

Morphology, Crystallization Behavior and Tensile Properties of β -Nucleated Isotactic Polypropylene Fibrous Membranes Prepared by Melt Electrospinning*

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Abstract β -nucleated isotactic polypropylene (iPP) fibers with diameters less than 5 μm were prepared through melt electrospinning. The effects of electrospinning process and rare earth β -nucleating agent (WBG) on the crystal structure of iPP fibers were investigated. The results indicate that the addition of WBG can improve the fluidity of iPP melt remarkably and help the formation of fine fibers with thinner diameter, while the electrostatic force applied on the iPP melt is not favorable for the formation of β -crystal in iPP fibers. In addition, the morphology and crystalline structure of WBG/iPP electrospun fibers depended on the content of WBG. Both the crystallinity and the percentage of β -crystal form of WBG/iPP electrospun fibers increase with the rise of the content of nucleating agent, which endows the prepared electrospun fibers excellent mechanical properties. The β -nucleated iPP electrospun fibrous membranes prepared in this study can be used for protective clothing material, filtration media, reinforcement for composites and tissue engineering scaffolds.

Keywords: Melt electrospinning; β -Nucleating agent; Crystallization; Polypropylene.

INTRODUCTION

Since 1981, when Larrondo and Manley designed the first melt electrospinning device and prepared polypropylene (PP) fibers with diameters of about 50 μm ^[1], melt electrospinning has been accepted as another method to fabricate polymer fibers and fibrous product with fiber diameters ranging from hundreds of nanometers to tens of micrometers^[2, 3]. The development of melt electrospinning is welcomed for several reasons: 1) availability in some engineering plastics like polypropylene (PP), polycarbonate (PC), polyethylene (PE), *etc.* which are not soluble in regular solvent at relatively mild temperatures and cannot serve in solution electrospinning; 2) safety assurance to the operators and the use of the end-product (no solvent is included); 3) smooth surface of the fibers compared to fibers with tiny pores on the surface prepared by solution electrospinning; 4) ease in preparation fibrous matrices with pore size of several microns that can be used in tissue engineering; 5) 100% output for melt electrospinning compared to 2%–10% of solution electrospinning,

* This work was financially supported by the National Natural Science Foundation of China (No. 20974010), Fundamental Research Funds for the Central Universities (No. ZZ1307) and Program for Changjiang Scholars and Innovative Research Teams in Universities (PCSIRT, No. IRT0807).

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Invited paper for the special issue of “Polymer Crystallization”

Received March 18, 2014; Revised April 11, 2014; Accepted April 21, 2014

doi: 10.1007/s10118-014-1465-2

the high output is a significant index in commercialization considering the economic effectiveness^[4–6].

The advantages of melt electrospinning have boosted the development of the technology, till now, several polymers, including polypropylene (PP) and polyethylene (PE), polycarbonate (PC), poly(lactic acid) (PLA), poly(ethylene glycol) (PEG), polycaprolactam (PCL) and polyamides (PA) have been applied in melt electrospinning^[6]. Polymer melts were electrospun into fabrics varying in shape and fiber arrangement according to specific applications. Melt electrospun products have been used in several fields, like gas and liquid filtration, protective clothing and coating, drug delivery, electronic circuit design and sensor industry^[7–11].

The exploration of polypropylene products with excellent performances and variation in product forms has never slowed down. Melt electrospinning of polypropylene now is mainly focusing on two aspects. One is preparation of fibers with fine diameter and the other is the preparation of *i*PP fabrics that can be used in certain fields. At present, polypropylene fibers with a diameter ranging from hundreds of nanometers to tens of micrometers can be prepared through melt electrospinning. A needleless melt electrospinning setup with a rotary metal disc spinneret was designed by Fang *et al.*^[12]. *i*PP fibers with diameter of 400 ± 290 nm were obtained at an optimized condition and by adding a cationic surfactant. An elevated temperature during the melt electrospinning process was adopted by Cho *et al.* and fibers with diameter of 2.4 μm were obtained. It was proved that the *i*PP fibrous webs are super hydrophobic^[13, 14]. The hydrophobic fabrics can be applied on the surface of solar cells to avoid contamination and expand lifetime of the solar cells^[7]. Protection clothing for agriculture workers to protect them from liquid pesticide was fabricated by Lee and Obendorf through melt electrospinning technology^[8, 15]. Furthermore, for the good air permeability and water repellency, it is promising that the *i*PP fibers can be directly used on wound as band-aid^[16, 17]. It is also anticipated that polypropylene electrospun fibrous membranes can be applied as battery separators due to their innate features of a large surface area and fine pore sizes. Although lots of work has been done on melt electrospinning of polypropylene, few investigations has been conducted on the effect of electrospinning process and nucleating agents on the crystal structure characteristics of the electrospun fibers which is a decisive factor for the mechanical performances of the products.

