

Fabrication and Morphology Development of Isotactic Polypropylene Nanofibers from Isotactic Polypropylene/Polylactide Blends

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ABSTRACT: The excellent characteristics of polymeric nanofibers with diameters less than 1 μm such as the enormous specific surface result in a dramatic increase in a variety of functional applications. In this article, polymer blends of isotactic polypropylene (iPP) and polylactide (PLA) were fabricated through a twin-screw extruder. The extrudates were prepared at various processing conditions and the iPP nanofibers were obtained by removal of the PLA matrix from the drawn samples. The influences of drawing ratio, the processing temperature, and the blend ratio of iPP/PLA on the morphology development of iPP

phase were investigated by scanning electron microscopy. It was found that the uniformed iPP nanofibers with averaged diameters less than 500 nm were fabricated by the suitable processing parameters. Otherwise, the processing immiscibility and rheological behavior of iPP/PLA blends were studied by means of dynamic mechanical analysis and capillary rheometer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2859–2866, 2012

Key words: blends; polyolefin; morphology; nanofiber

INTRODUCTION

Polypropylene (PP) or modified PP fibers have a large range of applications, such as soft tissue replacement, filter media materials, and reinforced composite materials.^{1,2} Despite reports of decreasing the diameters of the PP fibers, such as submicrometer or nanometer, there have been few studies on the production techniques and properties of PP fibers in such small sizes.³ A rapid development of researches on polymer blends has been witnessed during the past decades. Li et al. extensively investigated the morphology, rheological behaviors, and mechanical properties of many kinds of immiscible polymer blends named microfibrillar reinforced composites (MFC) or blends, which were fabricated via a die extrusion, hot stretching, and quenching. These blends included PET/PE,^{4,5} PC/HDPE,⁶ PET/iPP,^{7,8} and PET/HDPE,⁹ which consisted of a thermoplastic polymer as matrix and *in situ* thermoplastic polymer microfibrils as reinforcement. The distinct advantage of this process for microfibrillar

polymer blends is the high efficiency and energy saving since the required equipment is simple and the manipulation is also convenient. Recently, a novel technology of producing submicro or nano-sized thermoplastic fibers was developed through polymer blending method, including choosing two kinds of immiscible thermoplastic polymer, melt blending by a corotating twin-screw extruder, and removing the matrix phase and then nanofibers can be obtained at last.^{10–12} This method offers a good opportunity to prepare nanofibers of various kinds of thermoplastic polyolefins or polyesters, which cannot be made by traditional polymerization. Moreover, it has obvious predominance of high productivity, versatility of thermoplastics, controllability, and environmental friendliness in manufacturing thermoplastic fibers in the sub-micrometer to nanometer scope.

It is well known that Polylactide (PLA), a biodegradable polymer, which can also be produced from annually renewable resources has gained recently a growing attention, especially in environmental and biomedical uses.^{13,14} To modify various properties or to reduce the cost, many researches on PLA blends with other polymers have been carried out.¹⁵ Moreover, PLA has been reported to be not compatible with a wide variety of polyolefin resins, such as PE, PCL, and PBS.^{16–18} The miscibility, phase behavior, crystallization, and mechanical properties of PLA blends have been investigated in detail. Recently, Reddy et al. blended iPP and PLA to produce

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conjugated yarns with various blend ratios, researching the effort of composition ratio on the resistance to hydrolysis and biodegradation.¹⁹ However, the iPP/PLA blends have not been thoroughly analyzed, especially the morphology of iPP dispersed phase from iPP/PLA blends.

It is of great importance to know the morphology development of dispersed phase with different processing conditions, and then control them to meet our needs. There are many factors affecting the morphology of microfibrils in the blends, which include compatibility of components, viscosity ratio, drawing ratio, and blend ratio. This article focused on fabricating iPP nanofibers through the iPP/PLA blends and improving the processing parameters. Then the well-defined iPP nanofibers were prepared successfully by extrusion and subsequent drawing of blends and removing the PLA matrix. The morphologies of the iPP dispersed phase in various processing conditions were characterized. The miscibility and phase behavior of iPP/PLA blends were also studied.

EXPERIMENTAL

Materials

The resins used in this study include iPP and PLA. The iPP (Model Y2600T) is supplied by Shanghai Petrochemical Co., China. Its melt flow index (MFI) is about 20–30 g/10 min (230°C, 2.16 kg), and the particle diameter is 3 mm. The PLA (Model 2002D, NatureWorks Co.), was specifically designed for extrusion/thermoforming applications. Its residual monomer content is less than 0.3 wt %, and MFI is 4–8 g/10min (190°C, 2.16 kg).

Sample preparation

To avoid hydrolytic degradation, the PLA was dried under vacuum oven at 80°C for at least 12 h before processing. The iPP/PLA blends were prepared by melt extrusion using a corotating twin-screw extruder (EUROLAB16, $D = 16\text{mm}$, $L/D = 40$, Thermo-Haake Co., Germany). The procedures are briefly described as below: The mixtures of iPP and PLA were gravimetrically fed into the extruder and then were extruded through a die (4 mm in diameter). The extrudates were drawn at the die exit by a take-up device with two pinching rolls to facilitate the formation of the microfibrillar blends.

