compared with solution electrospun fibers, melt electrospun PP fibers are more uneven and with larger diameters. In this study, to remedy this problem, polar additives, namely stearic acid and sodium stearate, were added into pure PP. The effects of the additives were investigated. The results showed that in contrast to those of pure PP, the fiber diameter of PP with 8 wt. % stearic acid was decreased by 69.3 % (from 5.4 to 1.6 μm). The smallest fiber diameter was 600 nm and the smallest average fiber diameter was 1.8 μm when the sodium stearate contents were 10 and 8 wt. %, respectively. The addition of polar compounds altered not only the diameters of PP microfibers, but also the distribution of diameters, the processing current, and even the thermal properties of the fibers. The microcosmic mechanisms for these changes were interpreted.

Keywords: diameter; microfiber; non-polar polymer; sodium stearate; stearic acid; crystallization.

INTRODUCTION

Electrospinning from polymer solutions or melts are effective and direct techniques for producing nanofibers.[1–4] Solution electrospinning conducted at ambient temperature is a convenient way to obtain superfine fibers,[5,6] but not every polymer can be dissolved in an appropriate organic solvent at room temperature. Moreover, the volatility of organic solvents may lead to environmental pollution. A trace amount of organic solvent trapped in a spun polymer will negatively impact the mechanical properties of the resulting fibers.[7] Without

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polymer solvation, melt electrospinning compared with solution treatment is more environment friendly and highly efficient.[8–10] However, the development of melt electrospinning is slow because of the high viscosity of the melt, resulting in impaired flow and thick fibers (only a few can attain a thickness of several hundreds of nanometers).[11]

To decrease the viscosity and obtain small-diameter fibers, two ways have been attempted. The first was to change the conditions[12–16] of the melt electrospinning, such as the voltage, melt temperature, receiving distance, *etc*. The second was to change the polymer content, for instance the addition of a plasticizer,[12] or decreasing the molecular weight of the polymer,[5] *etc*. Malakhov *et al*.[17] used sodium stearate and oleate as additives to reduce the viscosity of polyamide 6 melt in electrospinning. They found that the addition of 10 wt. % additive decreased the average diameter of the fibers 40-fold because of the 60-fold decrease in the viscosity of the melt. Polyamide 6, sodium stearate and oleate are polar materials, so strong interactions exist among these molecules. Thus, using a polar additive is effective. However, non-polar polymers, such as polypropylene (PP), polyethylene, polybutadiene, polystyrene, *etc*., are very common in the fiber industry. Thus, whether a polar additive could also affect a non-polar polymer in melt electrospinning should be determined. □

A self-made melt electrospinning system[18–20] was used to spin PP fibers, which can be used in many fields, such as in filtration or clothing. Polar stearic acid or sodium stearate was added into the PP.[21–23] The detailed effects of polar additives on PP fiber diameter and other properties were studied.

EXPERIMENTAL

Materials

PP (iPP) was obtained from Shanghai Expert in the Developing of New Material Co., China. The melt flow index of the PP was 1500 g/10 min. Stearic acid and sodium stearate were purchased from Xilong Chemical Co., China. Stearic acid, with relative molecular mass of 284.48, is a short chain polymer. Sodium stearate, with relative molecular mass of 306.46, is an organic salt. All reagents were used as received without any further treatment.

Electrospinning equipment

A homemade electrospinning device, consisting of a heating system, a high-voltage supply device, and a collector, was used.[18-20] The collector was a square aluminum plate with edge length of 20 cm. The high-voltage supply device, purchased from Tianjin High Voltage Power Supply Plant, China, provided a maximum voltage output of 100 kV and a maximum current output of 2 mA. The electrical heating ring covering the cylinder was custom built with a power of 300 W. A piston controlled the flow rate of the polymer melt.

Preparation of the electrospinning materials

Nine PP samples containing 0, 6, 8, 10 and 12 wt. % stearic acid, as well as 6, 8, 10 and 12 wt. % sodium stearate, were prepared. To ensure that the stearic acid or sodium stearate was mixed uniformly with the pure PP, every sample was extruded using a miniature extruder (DYNISCO, LME-230, USA). The screw and die head temperatures were 145 and 140 °C, respectively. The screw speed was 30 rpm, and each sample had a mass of 0.5 g. Then, each sample was broken down into fine powders in a mill. The PP samples containing stearic acid or sodium stearate were considered as composites, while the pure PP sample was denoted as PP.

