

Study of Poly(ethylene terephthalate)/Polypropylene Microfibrillar Composites. I. Morphological Development in Melt Extrusion

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ABSTRACT: Poly(ethylene terephthalate)/polypropylene (PET/PP) blends of different compositions were extruded through a 2-mm capillary die using a corotating twin-screw extruder. The extrudates were cryogenically fractured and examined using scanning electron microscopy. The viscosity ratio of the constituent polymers alone was found to be unsuitable for explaining the polymer blend morphology. At a PET concentration of 20%, the extrudate consists of three regions. The skin layer, which is about 10 μm thick, has a lower concentration of the dispersed PET phase than the overall concentration. The intermediate region, which is about 400 μm thick, has profuse PET fibers and some small PET particles. The central region, which is approximately 800 μm in diameter, mainly contains PET particles that are generally bigger. A low barrel temperature, low die temper-

ature, and fast cooling rate helped to retain the fibers near the extrudate skin. Meanwhile, the variation of the barrel temperature, die temperature, and cooling media did not produce a significant affect on the PET particle size distribution in the central region of the extrudate. A high screw speed and a high postextrusion drawing speed were very effective in producing fibers in the extrudates through elongation of particles. At a PET concentration of 30%, coalescence of the PET phase was prevalent, leading to the formation of PET platelets near the extrudate skin and irregular PET networks in the central region of the extrudate. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1743–1752, 2003

Key words: composites; melt extrusion; morphology

INTRODUCTION

Morphology plays an important role in the mechanical properties of a polymer blend. A high degree of molecular orientation of the reinforcing polymer is essential in high performance polymer alloys. In an extrusion process, the development of the blend morphology depends not only on the intrinsic properties of the constituent polymers but also on the extrinsic factors such as the melt flow rheology through the die, the speed of postextrusion drawing, and the rate of cooling of the extrudate. In the development of so-called molecular composites, liquid crystalline polymers (LCPs) have been studied extensively because of their intrinsic ability to form fibrils in melt processing.^{1–9} However, LCPs are too expensive for general engineering applications. On the other hand, there are considerable supplies of poly(ethylene terephthalate) (PET) and polypropylene (PP) in the form of postconsumer scraps. These wastestreams of PET and PP

could be a low cost source of raw materials for forming polymer blends.

Unlike LCPs, the molecules of common thermoplastics relax rapidly during melt processing; therefore, a high degree of molecular orientation is difficult to achieve. By adding 18–22% PET to PP, Spreeuwiers and van der Pol¹⁰ produced a blend (AP-28) of fine PET fibers in a PP matrix, and it has an extraordinarily high tensile strength. Probably because of processing requirements, AP-28 is only produced in fiber or ribbon form. There is little information about its ability to undergo conventional molding processes into other forms of products. More recently, work has been reported on PET/polyamide-6 microfibrillar composites.^{11–13} The polymer fibrils are created by drawing the polymer blend. This leads to the orientation or fibrillization of both components, followed by melting or isotropization of the lower melting component and preservation of the oriented microfibrillar structure of the higher melting component.

We are presently engaged in a study on the development of a PET/PP microfibrillar composite that can be processed by conventional molding methods. The ultimate objective is to develop a technology for recycling PET and PP. In this study, the virgin polymers are blended in a twin-screw extruder to produce an extrudate with fibrous PET domains in a PP matrix. Subsequently, the extrudate is drawn in a solid state,

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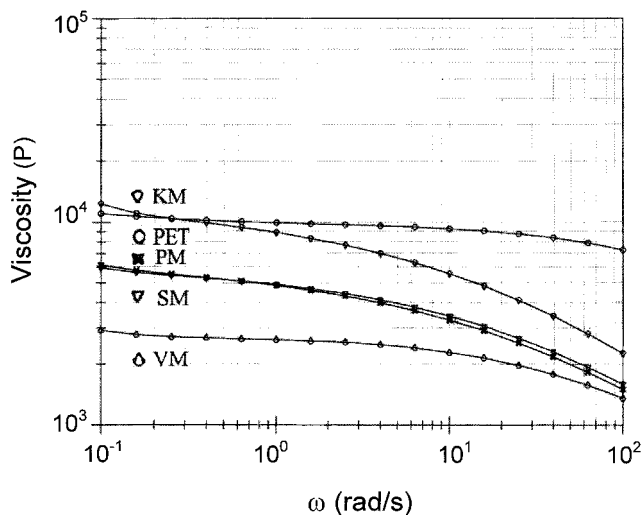


Figure 1 The effect of the angular velocity of the stress rheometer on the dynamic viscosity of PET and PP resins (KM, PM, SM, and VM) at a testing temperature of 270°C.

either at room temperature or an elevated temperature, to further enhance the molecular orientation of the PET fibers to give a microfibrillar composite. Eventually, the processability of the composite by conventional molding methods at a temperature above the melting point of PP but below that of PET is assessed. This article outlines the results on the morphological development of the PET/PP blends in melt extrusion.

EXPERIMENTAL

Materials and processing

The isotactic PP resins that were used were Shell KM6100 (KM), PM6100 (PM), SM6100 (SM), and VM6100 (VM) in granule form. Their melt flow indexes as provided by the manufacturer are 3.0, 5.5, 11, and 22, respectively. The PET resin was Arnite D04 300, a medium-viscosity extrusion grade. The blending process was carried out in a Prism corotating twin-screw extruder. It has a screw diameter of 16 mm and a length/diameter (L/D) ratio of 25. The capillary

die has a diameter of 2 mm and a length of 10 mm. Before blending, the PET resin was dried in an oven at 120°C for 4 h. It was then manually mixed with a predetermined amount of PP and fed into the extruder. There are four temperature control zones (T_1 , T_2 , T_3 , and T_4) along the barrel with T_1 next to the hopper and T_4 next to the die. After some preliminary trials, a basic set of extrusion parameters was determined as follows: zone T_1 was 160°C, T_2 was 220°C, T_3 and T_4 were 270°C, the die temperature was 270°C, the screw rotational speed was 50 rpm, and the postextrusion drawing speed was 15 m/min. The extrudate was cooled in a water bath at room temperature. To study the effect of a given extrusion parameter on the morphology of the extrudate, the parameter was changed while other parameters were kept at the basic setting.