In the study of the effect of drawing ratio, the iPP pellets were mixed with the dried PLA slices in a constant mass ratio of 20/80 (iPP/PLA) and at an identical processing temperature of 190°C and the screw rotation was maintained at 80 r/min. By changing the drawing speed, extrudates with vari-

ous draw ratios of 4, 7, 16, and 64 (the area of the transverse section of the die to that of the extrudates) were obtained. In the study of the influence of blend ratio, the iPP/PLA extrudates with appropriate blend ratios ranging from 5/95 to 30/70 were prepared at the same shear and elongated rate. In the study of the influence of processing temperature, iPP was mixed with PLA at the same screw speed of 80 r/min, the same drawing ratio of 16, constant mass ratio of 20/80, but different processing temperatures at 190, 200, 210, 220, and 230°C respectively.

Characterization and measurement

Dynamic Mechanical Analysis (DMA) was carried out with a DMA Q800 (TA Corp.) in the three-point bending mode. The dynamic loss ($\tan \delta$) and storage modulus (E') of iPP/PLA blends were determined at a frequency of 1 Hz and a heating rate of 3°C/min as a function of temperature from –100 to 150°C.

The apparent shear viscosities were measured by Advanced Capillary Rheometer (Model Instron 4467, Instron Corp.), which has a single barrel and capillary. The diameter of capillary die is 0.5 mm and the length/diameter ratio of capillary was 40 : 1. The barrel was preheated to the set temperature before loading. The whole process was under the different temperatures which match the various processing conditions.

The iPP/PLA extrudates prepared from melt extrusion were cut into small pieces and packed into the metallic netting and then underwent Soxhlet extraction in boiling chloroform for 2 h to remove the PLA matrix from the blends. In addition, some other extrudates were kept in liquid nitrogen and then quickly broken up. The fracture surface was used for Morphology observation. All the samples were sputtered with conductive gold, and then observed at a Scanning Electron Microscope (SEM, Mode S-3000). One hundred iPP nanofibers in the extrudates were measured to get the averaged diameters. And the number averaged diameters were calculated as follows:

$$D_N = \frac{\sum N_i D_i}{\sum N_i}$$

Where D_N is the number averaged diameter, N_i is the number of microfibrils or droplets with a diameter of D_i .

RESULTS AND DISCUSSION

Miscibility of iPP/PLA blends

The formation of microfibrils is based on the degree of incompatibility between matrix and dispersed

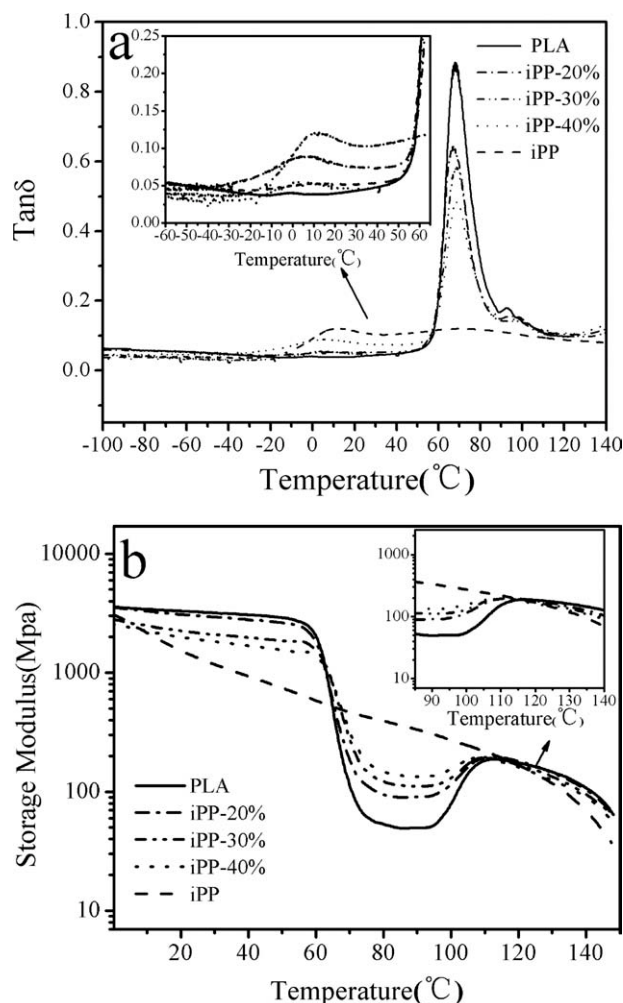


Figure 1 Dynamic viscoelastic curves for the iPP/PLA blends: (a) $\tan \delta$ versus temperature curves, (b) storage modulus versus temperature curves.