Electrospinning

The temperatures of the top and low electrical heating rings were set to 180 and 220°C, respectively. The distance between the spinneret head and the collecting plate was 10 cm. The samples were added into the cylinder individually. When the device reached the set temperature, it was maintained for 10 min. Subsequently, the piston weight was adjusted to control the quantity of the melt flow. When PP or its composite melts had uniformly covered the whole spray head, the high-voltage supply device was switched on and the voltage adjusted to approximately 37 kV.

Characterization

The diameters of the electrospun fibers were measured by scanning electron microscopy (SEM, Hitachi S4700). The fiber samples were coated with a 10 nm layer of platinum before observation. The scanning voltage was 20 kV. The average fiber diameters and their standard deviation (*SD*) were calculated from 100 fibers of one sample using software Image J 1.44P (National Institutes of Health, USA). The thermal transition of the PP was examined using differential scanning calorimetry (DSC, Perkin Elmer Pyrisl) to discuss the crystallization of PP. Fiber samples (3 mg) were loaded into the DSC pan. The scanned temperature range was from 25 to 300 °C, at a heating rate of 10 °C min^{-1}. The FT-IR measurements were realized over the wavenumber range 4000–400 cm^{-1}, using 32 scans at a resolution of 1 cm^{-1}, employing a Nicolet Avatar 320 FT-IR spectrometer.

RESULTS AND DISCUSSION

Effect of polar additives on the electrospinning current

The polar additive is easily polarized under a strong electrical field. Thus, the addition of a polar material in PP will result in a fundamental change in the electrospinning process. During the experiment, the current of the high-voltage generator was recorded when PP or its composites with different stearic acid contents were spun. Under the same spinning conditions, the current first increased with increasing stearic acid content, which illustrates that the polarized electron cloud of stearic acid increased the charge of the fibers containing additives (Fig. 1). However, the current decreased when the stearic acid content was increased from 10 to 12 wt. %. The explanation of this phenomenon is shown schematically in Fig. 2. Although the amount of tiny stearic acid particles in the surface layer of thick fibers is equal to or slightly higher than those in the surface layer of thin fibers, the charge density per surface area of the thick fibers is lower. Moreover, when the stearic acid content reached 12 wt. %, more stearic acid molecules probably aggregated to form larger domain phases while fewer molecules were dispersed in the PP melt phase. The stearic acid could not be uniformly distributed in the PP phase, which led to a discontinuous distribution that decreased the number of charges in a fiber unit. Hence, the current was lower when the stearic acid was 12 wt. % compared with that at 10 wt. %.

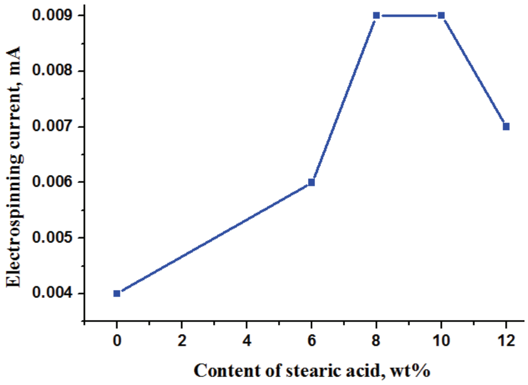


Fig. 1. Changes in the electrospinning current of PP containing different contents of stearic acid.