For the improvement of mechanical properties of *i*PP products, the crystal structure and morphology are significant factors to concern. Generally, *i*PP can crystallize in three crystal forms: α , β and γ ^[18–20]. α -crystal form is the thermal stable phase, while β - and γ -crystal forms are meta-stable and can easily transform into α -crystal form in proper conditions. In terms of mechanical properties, the α -crystal form leads to big spherulite size and brittle products while β -crystal form results in products with improved toughness^[21–24]. Besides, the thermal deformation temperature of β -crystal *i*PP is higher than that of α -crystal *i*PP^[25, 26]. Therefore, the difference in crystal forms and the corresponding mechanical properties of *i*PP offers a possibility to enhance the performance of *i*PP products through tailoring the crystal structure and morphology.

The addition of nucleating agent was accepted as the most effective way to prepare *i*PP material with excellent mechanical properties. Both inorganic and organic nucleating agents are included^[27–31]. A rare earth nucleating agent WBG ($\text{Ca}_x\text{La}_{1-x}(\text{LIG1})_m(\text{LIG2})_n$, x and $(1-x)$ are the ratio of Ca^{2+} and La^{3+} , while m and n are the coordinate number of LIG1 and LIG2, LIG1 is carboxylic acid and LIG2 is amino compound) with high β -crystal selectivity has been patented by Feng *et al.*^[32] and the nucleating effect of WBG on *i*PP has been studied by Luo *et al.*^[33]. The percent of β -crystal form can reach 90% at a 0.15% WBG content.

Besides, understanding of the crystallization habits of *i*PP on special occasion is very important for achieving good performance of the products. Yan *et al.* have done a lot of work on the crystallization behavior of *i*PP on different surfaces, like Kevlar and *i*PP fiber surface, PE film, *etc.* They studied the formation of β transcrystalline regions on *i*PP fiber and Kevlar fiber. The transcrystalline region on the fiber surface can serve as bondings in the composites and ensures good mechanical performance of the composites^[34, 35].

In this work, a highly effective β -nucleating agent (WBG) was blended with *i*PP melt and the β -nucleated isotactic polypropylene (*i*PP) fibers with diameters less than 5 μm were prepared through melt electrospinning. The crystallization behavior of WBG nucleated *i*PP melt electrospun fibers was investigated. The effect of applied voltage in electrospinning and the addition of β -nucleating agent on the crystal structure and the final

mechanical properties of the fibers were described. This work provides a new idea for producing high performance *i*PP fibrous product with potentials in relevant industries.

EXPERIMENTAL

Materials

Commercial isotactic polypropylene (*i*PP), PP-H-GD 150, with an isotacticity of 94%, melt flow index of 15 g/10 min (obtained at 230 °C with a load of 2.16 kg according to ASTM D1238) and melting temperature of 165 °C was kindly supplied by Shijiazhuang Refining Branch of China Petroleum & Chemical Corporation. The nucleating agent WBG with high β -crystal form selectivity was kindly supplied by Beijing Research Institute of Chemical Industry (SINOPEC, Polymer Research & Development Center).

Preparation of WBG/*i*PP Electrospun Fibers

The weight percent of WBG in each sample was set at 0.05 wt%, 0.5 wt% and 1.0 wt%. Compounding of WBG and *i*PP were completed in a mini single screw extruder (Dynisco LME-230) with a screw speed of 40 r/min and a temperature of 180 °C. A pure *i*PP sample was also prepared as the control sample.