phase, and incompatible polymers will be phase separated when mixed together.⁹ PLA and PP polymers are said to have poor compatibility.¹⁹ Figure 1 showed the dynamic viscoelastic curves for neat iPP, neat PLA, and iPP/PLA blends. In Figure 1(a), the glass transition temperatures (T_g) were calculated from the $\tan \delta$ peak temperature. As observed from the $\tan \delta$ curves, all of the blends showed two glass transitions, one for iPP at about 0°C and the other for PLA at about 68°C, indicating that the blends were not thermodynamically miscible.²⁰

The storage modulus (E') for iPP/PLA blends gradually decreased with increasing content of iPP. In Figure 1(b), the E' of neat PLA dropped abruptly, at about 60°C, due to the glass transition, and then rose at around 110°C because of the cold crystallization of PLA.^{21,22} The values of E' started to increase, due to the crystallization of the PLA component, and shifted to a lower degree with the addition of iPP. This result suggested that the incorporation of iPP enhanced the cold-crystallization ability of PLA

and therefore decreased the temperature of PLA in the blends.¹⁵

Moreover, Figure 2 gave the SEM images of fracture surface for the iPP/PLA blends with kinds of blend ratios. All these SEM images exhibited a clearly phase-separated morphology with iPP dispersed in the PLA matrix. This phase-separated structure of the blends was in agreement with the two T_g s obtained from the DMA measurements.²³

Rheological behavior of iPP/PLA blends

The performance of immiscible polymer blends not only depends on properties of the polymer pairs used but also highly depends on the morphology, which change significantly during processing. To optimize final properties of this blend material, good insight into the relation between the morphology development and rheological response is essential.^{6,17,24}

It is very important to explore the rheological properties of the immiscible iPP/PLA blend. The melt flow behaviors of iPP and PLA were shown in Figure 3. On increasing the apparent shear rate, the apparent shear viscosity decreased. Otherwise, the viscosities of these two materials were temperature sensitive. With increasing temperature, the apparent shear viscosity decreased.²⁵ For iPP, the apparent shear viscosity changed slightly. Furthermore, at the identical temperature, for example at 190°C, the viscosity of iPP was higher than that of PLA. This phenomenon implied that the viscosity ratios of iPP to PLA might vary accordingly with the change of viscosity at different temperatures.

It is well known that viscosity ratios (η_d/η_m , η_d is the viscosity of the dispersed phase, η_m is the viscosity of the matrix phase) played an important role on the deformation of the dispersed phase, and subsequently affected the morphology of microfibrils.⁹ Researches indicated that good fibrillation can be achieved when the viscosity ratio in the range of $0.1 < \eta_d/\eta_m < 10$. To investigate the variation of viscosity ratio, the apparent shear viscosity ratio of iPP to PLA versus apparent shear rate at 190, 200, 210, 220, and 230°C were shown in Figure 4 and the similar conclusion was obtained in this research. The viscosity ratios of iPP to PLA at different temperatures ranged from 1.0 to 5.0. Furthermore, it can be seen that the viscosity ratios were close to one at 190 and 200°C in the range of experiment shear rate. When the temperature increased to 230°C, the viscosity ratio was higher than those at low temperatures.

Morphology development of iPP nanofibers

The highly elongated morphology of the dispersed phase obtained after melt blending and extrusion can be considered as an overall result of breakup,