Viscosity measurement

The dynamic viscosities of the polymers were measured by a Rheometrics dynamic stress rheometer (SR-200) as a function of the frequency at 270°C in nitrogen. The experiments were performed at a strain of 5% and the gap between the parallel plates was 1 mm.

Scanning electron microscopy

The morphology of the PET/PP extrudates was studied with a Cambridge S440 scanning electron microscope. The composite extrudates were cryogenically fractured by simple bending to give a cross-sectional view or by splitting to give a longitudinal view. The fracture surfaces were sputtered with a layer of gold-palladium before examination.

Measurement of PET fiber diameter and particle size

The diameters of the PET fibers within the extrudates were measured from the scanning electron microscopy micrographs. More than 200 measurements were taken for a given sample. The fibers were graded and

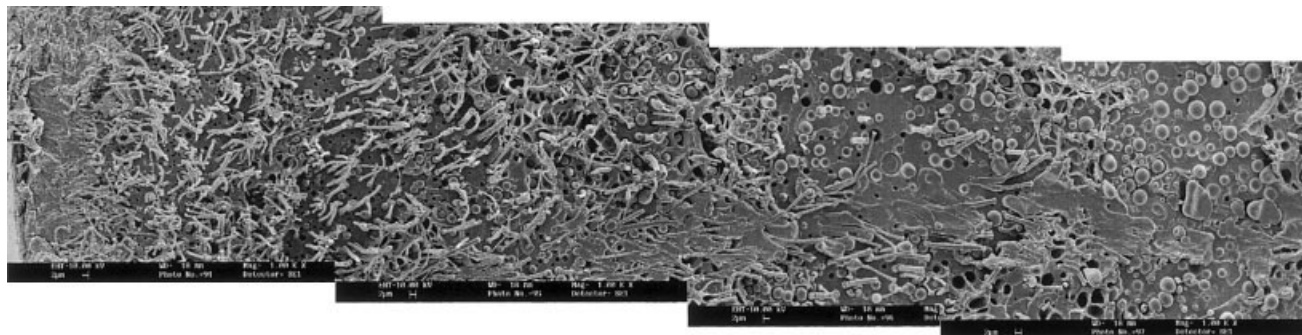


Figure 2 A cryogenically fractured cross section of a PET/VM(20/80) extrudate showing PET fibers near the skin (left) and PET particles in the central region (right).

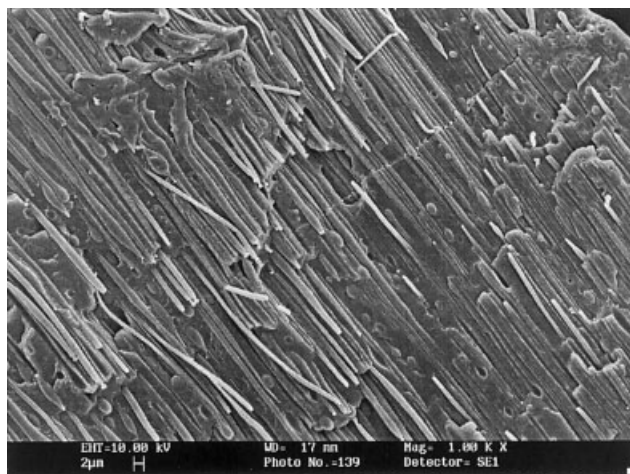


Figure 3 A longitudinal section near the skin of a PET/VM (20/80) extrudate prepared under the basic extrusion setting.

then the ratio between the number of a certain grade (N_i) and the total number (N) of measurements was plotted against the fiber diameter to give a diameter distribution graph. Similarly, diameter distribution graphs were also obtained for PET particles within the extrudates.

RESULTS AND DISCUSSION

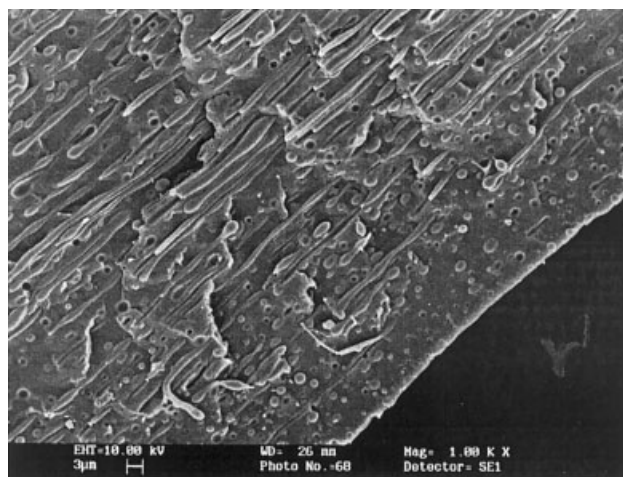
Effect of viscosity ratio

It has been reported that the dispersed phase is more likely to form fibers during extrusion when the viscosity ratio (viscosity of dispersed phase/viscosity of matrix polymer) is close to unity.^{14,15} Figure 1 shows the curves of the dynamic viscosity versus the frequency of the polymers. The viscosity ratio of PET/KM is closer to unity than those of the other blend pairs within the tested range of angular velocities (ω) or "shear rates." At an ω of 10^2 rad/s, the viscosity ratio of PET/KM is approximately 3.7 and that of PET/VM is 6.8. According to Taylor,¹⁶ a drop of fluid with a viscosity that exceeds the viscosity of the suspending fluid by a factor of more than approximately 4 does not become stretched in a simple shear flow, but rather achieves a steady, slightly deformed shape for all large shear rates. This suggests that PET/KM should give a more fibrous morphology than the other blend pairs and PET/VM should be less fibrous. On the contrary, more fibers were observed in the PET/VM blend than any other blends under the basic extrusion setting. Perhaps the viscosity ratio alone is not suitable for explaining the polymer blend morphology.¹⁷