A self-designed melt eletrospinning device^[3] was employed, and the extruded compounds of WBG/*i*PP were transferred to the melt electrospinning device to fabricate fibrous membrane. The temperature was set at 265 °C to ensure good fluidity of polymer melt and the continuity of *i*PP fibers. A positive high voltage supply was attached to the spinning nozzle. The cathode is a copper plate covered by alumina foil on which the fibers were collected and formed fibrous membrane. To investigate the effect of applied voltage on the morphology and crystal structure of the electrospun fibrous membrane, the applied voltage was set at 35, 40 and 45 kV respectively. According to our previous work, the appropriate distance between the spinneret and the collector was 12 cm^[14].

Preparation of WBG/*i*PP Films

To investigate the effect of electrospinning process on the β nucleation effect of WBG, the melt-pressed *i*PP films were prepared as control samples in this work. All blend samples of *i*PP with different WBG contents were first sandwiched between two polyimide films and melt-pressed at 265 °C and 15 MPa to form a polymer film with a thickness of *ca.* 100 μ m. After that, the pressed films were cooled down directly to room temperature without any thermal treatment.

Characterizations

The morphologies of WBG/*i*PP elctrospun fibers were examined with a field emission environment scanning electronic microscope FEI XL-30 at 20 kV. All samples were first sputter-coated with a gold layer under vacuum situation.

Wide angle X-ray diffraction (WAXD) experiments were conducted with PaNalytical (Holland) X' pert Pro MRD diffractometer (CuK α , $\lambda = 0.154$ nm, 40 kV, 40 mA, reflection mode) to study the crystal structure of the samples. Electrospun WBG/ *i*PP fibrous membranes with a dimension of 15 mm $\times$ 15 mm were cut down from the whole membrane to undergo the WAXD test. The experiments were performed with a 2θ range of 10°–30°, at a scanning rate of 2 °/min and a scanning step of 0.02°. The specific reflections of different crystal forms in the WAXD profiles of *i*PP are as follows: (110) at $2\theta = 14.1^\circ$, (040) at 16.9° , (130) at 18.5° are the principal reflections of the α -crystal form, while (300) at about 15.9° is the principal reflection of the β -crystal form^[36, 37]. The amorphous part is a flat reflection on the profile. Thus, the crystallinity (X_c) and the fraction of β form (K_β) present in each sample can be determined by the following formulas^[38]:

$$X_c = 1 - \frac{A_{\text{amorphous}}}{\Sigma(A_{\text{amorphous}} + A_{\text{crystallization}})} \quad (1)$$

$$K_\beta = \frac{A_{\beta(300)}}{A_{\alpha(110)} + A_{\alpha(040)} + A_{\alpha(111)} + A_{\beta(300)}} \quad (2)$$

where X_c expresses the crystallinity, $A_{\text{amorphous}}$ is the area of the amorphous phase, $A_{\text{crystallization}}$ is the area of the crystallization phase, K_β represents the relative content of β -crystal form, $A_{\alpha(110)}$, $A_{\alpha(040)}$ and $A_{\alpha(111)}$ represent the intensities of (110), (040), and (111) crystal planes of α -crystal, while $A_{\beta(300)}$ represents the intensity of β (300) reflection. Curve-fitting software was used to calculate the peak intensities of WAXD profiles. The deconvoluted peaks can be obtained by using the mixed function of Gauss and Lorentz.

Crystal structures of the samples were also studied by a TAQ200 differential scanning calorimeter (DSC). The samples were heated from 80 °C to 220 °C in a flowing N₂ atmosphere at a heating rate of 10 K/min.

Mechanical tests were conducted using a Gotech TCS-2000 tensile tester to study the static mechanical properties of the fibrous membranes. At least five specimens with length of 50 mm and width of 10 mm were prepared for each sample. The testing rate was 50 mm/min.

RESULTS AND DISCUSSION

Morphology of the Electrospun WBG/iPP Fibrous Membranes

Electrospinning has been known as a common method to prepare nonwoven fabric with many applications. The morphologies of the melt electrospun iPP fibers with different WBG contents prepared under different voltages are shown in Fig. 1.