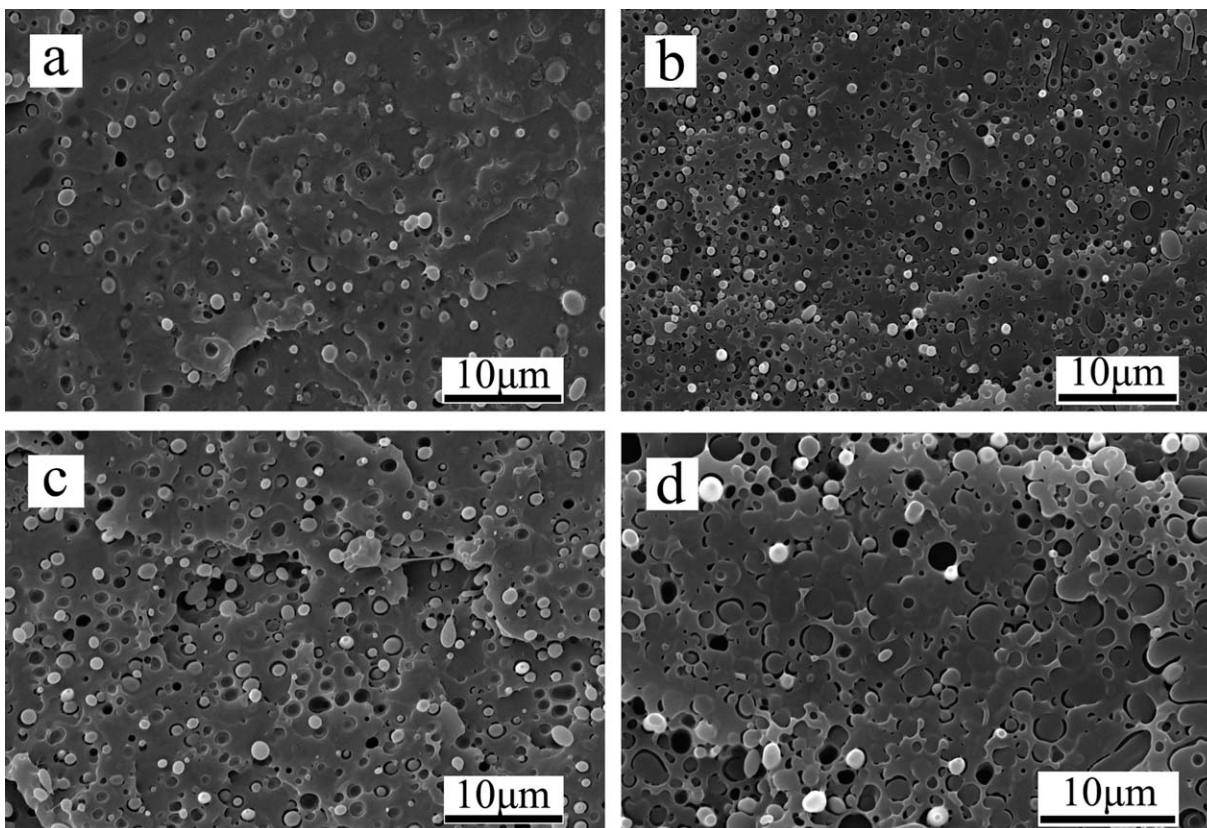


Figure 2 Fracture surface of iPP/PLA samples with various blending ratios (w/w):(a)5/95, (b)10/90, (c) 20/80, and (d)30/70.

single particle deformation and coalescence of the dispersed phase in the matrix. It is generally believed that the main factors influencing the morphology development of dispersed phase would be composition ratio, viscosity ratio (η_d/η_m), and processing parameters.^{11,25,26} This work will demonstrate the systematic investigation that provides clear evidence of the morphology evolution of iPP phase in the immiscible iPP/PLA blends and understanding of the influences of these factors.

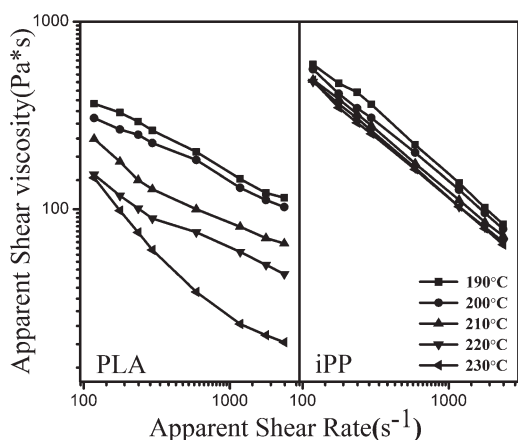


Figure 3 Apparent shear viscosity of PLA and iPP versus apparent shear rate at 190, 200, 210, 220, and 230°C.

Effect of drawing ratio on the morphology of iPP nanofibers

It is well known that during shear flow, molecule chains will disentangle and orient along the flow direction, which results in less energy required for flow of the molecules.^{8,11} It is predicted that when the melt flow of iPP/PLA blends through the

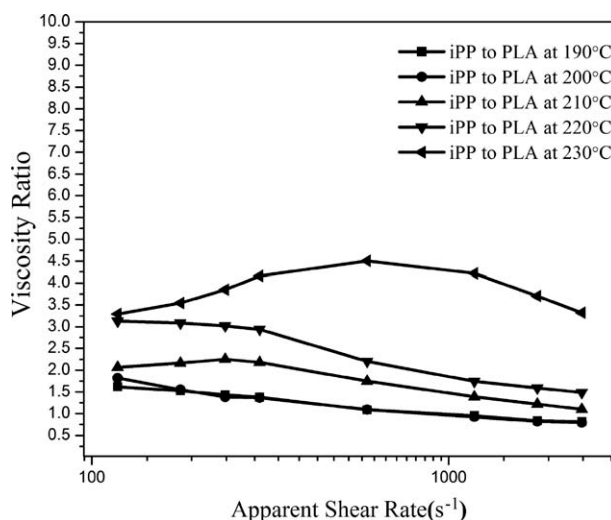


Figure 4 Apparent shear viscosity ratio of iPP to PLA versus apparent shear rate at 190, 200, 210, 220, and 230°C.