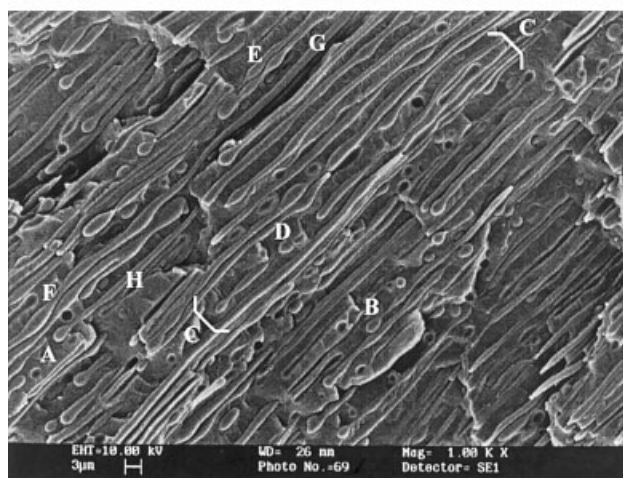
Morphology of PET/VM (20/80) blend

Figure 2 shows the typical view along a radius of the cross section of the PET/VM (20/80) extrudate pre-

pared under the basic extrusion setting. The region near the skin (left) contains many pulled out PET fibers and some small PET particles. However, the number of fibers decreases towards the central region (right) of the extrudate, giving way to some large particles. Figure 3 shows the longitudinal section near the skin of the extrudate. The PET fibers generally have a diameter of about $1 \mu\text{m}$ and their length/diameter ratio is large. There are signs of necking at



(a)



(b)

Figure 4 (a) A longitudinal section of the skin region of a PET/VM (20/80) extrudate; the postextrusion drawing speed is 6 m/min. (b) A longitudinal section near the skin of a PET/VM (20/80) extrudate: Points A and B are the fiber ends breaking away from the main body of the fibers, point C with the bracket is the fiber breaking into several sections simultaneously, point D is the broken fiber section shrinking into a particle, points E and F are neighboring fibers with conformable shapes, and points G and H are the coalescence of fibers. The postextrusion drawing speed is 6 m/min.

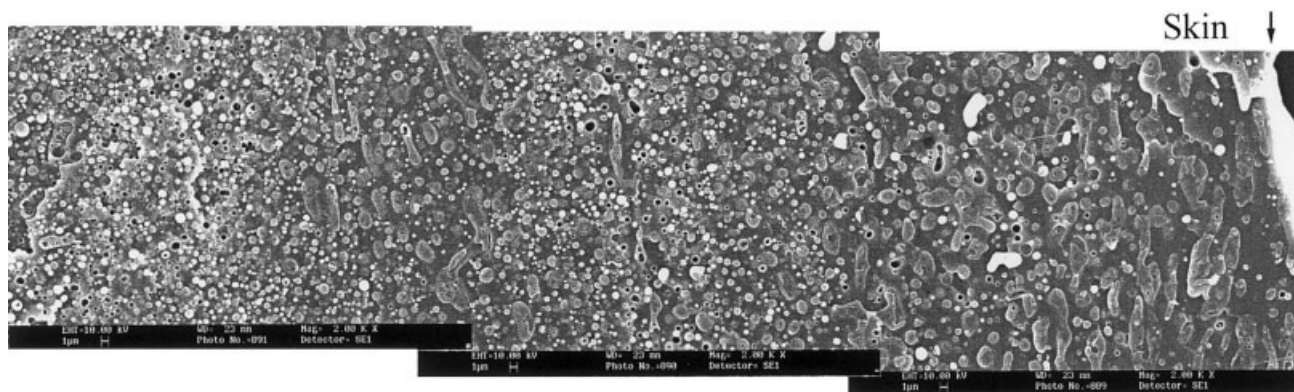


Figure 5 A cross section of a PET/KM (30/70) extrudate: the skin (right) and halfway between the skin and the extrudate center (left).

some of the fiber ends, which are caused during fracture of the extrudate.

Figure 4(a) shows the longitudinal section of another extrudate prepared under very similar conditions except at a lower postextrusion drawing speed of 6 m/min. There is a skin layer, $\sim 10 \mu\text{m}$ thick, with a lower concentration of PET. This is probably a result of migration of the dispersed PET phase toward the low stress in the capillary center.^{18–20} Figure 4(b) shows another region near the skin. The phenomenon of capillary instability is obvious.²¹ The enlarged fiber ends often break away from the main body of the fiber (Fig. 4, points A and B). A fiber may break into several sections simultaneously (Fig. 4, point C with bracket). The broken sections will then shrink into particles under the influence of interfacial tension (Fig. 4, point D). When two fibers are brought very close together, their shapes become conformable with each other (Fig. 4, points E and F) and eventually the neighboring fibers may merge together (Fig. 4, points G and H).

Morphology of PET/KM (30/70) blend

Melt fracture occurred when extruding a blend of 30% PET and 70% KM6100 using the basic extrusion setting. When a die with a diameter of 2 mm and a length of 20 mm was used, the extrudate became smooth. The longer die allowed more time for the deformed PET phase to relax, thus reducing the degree of die swell and eliminating the phenomenon of melt fracture. Chapleau and Favis²² found that a L/D ratio that was too high could not give a fibrous morphology in polycarbonate/PP (5/95) blends because of the back recoil or recovery of the deformed phase.