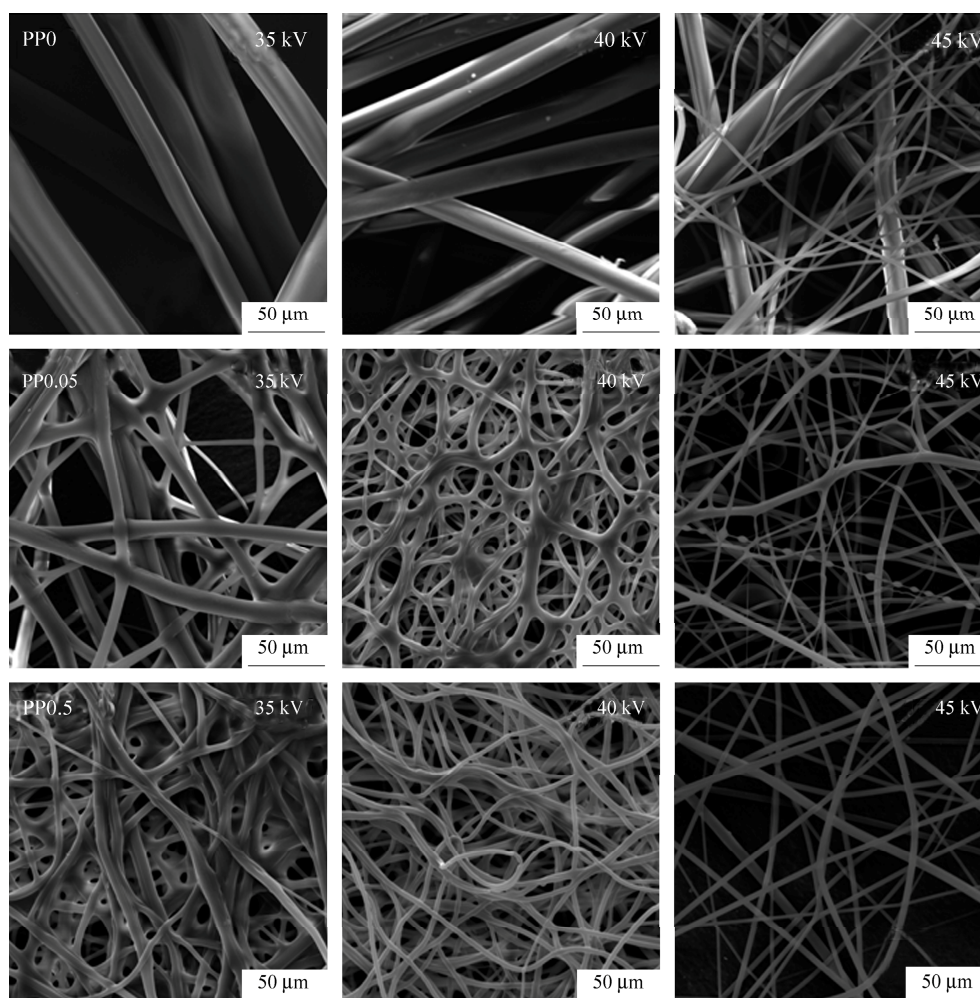


Fig. 1 SEM micrographs of melt electrospun WBG/iPP fibers with different nucleating agent contents prepared under different voltages

It is obvious that the melt electrospun *i*PP fibers are continuous and smooth. The diameter of the fibers depends on the content of WBG and the applied voltage during the electrospinning process. For fibers at a given WBG content, as the applied voltage changes from 35 kV to 45 kV, the diameter of fibers decreases gradually. The changing pattern was also found by Detta in the melt electrospinning of PCL fibers^[39]. It seems that when the applied voltage is 40 kV, the *i*PP fibers exhibit the best uniformity and continuity. During the electrospinning process, when the applied voltage is too low, polymer melt cannot be stretched enough to form fibers with thin diameters, and when the applied voltage is too high, the polymer fibers formed between the cathode and anode suffer strong electrostatic force and whip violently, which is not favorable for the formation of continuous fibers.