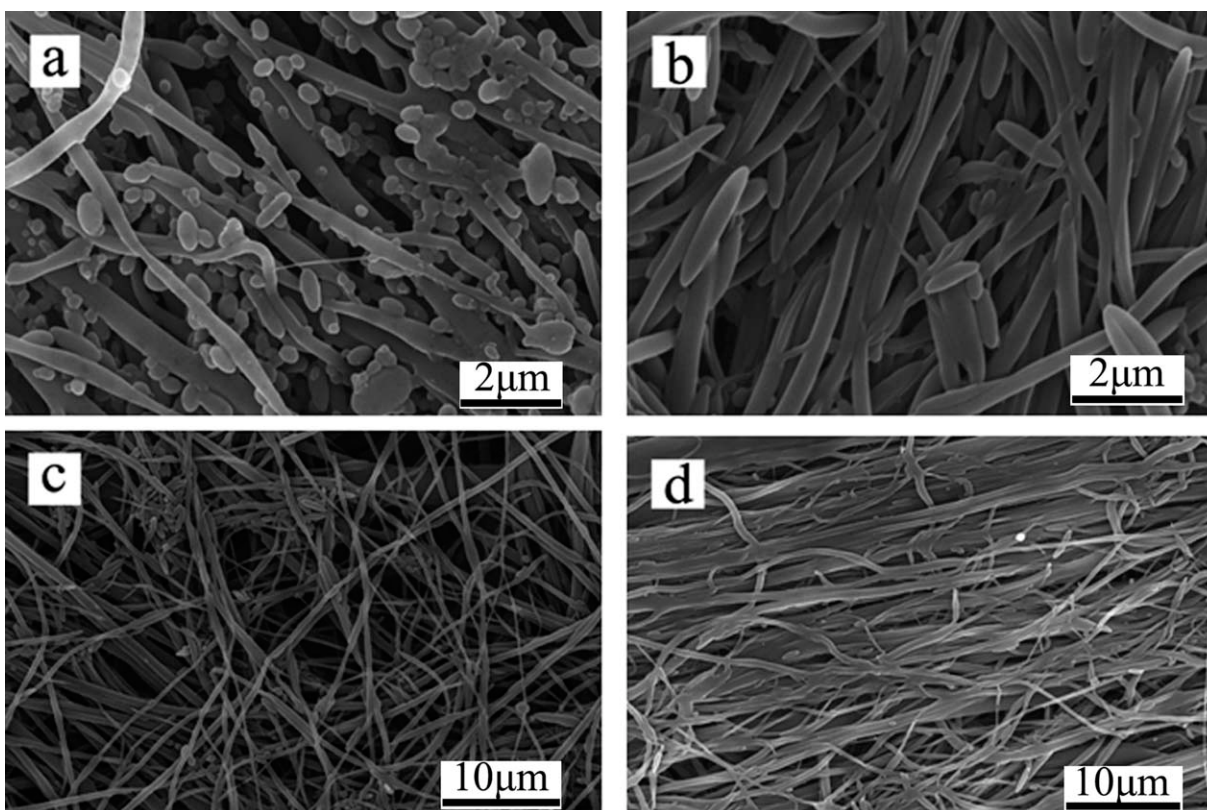


Figure 5 iPP nanofibers extracted from extrudates (iPP/PLA = 20/80) with drawing ratios of (a) 4, (b) 7, (c) 16, and (d) 64.

entrance of the rodlike die during the extrusion, the melt would undergo the elongation flow field because of the convergence effect at the entrance. Thus, the elongation flow field would be of great importance to the morphology development.

SEM images of iPP nanofibers obtained after removal of PLA matrix from the extrudates were shown in Figure 5. It can be seen that iPP existed mainly in the form of fibers and spheres when the drawing ratio was 4 in Figure 5(a). And then it should be noted that more ends and elongated ellipsoids can be observed from the iPP nanofibers with drawing ratio of 7 in Figure 5(b). When the drawing ratio was increased to 16 or 64, uniform iPP nanofibers with average diameters of about one to several hundred nanometers were observed from the samples in Figure 5(c,d), almost without the presence of spheres or elongated ellipsoids. Thus, the difference in the diameters of the iPP dispersed phase could be minimized during elongation and deformation process and higher drawing ratio resulted in iPP nanofibers becoming smaller and more uniform in diameter.

Effect of processing temperature on the morphology of iPP nanofibers

Figure 6 displayed the morphology of iPP dispersed phase prepared after removing the PLA matrix of

blends with different processing temperatures. With the increase of the processing temperature to 230°C, lots of microspheres or elliptical spheres could be observed in Figure 6(e), whereas the continuous iPP nanofibers were fabricated during the processing temperature ranged from 200 to 220°C, which were shown in Figure 6(b,c, and d).