Figure 5 shows the cross section of a PET/KM (30/70) extrudate from the skin to about halfway toward the center. A layered structure is present. The layer next to the skin, which is approximately $70 \mu\text{m}$ thick, contains large domains of PET with an elongated cross section. These are actually PET platelets with the long

axis along the flow direction. They were formed as a result of coalescence. It was reported that when the minor phase concentration was increased to 20%, coalescence became obvious.²² The PET platelets are approximately parallel to the circumferential direction of the extrudate, suggesting that coalescence tends to occur within layers of constant shear.

Further away from the skin, the elongated cross section of the PET domains gradually gives way to a circular cross section. This implies that most PET domains are now in the form of dispersed fibers or particles. This second layer has a thickness of approximately $60 \mu\text{m}$. There are some holes within this layer, which is an indication of fiber pull-out. The third layer has a morphology similar to the first layer but the thickness is much smaller. It is followed by another fibrous region similar to the second layer. At present, it is not fully understood how such an alternating layered structure developed; nevertheless, it should be related to the flow rheology through the die. Figure 6 shows the central region of the extrudate. Many of the

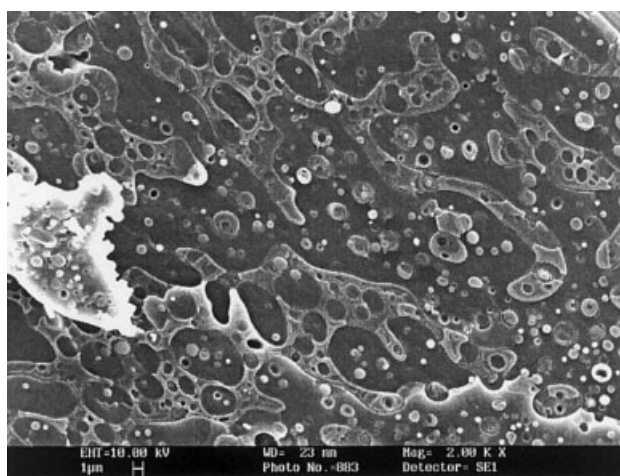


Figure 6 The central region of a PET/KM (30/70) extrudate showing PET networks with entrapped PP fibers.

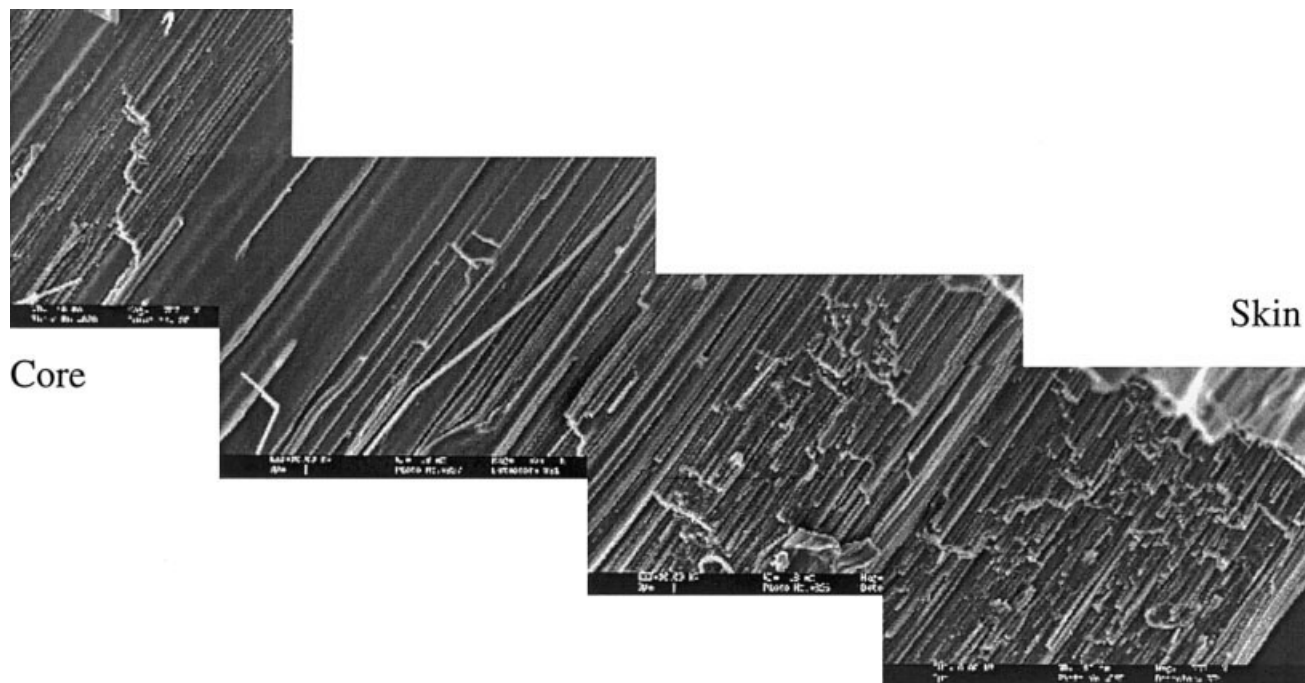


Figure 7 A longitudinal section of a PET/KM (30/70) extrudate.

PET domains are irregular in shape and some of them are merged together to form a network. Within these networks some entrapped PP domains are found in the form of fine fibers.

Figure 7 shows the longitudinal view of the PET/KM (30/70) extrudate through the center. No obvious PET particles are seen, which is a strong indication that coalescence of the minor phase is prevalent at a concentration of 30%. The skin region (right) exhibits an extremely fibrous morphology, which is partially due to dispersed PET fibers and partially due to the edge-on view of the PET platelets near the extrudate surface. The central region (left) gives a smooth filmlike structure. This can be explained by the fact that the PET platelets or networks in the central region are less oriented. During splitting of the extrudate, failure occurred along the PET/KM interfaces that were roughly parallel with the fracture plane. The clean fracture surface indicates that the adhesion between the polymers is poor.