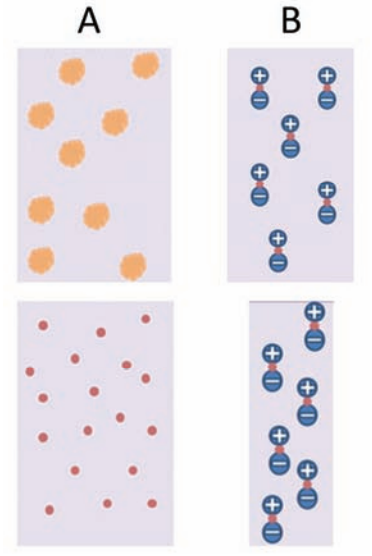
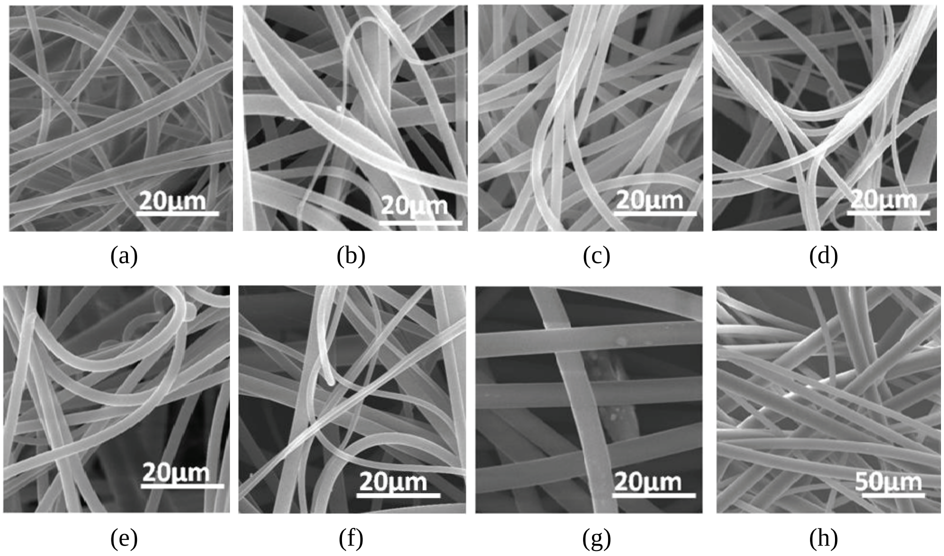


Fig. 2. Mimic diagrams of different PP fibers containing additives. The dark rectangles represent fibers. A shows the PP fibers with sodium stearate (irregular particles) (upper) and with stearic acid (points) (lower). B shows the PP fibers with stearic acid (dipole) electrospun at low (upper) and high (lower) voltages.

Effect of polar additive on the fiber diameters

The polar additive apparently affects the fiber diameters of PP. The SEM images of PP with different contents of polar additive are illustrated in Fig. 3 and the statistical data are listed in Table I. The average fiber diameter of the PP composite initially decreased with increasing stearic acid or sodium stearate content (Fig. 4 and Table I). When stearic acid content was 8 wt. %, the minimum diameter was 1.65 μm, but the *SD* was not the smallest. The minimum *SD* appeared at 10 wt. % stearic acid. However, the average diameter increased when the content exceeded 10 wt. %.

The possible reason for the variations in the diameters is the presence of the carboxyl group in the stearic acid molecule. Under a high electric field, the electron cloud of the carboxyl oxygen double bond and the carboxyl oxygen single



(a) (b) (c) (d)

(e) (f) (g) (h)

Fig. 3. SEM images of PP fibers containing different contents of additive, electrospun at 220 °C, 10 cm spinning distance, and 30 kV. a) 6 wt. % stearic acid; b) 6 wt. % sodium stearate; c) 8 wt. % stearic acid; d) 8 wt, % sodium stearate; e) 10 wt. % stearic acid; f) 10 wt. % sodium stearate; g) 12 wt. % stearic acid; h) without additives.

TABLE I. Statistical data of diameters of PP fibers containing different additive contents (*AVG*: average diameter, *SDEV*: standard values of deviation, *MIN*: minimum value)