To study the morphology development of iPP dispersed phase accompanied with various processing temperatures intensively, the average diameters and distributions of iPP phase were shown in Figure 7. The standard deviations for the averaged diameters at different processing temperatures from 190 to 230°C were 0.1082, 0.09897, 0.09767, 0.08768, and 0.08336 respectively. As a whole, increasing the processing temperature resulted in iPP nanofibers becoming smaller and more uniform in diameter distribution. It can be seen that when the processing temperatures were 190 and 200°C, the iPP nanofibers obtained had broader diameter distributions ranging from 200 to 1000 nm, as well as the larger number average diameter of 429 and 411 nm in Figure 7(a,b). Although the diameter distributions were narrowed to a range of 100–800 nm and the number average diameters were reduced to 339 or 308 nm with an increase in the temperatures from 210 to 220°C, shown in Figure 7(c,d). Otherwise, the narrowest diameter distribution of the iPP nanofibers from 200

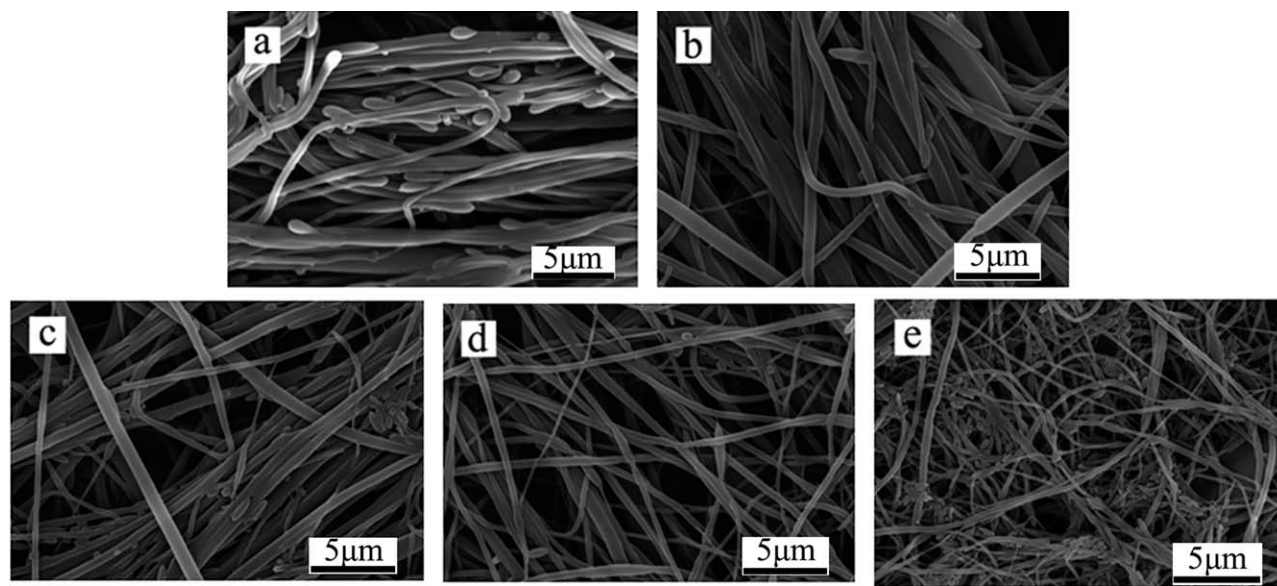


Figure 6 iPP nanofibers extracted from extrudates (iPP/PLA = 20/80) with different processing temperatures of (a) 190, (b) 200, (c) 210, (d) 220, and (e) 230°C.

to 650 nm and the smallest average diameter of 296 nm were occurred at 230°C, observed in Figure 7(e), but 230°C was not an appropriate processing temperature to fabricate continuous iPP nanofibers because of so many microspheres or elliptical spheres. It is indicated that suitable processing temperatures had positive effect to decrease the distributions and average number diameters of iPP nanofib-

ers, since they affected the rheological behaviors of iPP and PLA in the blends.²⁷

Effect of blend ratio on the morphology of the iPP nanofibers

The blend ratio of immiscible polymer blends, such as iPP/CAB,^{11,12} PCL/PLA,¹⁷ and LDPE/CAB,²⁸