Effect of barrel temperature

The effect of the barrel temperature was studied by changing T_3 and T_4 while keeping other extrusion parameters fixed. Four temperature settings were used; zones T_3 and T_4 were 260, 270, 280, and 290°C. In general, the morphologies for zones T_3 and T_4 at 260 and 270°C are similar (Fig. 2), and the fiber diameter distributions of the extrudates are shown in Figure 8. Apparently, a lower barrel temperature or melt temperature favors the formation of finer PET fibers. In

contrast, there are basically PET particles but no fibers in the extrudates prepared at 280 and 290°C. Vainio et al.²³ analyzed the particle size distribution in order to optimize the screw configuration for extrusion. In this study the particle size distributions both near the skin and in the central region were investigated for extrudates prepared at different barrel temperatures. Near the skin [Fig. 9(a)] the particle size generally increases with increasing barrel temperature; the peak particle size shifts from 1.5 μm at 260°C to 4 μm at 290°C. In addition, a broader particle size distribution is observed for the higher barrel temperature. In the central

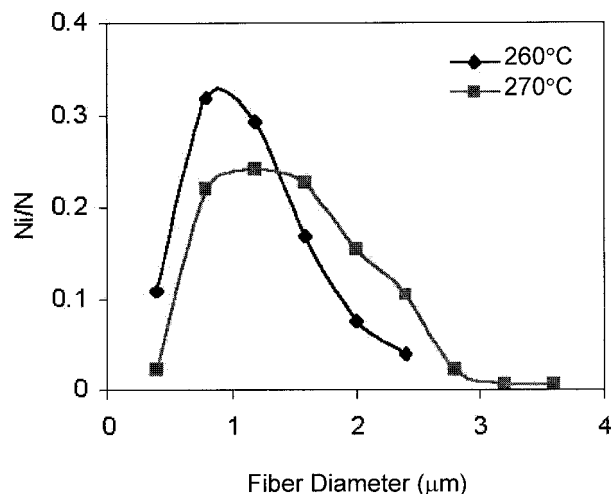
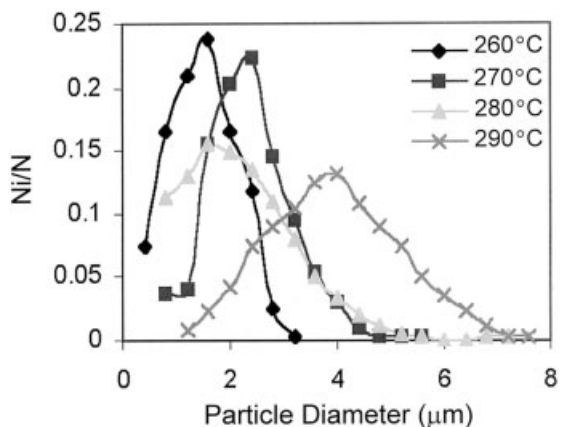


Figure 8 The effect of the barrel temperature on the PET fiber diameter distribution in PET/VM (20/80) extrudates.

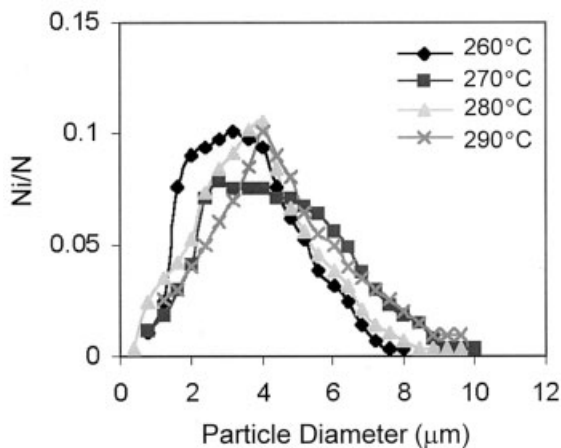
region [Fig. 9(b)] the particles are generally larger and their size distributions do not change much with the barrel temperature. The longer cooling time has probably enhanced coalescence of the smaller particles and allowed contraction of the elongated PET domains back into spherical particles. In the sample extruded at 290°C, it is noteworthy that the particle size distributions near the skin and in the central region are very similar. This suggests that slow cooling of the extrudate is not favorable for fiber formation because it allows the elongated PET domains to shrink back into spherical particles.

Effect of die temperature

Three die temperatures were studied (240, 260, and 290°C). The particle size near the skin [Fig. 10(a)] increases slightly with an increasing die temperature. The increase in the peak particle size (from 2 to 2.5 μm) between 260 and 290°C is smaller than the effect

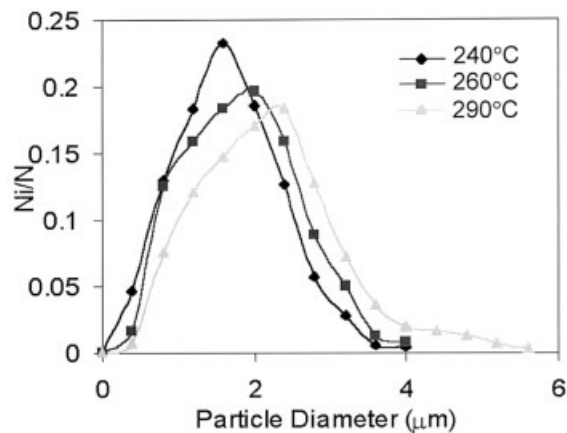


(a)

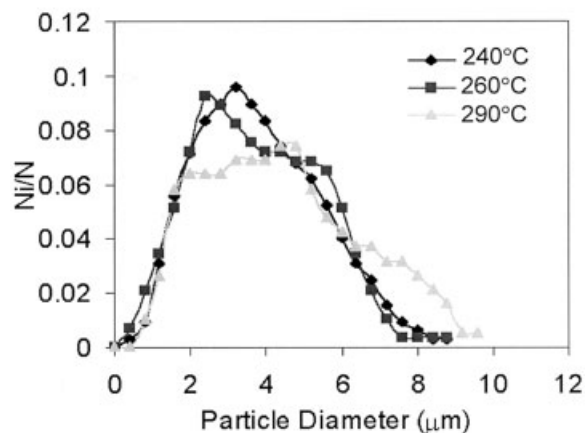


(b)

Figure 9 The effect of the barrel temperature on the PET particle size distribution in PET/VM (20/80) extrudates: (a) near the skin and (b) in the central region.