Parameter	6 wt. % stearic acid	6 wt. % sodium stearate	8 wt. % stearic acid	8 wt, % sodium stearate	10 wt. % stearic acid	10 wt. % sodium stearate	12 wt. % stearic acid	Without additives
AVG / µm	2.1	2.4	1.6	1.8	2.1	2.2	4.9	5.4
SDEV	0.2	0.7	0.1	0.8	0.1	2.2	0.2	1.7
MIN / µm	1.7	0.9	1.3	0.8	2.0	0.6	4.5	3.0

bond is easily changed and polarized. Then, the polymer chains connected, entangled or wrapped with stearic acid will bear a strong electric field force. Moreover, stearic acid can plastify PP. With the increase in stearic acid content, the PP composite melt suffered more force from the electric field. Under a high tensile force, the diameter of the PP microfibers that formed at the end of the Taylor cone was small. However, when the stearic acid content was increased to 12 wt. %, the fiber diameter became thick again, reaching 4.8 µm. This condition may have been caused by the increased formation of tiny phases of stearic acid molecules, with low molecule dispersal in the PP melt phase, when stearic acid content reached 12 wt. %. Therefore, the continuous stearic acid phase moved very easily and the PP melt phase became more viscous, resulting in a second increase in the fiber diameter.

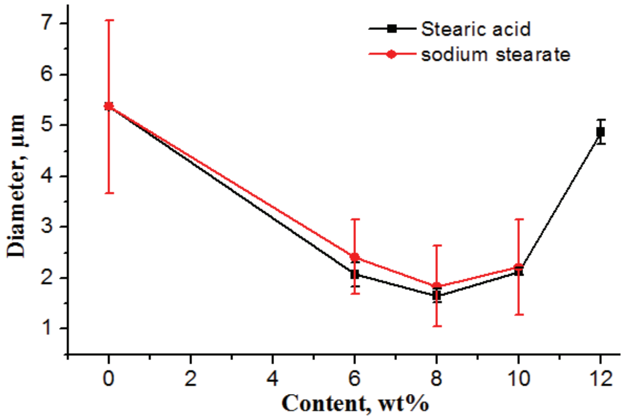


Fig. 4. Changes in the average diameter of PP fibers containing additives at different contents of stearic acid and sodium stearate.

The minimum fiber diameter of PP with sodium stearate was significantly smaller than that achieved with stearic acid (Fig. 4 and Table I), probably because sodium stearate is a salt. Salts can be easily ionized in an electric field. The positive and negative ions move to opposite ends and then produce an electric force along the direction of the electric field. For the stearic acid under a strong electric field, only a shift in the electron cloud occurs, and the polarization is much smaller than that obtained with sodium stearate. The force from the electron movement is significantly greater than the force from the electron cloud shift. Thus, the fiber diameters of the PP composites containing sodium stearate were smaller than those containing stearic acid. However, the diameter distributions of the PP with sodium stearate were extremely inhomogeneous compared with those containing stearate acid. This condition may have been because sodium stearate is a hydrophilic salt, which has no plastification effect on the organic PP melt. Stearic acid as an organic material can be evenly distributed in the PP melt and had an apparent plastification effect on the melt. This phenomenon resulted in the presence of both thick and thin fibers from the PP with sodium stearate, which led to uneven diameter distributions.

Effect of polar additive on the diameter distribution of PP fibers

The effect of polar additive on the fiber diameter distribution varied with the additive content. The diameter distribution of PP fibers containing different amounts of stearic acid is shown in Fig. 5. The PP (0 wt. % stearic acid) showed a broad and multiple peak distribution of the fiber diameters. The distribution peak generally shifted to the large diameter side with increasing stearic acid content, but the distribution remained at the small fiber diameter side when the stearic acid content was at 6 wt. %. The average diameter of the PP fibers with

8 wt. % stearic acid was 1.6 μm, which was smaller than that (2.1 μm) of the PP fibers with 10 wt. % stearic acid, but had a larger *SD* (Table I and Fig. 4). The data from Table I agree well with those of Fig. 5. The fiber diameters of PP with 8 wt. % stearic acid had a distribution range from 1.0 and 1.75 μm. A bimodal fiber diameter distribution was visible on the curve. However, the fiber diameters of PP with 10 wt. % stearic acid had a distribution range from 2.0 to 2.25 μm with one major peak. Thus, the diameter distribution of PP with 8 wt. % stearic acid was broader than that with 10 wt. % stearic acid, but both composites had narrower diameter distributions than that of PP.