Decrease in fiber diameter is more obvious as the content of WBG in fibers increases, indicating good lubricant effect of WBG on *i*PP melt and therefore, fibers with fine diameters can be obtained through adding more WBG. It could be concluded that the addition of WBG in *i*PP results in thinner fibers than pure *i*PP. In Fig. 1, the diameter of pure *i*PP fibers (PP0) ranges from 15 μm to 20 μm , while after the addition of WBG, the diameter of *i*PP fibers is reduced to less than 5 μm .

Furthermore, the elevated electrospinning temperature (265 $^{\circ}\text{C}$) leads to the formation of fuse-bondings among fibers and formed network products. The fused bondings in the network can act as physical crosslinks which will profoundly influence the mechanical properties of the fibrous membrane. The importance of inter-fiber interactions for the mechanical properties of the fibrous network as well as the plastic deformation behavior of the fuse bonding fibers has been highlighted and described through theoretical methods by several groups^[40]. Theoretical analysis indicated that the fuse bonding or the inter-fiber interactions can lead to energy dissipation through plastic deformation. Such fibrous networks are popular in biomaterials for preparation of 3D-scaffolds as well as in clothing.

Crystal Structure of the Electrospun WBG/iPP Fibrous Membranes

Thermal history and crystallization condition are determinable factors for the crystallization of *i*PP. During the electrospinning process, the *i*PP chains are stretched by the electrostatic force in the electric field and therefore form highly ordered structures inside the fibers. Besides, when the polymer melts flow out the spinneret and form fibers, they go through a fast cooling process (from 265 $^{\circ}\text{C}$ to room temperature in seconds), leading to the formation of inner stress in *i*PP fibers.

The crystallization characteristics of the electrospun *i*PP fibers with different WBG contents were investigated by DSC, and the results are shown in Fig. 2. In this work, all sample pieces for DSC tests were cut from almost the same spot of the fibrous membrane of each sample. Since the morphology of pure *i*PP fibers electrospun at voltages of 35 kV and 45 kV are not good enough to be employed for studying the effect of voltage on crystal structures of *i*PP fibers, only the DSC data of pure *i*PP fibers electrospun at 40 kV are provided in Fig. 2(a). In Fig. 2(a), on the DSC curve of pure *i*PP fibers electrospun at voltage of 40 kV, only α -crystal form of *i*PP can be found and there is no melting peak of β -crystal form. While in Figs. 2(b), 2(c) and 2(d), β -crystal form melting peak shows up besides α -crystal form. At the same time, with increasing the voltage in the electrospinning process, the content of β -crystal form first increases and then decreases. We suggest that the external electric force is the dominate factor that determine the crystal structure of the fibers, and the stretching force at voltages of 40 kV is suitable for the formation of β -crystal form in the fibers, while the stretching force at voltages of 35 kV and 45 kV are too weak or too strong to form β -crystal form. Too weak or too strong voltage will result in weakened control on the ordered β -crystal structure due to the unstable whipping of the fibers, which can be proved by the morphology of the fibers in Fig. 1. Furthermore, in these fibers, polymer chains are stretched and fast quenched in the solidification of polymer melt, which results in the formation of inner stress.

Except the electrospinning voltage, the content of β -nucleating agent also has a great influence on the crystal structure of *i*PP electrospun fibers. Under the same electrospinning voltage, the peak intensity of β -crystal form in Fig. 2 increases with the rise of the content of nucleating agents, indicating the obvious β -nucleation effect of WBG. The above results indicate that when electrospun fibrous products are prepared with targeted mechanical properties, it is very important to balance the effect of nucleating agent and the effect of applied voltage on the final crystal structure of the fibers.