(a)



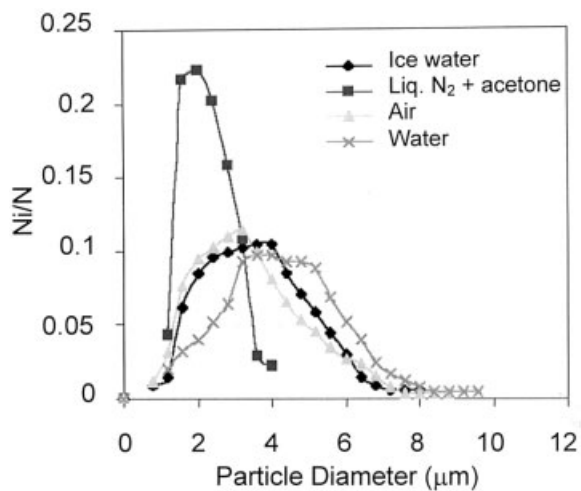
(b)

Figure 10 The effect of the die temperature on the PET particle size distribution in PET/VM (20/80) extrudates: (a) near the skin and (b) in the central region.

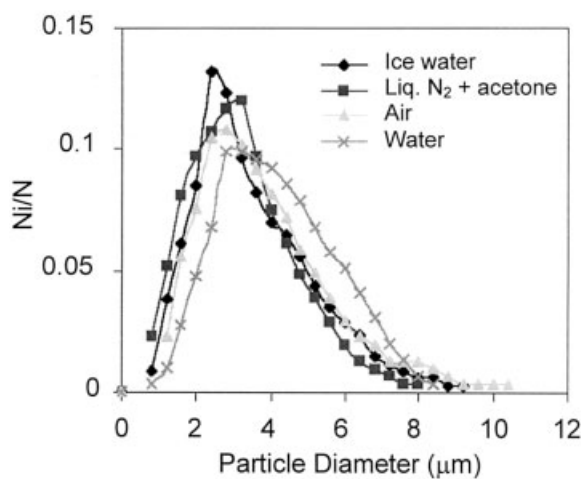
of the barrel temperature because of the short residence time of the melt in the die. The effect of the die temperature on the particle size distribution is not obvious in the central region of the extrudate [Fig. 10(b)]. Nevertheless, there is a slight drop in the peak intensity and an increase in the number of bigger particles at 290°C. This is probably a result of the slower solidification process, which enhances coalescence of smaller particles.

Effect of cooling medium

Four cooling media, namely air, water (room temperature), ice water (0°C), and a mixture of liquid nitrogen and acetone ($\sim -80^\circ\text{C}$), were used for this study. The melt was extruded directly into a beaker containing the liquid cooling media, while the extrudate was supported on a piece of wood after the die using air as the cooling medium. No postextrusion drawing was applied on the extrudates; therefore, the flow was no longer elongational after the die. In fact, there was a



(a)



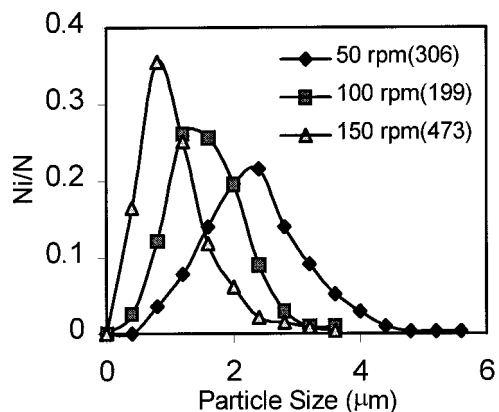
(b)

Figure 11 The effect of the cooling media on the PET particle size distribution in PET/VM (20/80) extrudates: (a) near the skin and (b) in the central region.

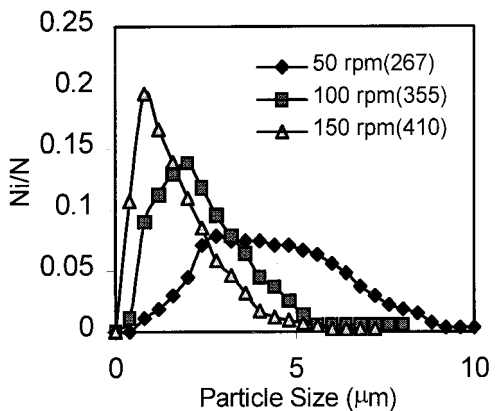
slight radial flow due to die swell. Some coarse fibers were found near the skin, particularly in extrudates cooled in the mixture of liquid nitrogen and acetone. Obviously, the fibers were formed inside the die, most probably because of the elongational flow generated at the convergent die entrance, and they were preserved by the high cooling rate.