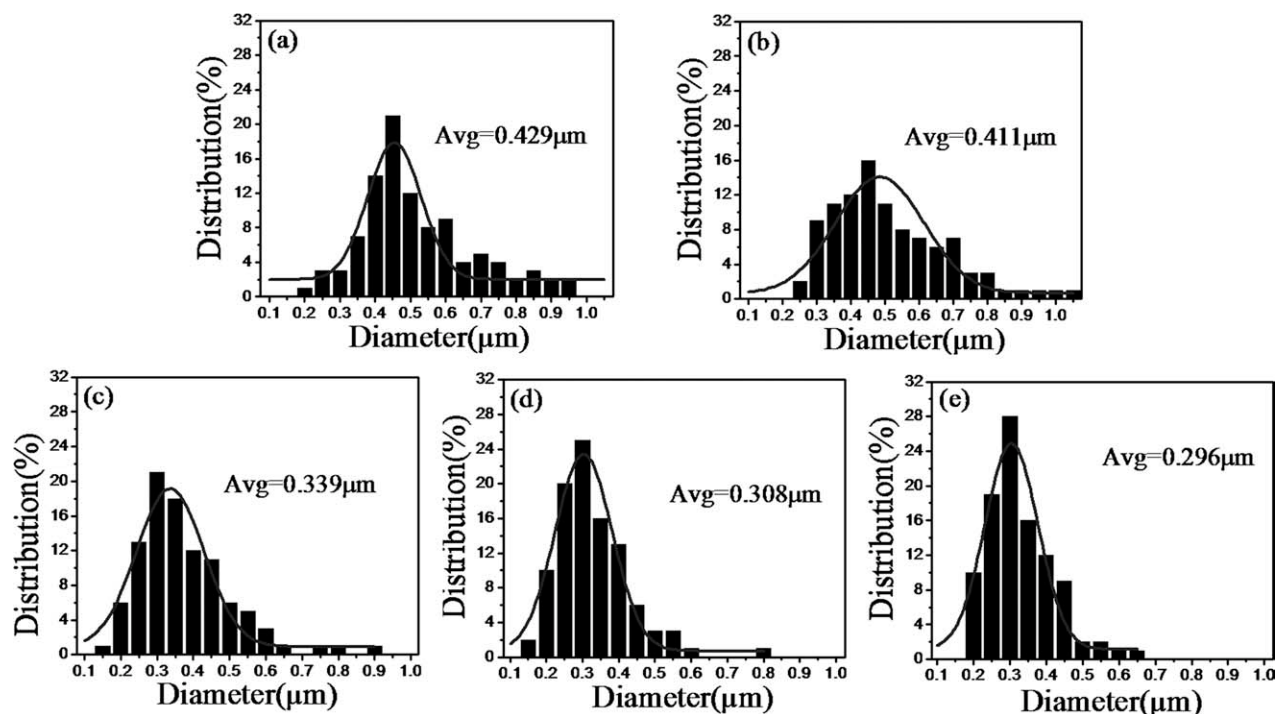


Figure 7 Diameter distributions of iPP nanofibers prepared from removing the PLA matrix of iPP/PLA = 20/80 with different processing temperatures at (a) 190, (b) 200, (c) 210, (d) 220 and (e) 230°C.

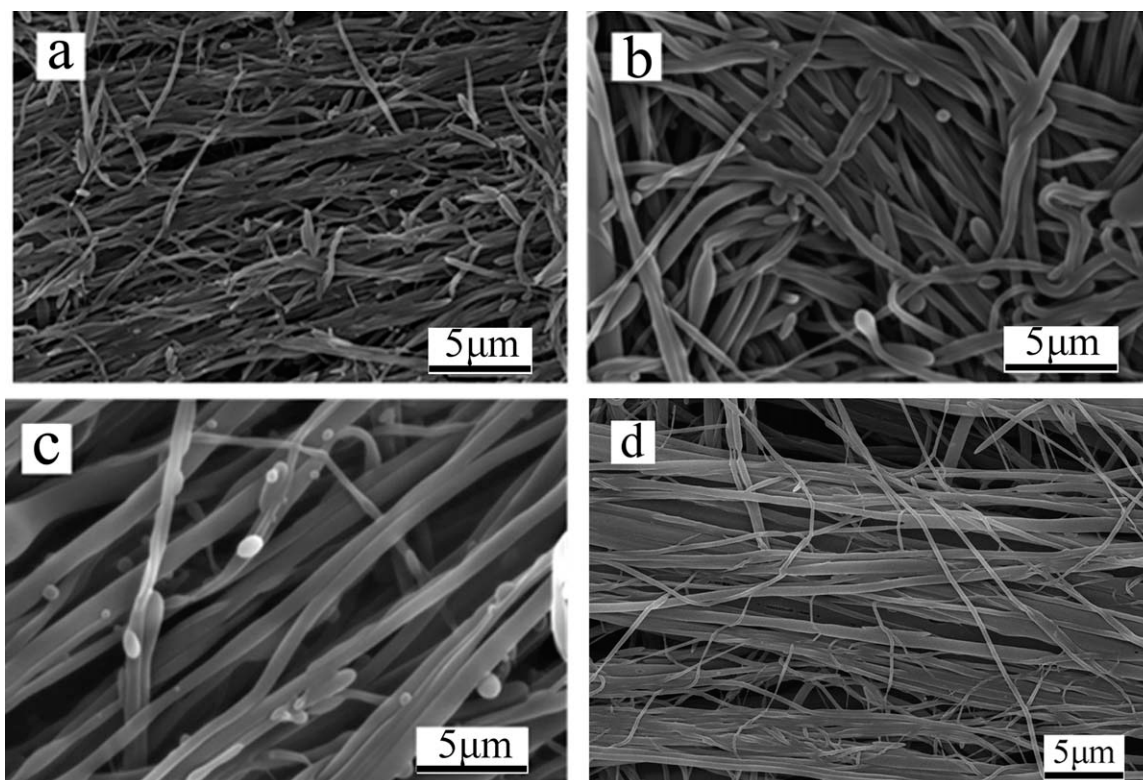


Figure 8 iPP nanofibers extracted from extrudates (iPP/PLA) at different blend ratios: (a) 5/95, (b) 10/90, (c) 20/80, and (d) 30/70.