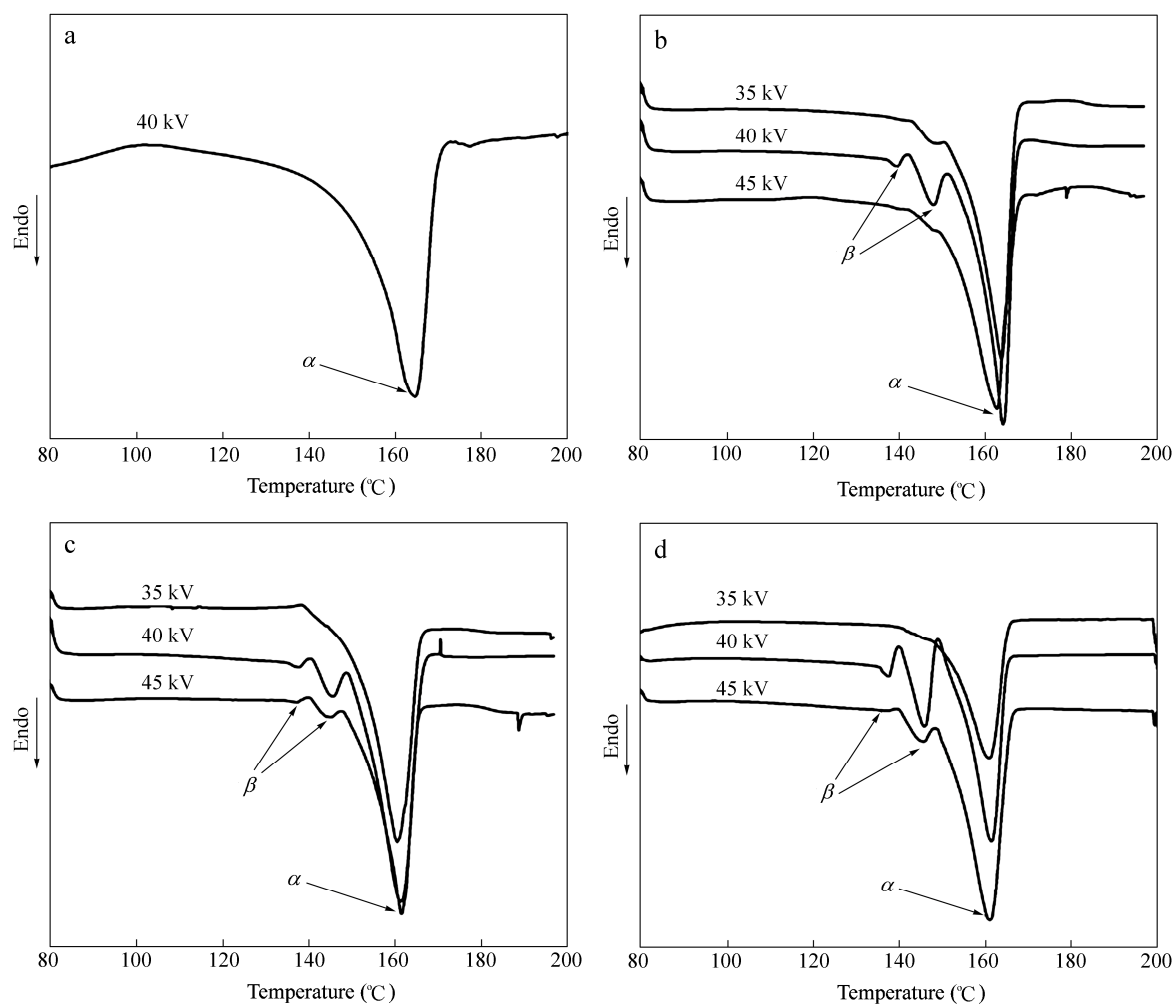


Fig. 2 DSC diagrams of WBG/*i*PP melt electrospun fibers at different applied voltages and different WBG contents (a) 0 wt%, (b) 0.05 wt%, (c) 0.5 wt% and (d) 1.0 wt%

In order to further illustrate the electrospinning process and the addition of β -nucleating agent on the crystal structure of *i*PP electrospun fibers, WAXD was adopted to investigate the variation of the crystallinity (X_c) and the content of β -crystal form (K_β) in *i*PP films and *i*PP fibers. By a comparison of Fig. 3 and Fig. 4, it can be found that, due to the stretching effect, the diffraction peaks of *i*PP electrospun fibers are wider than those of melt-pressed films. The crystallization of *i*PP in the confined fibers (fiber diameter of *ca.* 5 μm) is quite different from that in films (thickness of *ca.* 100 μm). During the electrospinning process, the *i*PP chains were stretched along the fiber axis, the growth of spherulite was restrained, and the ordered crystal structure was seriously deformed.