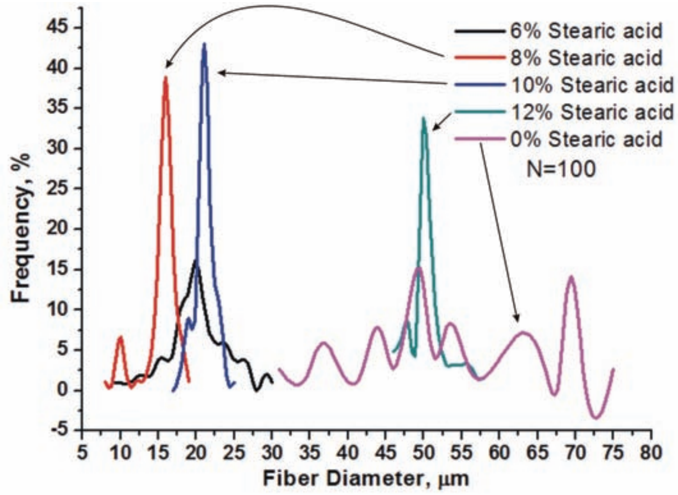


Fig. 5. Diameter distribution of PP fibers containing different contents of stearic acid. *N* = 100 indicates 100 fibers from each photomicrograph measured.

Effect of the polar additives on fiber crystallization

The degree of crystallinity is very important for the performance of fibers. DSC was used to check the thermal properties of the fibers. The thermal analysis curves of PP powder, PP fibers, and microfibers of PP with 10 wt. % stearic acid are shown in Fig. 6. PP had the maximum melting peak, as shown by the thermogram. The peak shifted to a low temperature and its magnitude was decreased after the PP had been electrospun. The smallest peak value and the lowest temperature were exhibited by the PP fibers with 10 wt. % stearic acid. A cold crystallization peak was found on the curves of the PP fiber and the PP fibers containing additives, indicating that crystallization in the two types of fibers was complete. The size of the melting peak reflects the degree of crystallinity. The decrease in the melting peak of electrospun microfibers, as well as the appearance of cold crystallization, showed the decrease in PP crystallinity. PP is a slow crystallizing polymer, and its crystallization needs sufficient time. As the electrospinning process is very fast, the PP melt jet did not have sufficient time to crystallize before falling on the collection plate and cooling quickly. On the other hand, the fluidity of the PP melt increased for two reasons, one is the plastification effect of stearic acid and another is the movement of the electron cloud of stearic acid that increased the force on the PP melt in the electric field. The faster is the flow, the shorter is the time to crystallize. Hence, the degree of crystallinity of PP with stearic acid was the smallest and its crystallization was the most imperfect, as evidenced by the minimal height of the melting peak.

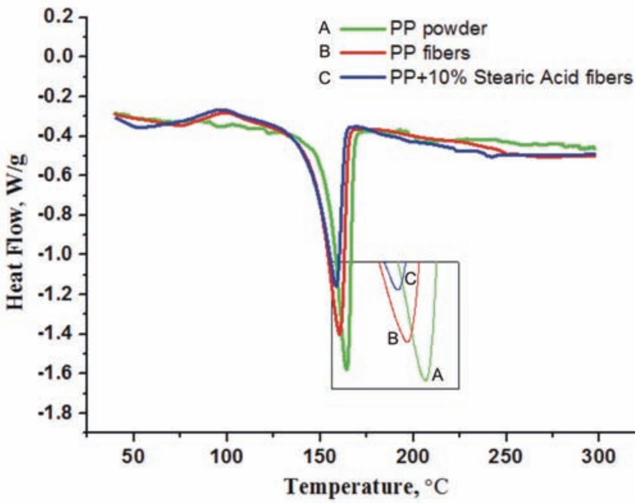


Fig. 6. DSC thermograms of PP powder, PP fibers, and PP fibers containing 10 wt. % stearic acid. The inset is the enlarged tip area of the main curves.