Basically there are two mechanisms for fiber formation, which are elongation and coalescence of the dispersed phase. Assume the dispersed PET domains are in the form of spherical particles at the die entrance where the cross section of the flow channel is wide and the speed of the flow is low. As the flow converges to the exit orifice, it is accelerated and a highly elongational flow is favorable for fiber formation.^{24,25} An increase in the number of fibers always causes a corresponding drop in the number of big particles,

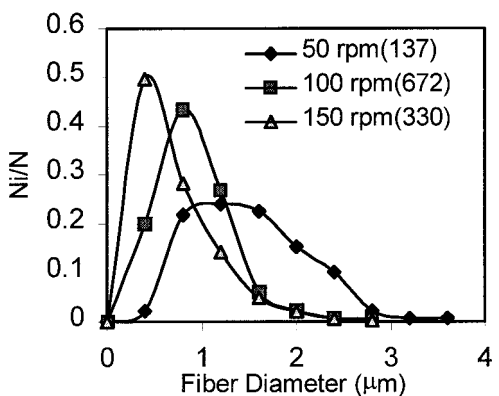
suggesting that elongation of these particles plays an important role in fiber formation. Although the phenomenon of coalescence of the dispersed PET phase is observed after the die (Fig. 4), its frequency of occurrence is not very high. Nevertheless, the possibility of



(a)



(b)



(c)

Figure 12 The effect of the screw speed on the domain size distribution of the PET phase in PET/VM (20/80) extrudates: (a) the particle size near the skin, (b) the particle size in the central region, and (c) the fiber diameter near the skin. The number of particles counted are shown in parentheses.

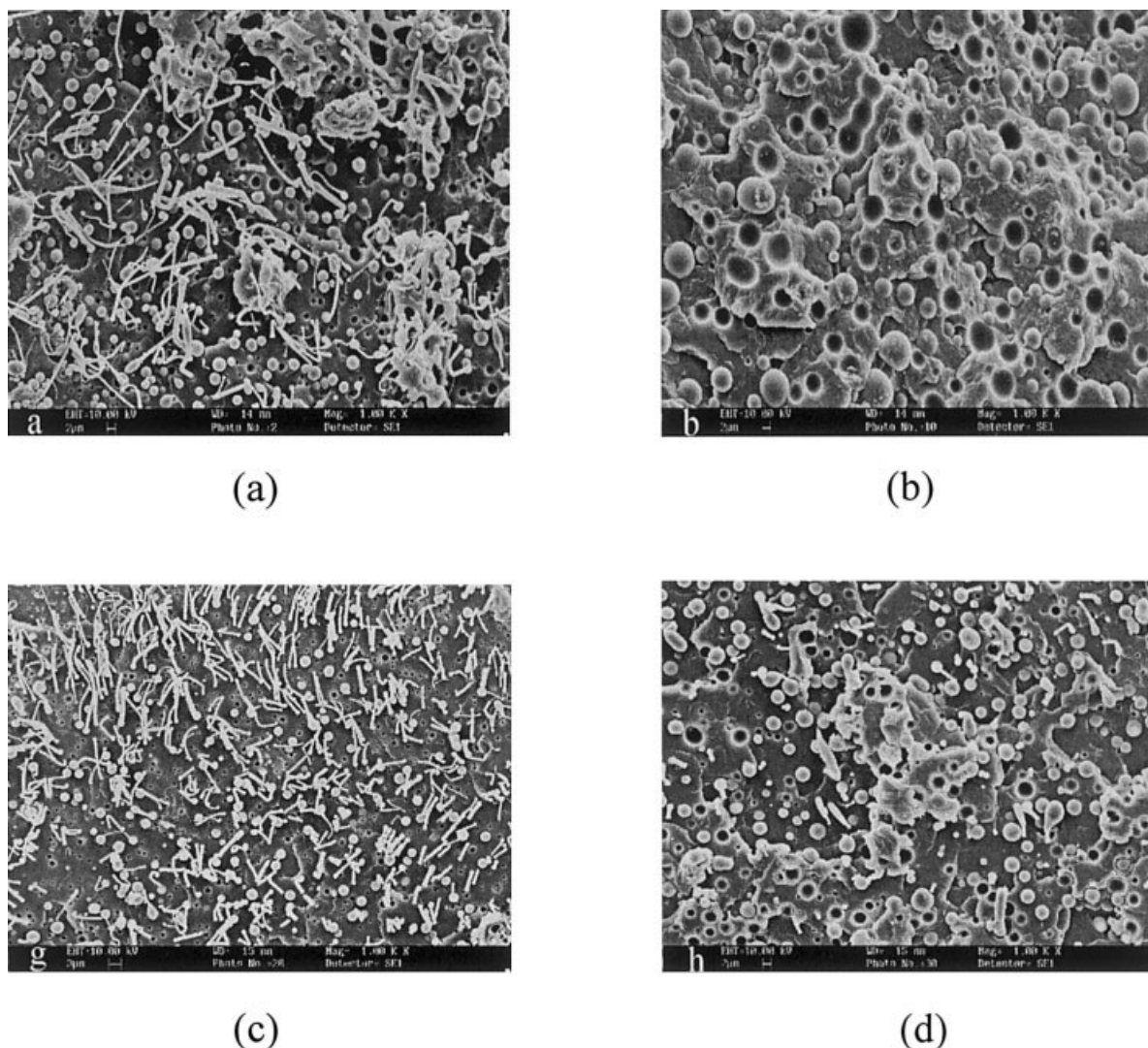


Figure 13 The cross-sectional morphology of PET/VM (20/80) extrudates prepared at different postextrusion drawing speeds: (a) 10 m/min near the skin, (b) 10 m/min in the central region, (c) 25 m/min near the skin, and (d) 25 m/min in the central region.

vigorous coalescence along the upstream of the die cannot be ruled out.

Figure 11(a) shows the particle size distribution near the skin. The liquid nitrogen and acetone mixture produces a narrower band of small PET particles, while the other three cooling media give a wider distribution with more large particles. The liquid nitrogen and acetone mixture was able to freeze the melt shortly after contact; therefore, the morphology is similar to that just after the die. The increase in particle size in samples cooled in the other three media was probably a result of shrinkage of the elongated PET domains and coalescence of particles facilitated by the slower cooling rates. As expected, the particle size distribution in the central regions of the extrudates cooled in the different media does not vary significantly [Fig. 11(b)], because of slow cooling.