The variation of X_c and K_β in *i*PP films and *i*PP fibers is shown in Fig. 5. It can be observed that both X_c and K_β of the electrospun fibers and melt-pressed films increase with rise of the content of WBG. However, at identical WBG content, both X_c and K_β of the electrospun fibers are lower than those of melt-pressed films. This can be explained that, in the electrospinning process, the crystallization of polypropylene happens in confined fibers. The fast cooling and strong stretching effect disturbed the arrangement of polymer chains into regular crystal lattices which resulted in imperfect crystal structures in the fibers. While for *i*PP films, the polymer chains crystallized in bulk condition and they had enough time to arrange into crystal lattice thus resulted in perfect crystals. Besides, the addition of β -nucleating agent in *i*PP brought high β -crystal form fraction in the

fibers, which is an attractive factor for preparing *i*PP electrospun fibers with high mechanical performance. In our work, the K_β of the prepared *i*PP melt electrospun fibers is up to 66.2% by adding a highly effective β -nucleating agent.

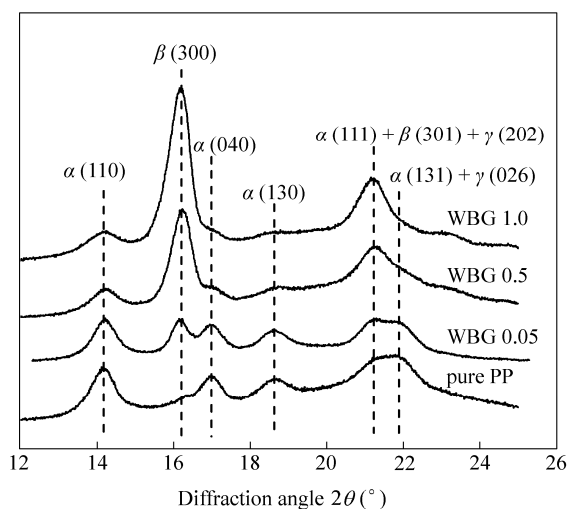


Fig. 3 WAXD patterns of pure *i*PP and WBG/*i*PP electrospun fibers electrospun at 40 kV

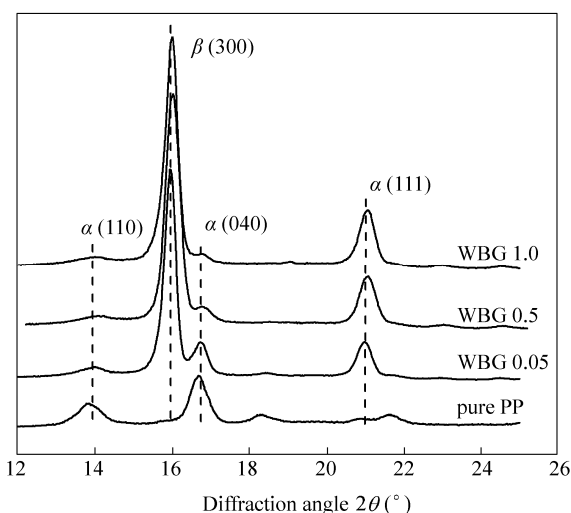


Fig. 4 WAXD patterns of pure *i*PP and WBG/*i*PP films

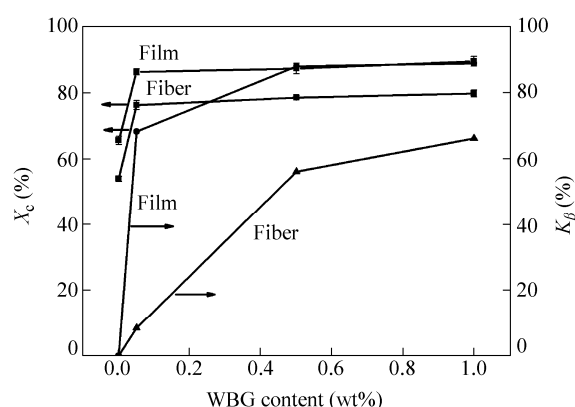


Fig. 5 The variation of the crystallinity and the content of β -crystal form in *i*PP films and *i*PP fibers