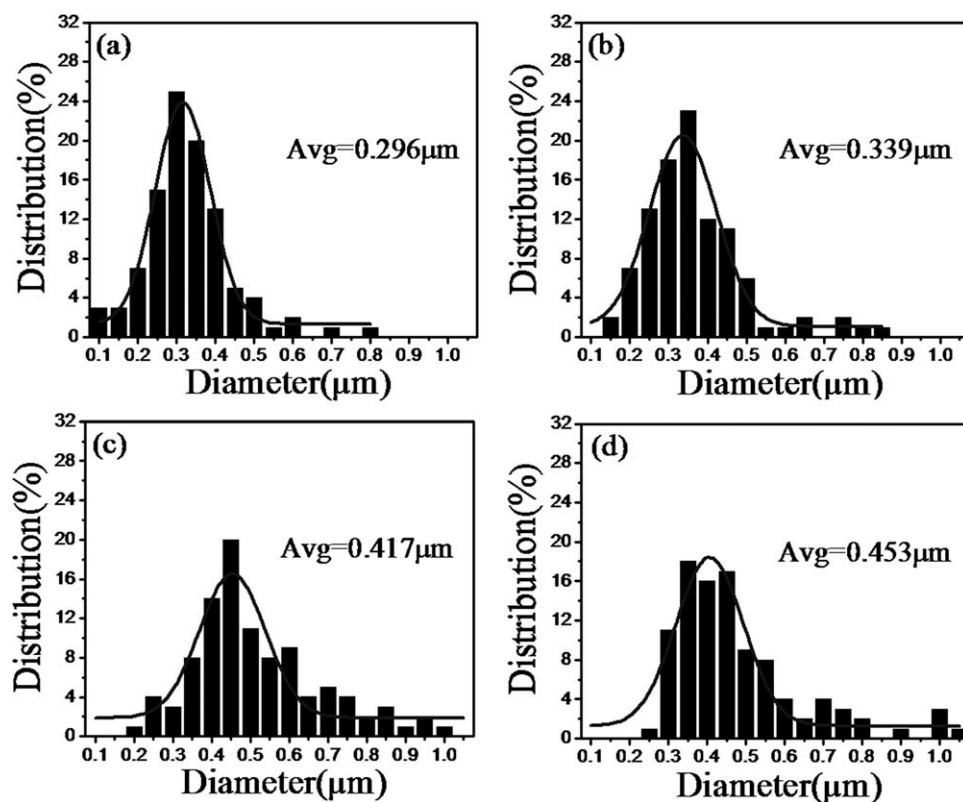


Figure 9 Diameter distributions of iPP nanofibers prepared from removing the PLA matrix of iPP/PLA with blend ratios of (a) 5/95, (b) 10/90, (c) 20/80, and (d) 30/70.

plays an important role in determining the morphological structure of blends and possibly in controlling the sizes of the formed dispersed phase microfibrils. Thus, the SEM photographs of iPP nanofibers were shown in Figure 8.

On the whole, however, only when the amount of iPP was fewer than 30% in the blends did the iPP dispersed phase start to form microfibrils after extrusion. This phenomenon was a reflection of iPP dispersed phase in the matrix PLA system. It might be due to the fact that the larger amount of PLA matrix reduces the possibility of coalescence of elongated iPP ellipsoids.^{11,12} Moreover, the bundles of iPP nanofibers were obtained when the blend ratio reached 30/70, shown in Figure 8(d). The fibers became very tight somewhat like cords or sheets. On one hand, this could be due to the result that the dispersed phase was easy to be propelled by the matrix because of their immiscibility. On the other hand, the value of the viscosity ratio of iPP to PLA had a slightly higher than one, resulting in parallel coalescence of fibers.²⁵

The diameter distributions of iPP nanofibers became narrower and the averaged diameters decreased from 453 to 296 nm, measured in Figure 9. The standard deviations for the averaged diameters at various iPP contents in blends from 5 to 30% were 0.08468, 0.09152, 0.09841, and 0.1104 respectively. These results clearly revealed that the diameters of iPP nanofibers in the PLA matrix could be well controlled by the composition ratio.

CONCLUSIONS

In this study, iPP nanofibers with averaged diameters less than 500 nm were successfully fabricated by blending iPP with PLA in a corotating twin-screw extruder, melt extruding the immiscible blends through a rodlike die, drawing the extrudates through the die, and then selectively removing the PLA matrix from the extrudates. It was clearly revealed that the morphologies of iPP nanofibers could be well controlled by the suitable processing conditions including the drawing ratio (16–64), the processing temperature (190–230°C), and the composition ratio of iPP/PLA blends (5/95–30/70). However, high degree of deformation induced from exceedingly high drawing ratio or blend ratio or processing temperature may facilitate the coales-

cence of elongated ellipsoids or continuous nanofibers.

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