Effect of screw speed

The domain size of the dispersed PET phase decreases with increasing screw speed and the PET particles near the skin are generally smaller than that in the central region (Fig. 12). The rotating screws input mixing energy into the melt, resulting in a decrease in the domain size of the dispersed phase along the barrel. The melt is then forced through the die. Some dispersed particles are deformed into fibrous domains or even broken into smaller particles as a result of capillary instability. If the size and shape of the minor phase during melt extrusion of incompatible polymer blends are the result of melt viscosity effects being balanced by interfacial tension, then the size of the minor phase will decrease continually to a final equilibrium size with increasing input energy of mix-

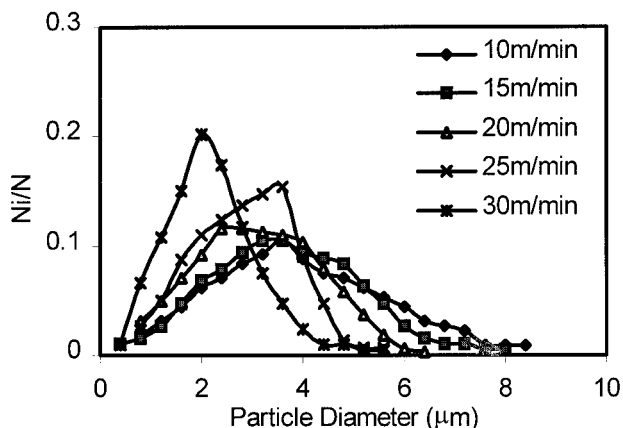


Figure 14 The effect of the postextrusion drawing speed on the PET particle size distribution in the central regions of PET/VM (20/80) extrudates.

ing.^{15,16} It has been reported that most significant particle size deformation and disintegration processes took place within the first 2 min of mixing,²⁶ and after 2 min very little reduction in the size of the minor phase was observed up to 20 min of mixing. Plochocki et al.²⁷ proposed that an abrasion mechanism was responsible for the early stage of the dispersion process and that the final domain size might be controlled by a dispersion-coalescence equilibrium.

Effect of postextrusion drawing

Hot stretching is very effective in transforming the dispersed minor phase into fibers.²⁵ Figure 13 shows the extrudates prepared at drawing speeds of 10 and 25 m/min, corresponding to draw ratios of 1.7 and 4.1, respectively. The higher drawing speed noticeably reduces the diameter of the PET fibers in the skin region, but it does not change the size of the PET particles significantly. This is probably due to the fact that the large PET particles in this region were deformed into fibers and only the smaller ones would survive the flow. In contrast, the PET particles in the central region of the extrudate prepared at 10 m/min are considerably bigger. Figure 14 shows the size distribution of the PET particles within the central regions of the extrudates prepared at different postextrusion drawing speeds. Furthermore, some coarse fibers are found in the central region of the extrudate prepared at 25 m/min [Fig. 13(d)]. This can be attributed to the fact that at a high drawing speed the flow remained highly elongational even after the die. It suppressed recovery of the elongated fibers formed in the die or even increased the aspect ratio of those fibers. Also, reduction of the extrudate diameter, caused by the higher draw ratio, increased the cooling rate in the extrudate center, thus preventing the elongated PET domains from shrinking back to particles.

CONCLUSIONS

The typical morphology of the PET/VM (20/80) extrudate consists of three regions: a skin layer, an intermediate region, and a central region. The skin layer, which is about 10 μm thick, has a lower concentration of PET. The intermediate region, which is about 400 μm thick, has profuse PET fibers and some small PET particles. The central region is approximately 800 μm in diameter and mainly contains PET particles that are relatively larger. The elongation of particles appears to be a major mechanism of fiber formation because an increase in the number of fibers always results in a decrease of big particles. Although the phenomenon of coalescence is observed in the PET/VM (20/80) blend, it is difficult to assess its contribution to fiber formation. In comparison, coalescence is prevalent in the PET/KM (30/70) blend, forming PET platelets near the skin of the extrudate and irregular networks in the central region.

All the extrusion parameters show some effects on the peak particle size near the skin (Table I). In particular, the screw speed is the most prevalent factor in changing the particle size: the higher the screw speed, the smaller the particle size. A lower barrel temperature and a lower die temperature produce a smaller peak particle size and a large number of fibers. When different cooling media were used, only the mixture of liquid nitrogen and acetone gave a smaller peak particle size near the skin. The fast cooling rate had probably suppressed the shrinkage of elongated PET domains into big particles. Within the range of barrel temperatures, die temperatures, and cooling media used in this study, the size distribution of the PET

TABLE I
Effects of Extrusion Conditions on Peak Particle Size of Dispersed PET Phase in PET/VM (20/80) Extrudates

| Extrusion Condition | Peak Particle Size | |
|---------------------------------|-----------------------------|----------------------------------|
| | Near Skin (μm) | Central Region (μm) |
| Barrel temperature | | |
| 260°C | 1.5 | 3.5 |
| 270°C | 2.5 | 3.5 |
| 290°C | 4.0 | 3.5 |
| Die temperature | | |
| 240°C | 1.5 | 3.0 |
| 260°C | 2.0 | 3.0 |
| 290°C | 2.5 | 3.0 |
| Cooling medium | | |
| Liquid N ₂ + acetone | 2.0 | 3.0 |
| Others | 3.0 | 3.0 |
| Screw speed | | |
| 50 rpm | 2.5 | 3.5 |
| 100 rpm | 1.5 | 2.0 |
| 150 rpm | 0.8 | 0.8 |
| Postextrusion drawing speed | | |
| 15–20 m/min | 2.5 | 3.5 |
| 25–30 m/min | 2.0 | 2.0 |

particles did not change significantly in the central region. Moreover, a higher screw speed and postextrusion drawing speed reduced the peak particle size significantly. The former increases the mixing energy input and the latter keeps the flow in a highly elongational state after the die. Some fibers were found in the central regions of the extrudates prepared at a postextrusion drawing speed of 25 m/min or higher. In contrast, very few or no fibers were found in the central regions of the extrudates prepared under other extrusion conditions.

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