Mechanical Properties of the Fibrous Membrane

For crystalline polymers, the crystal structure has great influence on the mechanical properties of polymer products. Generally, higher β -crystal content will endow *i*PP electrospun fibers better toughness and tensile strength. To further illustrate the structure-property relation of polymer and fabricate high performance electrospun fiber materials, the tensile properties of *i*PP fibrous membranes prepared by melt electrospinning are investigated in this work and the results are shown in Fig. 6.

It is apparently shown in Fig. 6 that the tensile strength of *i*PP fibrous membranes increases with increasing the content of WBG content, which is consistent with the changing patterns of X_c and K_β shown in Fig. 5. All the electrospun samples show an obvious yield behavior in Fig. 6, indicating toughness of the fibrous membranes, which is quite different from the CNTs reinforced *i*PP electrospun fibers we reported previously^[14]. For pure *i*PP, the yield is attributed to the amorphous phases ($X_c = 53\%$) which act as bondings between spherulites in *i*PP material, but the effect of amorphous region on the toughness of the material is very limited. For fibrous membranes blended with WBG, the increase in the content of β -crystal form imparts the material improved

toughness, which is proved by the higher deformation of the fibrous membranes. According to the study of Varga^[34], the crystal structure of β -crystal form is composed of sheaf-like spherulites with hedrites formed by clusters of multilayer lamellar crystallites. On the surface of the etched lamellae hexagonal boundaries, they are screw dislocations responsible for the branching and proliferation of lamellae. This is quite different from the structure of α -crystal form with rigid spherulites and clear spherulite boundaries. The special crystal structures of β -crystal explain the improved toughness of WBG/*i*PP fibrous membranes.

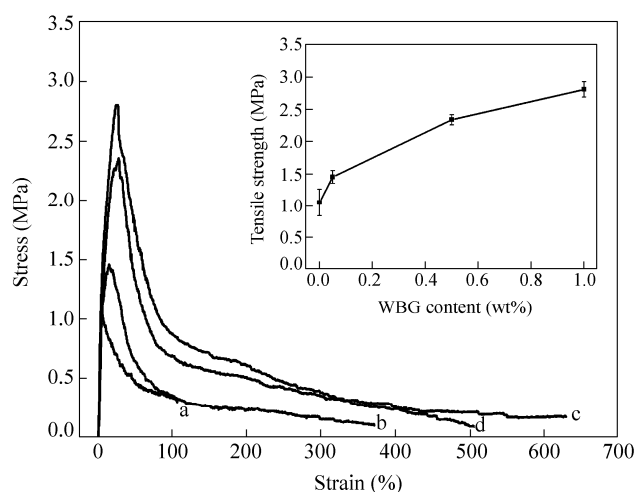


Fig. 6 Mechanical properties of *i*PP electrospun fibrous membranes with different WBG contents (a) 0 wt%, (b) 0.05 wt%, (c) 0.5 wt% and (d) 1.0 wt%

CONCLUSIONS

In this work, WBG/*i*PP fibrous membranes with fused network structure were prepared *via* melt electrospinning. The effect of electrospinning process and rare earth β -nucleating agent (WBG) on the crystal structure, morphology and mechanical properties of the *i*PP fibers were investigated. It was found that the addition of WBG can improve the fluidity of *i*PP melt remarkably and help to form *i*PP fibrous membranes with thinner diameters (less than 5 μ m), while the electrostatic force applied on the *i*PP is not favorable for the formation of β -crystal in *i*PP fibers because the ordered crystal structure was seriously deformed during the electrostatic stretching process. In addition, the tensile strength of *i*PP fibrous membranes increases with increasing the WBG content, which is consistent with the changing patterns of X_c and K_β .

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