Effect of polar additive on the structure of the fibers

To gain some insight into the change in chemical structure of PP accompanying electrospinning, IR spectroscopy was conducted on the PP before and after spinning. The results are shown in Fig. 7 for the PP powder, PP fibers containing 10 wt. % stearic acid and PP fibers. The representative bands can be assigned as follows: the intense bands extending from 1350 to 1470 cm^{-1} are super-positions of alkanes, $\nu_{C–H}$. The bands extending between 2500 and 3000 cm^{-1} mainly resulted from different stretch vibrations of C–H bands ($–CH_3$ and $–CH_2$). The peak at 1709 cm^{-1} can be assigned to $\nu_{C=O}$ of a carboxylic acids. As seen in Fig. 7 (curves A and C), no appreciable difference could be observed in the IR spectra between the virgin powder and the PP fibers, except for the change of 2361 cm^{-1} that arises from CO_2 absorbed by the fibers. Comparing the IR spectra of Fig. 7B and C, one new peak appeared at 1709 cm^{-1}, corresponding to $\nu_{C=O}$. This phenolmenon can be attributed the stearic acid. No other chemical changes were apparent. Hence, the polar additive did not change the structure of the fibers.

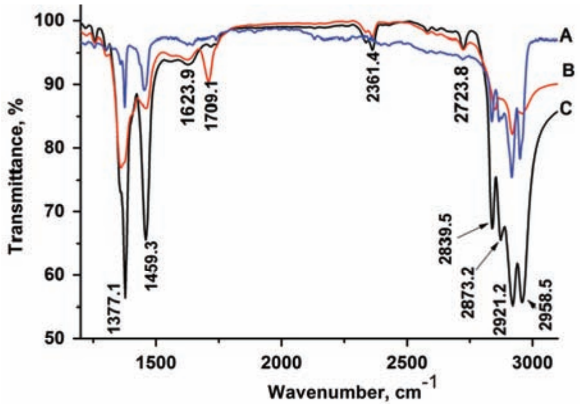


Fig. 7. FT-IR spectra of: A) PP powder; B) fibers of PP containing 10 wt. % stearic acid; C) PP fibers.

CONCLUSIONS

In summary, stearic acid and sodium stearate are promising additives for decreasing the fiber diameter and the diameter distribution in the electrospinning of PP because of their polarity and plastification effect. The smallest fiber diameter was 600 nm and the smallest average fiber diameter was 1.8 μm when the sodium stearate content was 10 and 8 wt. %, respectively. The narrowest diameter distribution appears when the stearic acid content was 10 wt. %. Both additives can reduce the fiber diameter and diameter distribution when compared to the fibers from neat PP.

The crystallinity of resulting PP fibers containing additives was smaller than those of PP and electrospun PP fibers, indicating that the addition of polar compounds in PP can alter not only the diameter of resulting fibers, but also the thermal property and microstructure.

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ИЗВОД

УТИЦАЈ ПОЛАРНИХ АДИТИВА НА ПРОЦЕС ИЗРАДЕ НЕПОЛАРНИХ ПОЛИПРОПИЛЕНСКИХ ВЛАКАНА ЕЛЕКТРОСПИНИНГОМ ИЗ РАСТОПА

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Полимерна влакна нанометарских димензија могу се добити електроспинингом из раствора или растопа, који је веома ефикасан и директан поступак. Како је поли(пропилен) (PP) тешко растваран на собној температури, његова влакна се израђују електроспинингом из растопа. Међутим, у поређењу са влакнима добијеним електроспинингом из раствора, PP влакна из растопа су неуједначених димензија и већих пречника. Да би се побољшао поступак прераде из растопа, неполарном PP се додају поларни адитиви, као што су стеаринска киселина и натријум-стеарат. Утицај додатка поларних адитива на процес израде PP влакана електроспинингом из растопа је приказан у овом раду. Резултати су показали да у поређењу са полазним PP влакнима, пречници влакана PP са 8 мас. % стеаринске киселине су смањени за 69,3 % (од 5,4 до 1,6 µm). Најмањи пречник влакана од 600 nm је добијен у присуству 10 мас. % натријум-стеарата у полимерној матрици, док је најмањи средњи пречник влакана износио 1,8 µm при садржају од 8 мас. %. Додатак поларних једињења утиче не само на пречник PP микровлакана, већ и на расподелу величина влакана, јачину струје при преради, као и на термичка својства добијених влакана. У раду је предложен механизам деловања поларних адитива на поступак израде PP микровлакана.

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