Morphology Development of PBT/PE Blends during Extrusion and Its Reflection on the Rheological Properties

Joung Sook Hong, Jeong Lim Kim, Kyung Hyun Ahn, Seung Jong Lee

School of Chemical Engineering, Seoul National University, Seoul 151–744, Korea

ABSTRACT: In this study, we have investigated morphology evolution of polymer blends during extrusion. By choosing two polymers, high density polyethylene (PE) and poly (1,4-butylene terephthalate) (PBT), having a large difference in melting temperature, we could control the viscosity ratio of the blend as well as the morphology. The morphology of the dispersed phase evolved from film to fibril and to droplet structure depending on thermal and deformation history. We could maintain the film or fibril structure in a final product by keeping the dispersed phase deformable and rigid enough to avoid the relaxation that is related with instability originating from the interfacial tension. The anisotropic structures (film and fibril) were found to enhance the rheological properties significantly, but in different manners under shear and extensional flow fields. This study shows that diverse morphology can be obtained by controlling processing conditions, and the rheological properties can be dramatically enhanced by morphology control. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1702–1709, 2005

Key words: rheology; morphology; fibrils; films

INTRODUCTION

Most polymer blends have multiple phases due to the lack of thermodynamic interaction, and the final morphology of the blend has a significant influence on its properties. The morphology is determined by various parameters, such as composition, interfacial tension, viscoelasticity, shear rate, flow field, and so on.[1,2] Depending on these parameters, various types of morphology of the dispersed phase, like nodular, laminar, and fibril, can be obtained. In general, blending would be achieved in an extruder with the goal that the dispersed phase is dispersed and distributed well into the matrix with the desired size and shape. To achieve this goal, therefore, it is meaningful to understand the morphology development in an extruder and to know how the structure is evolving. Moreover, it is necessary to control the morphology to achieve the required performance.

There are many researches concerning the morphology development of polymer blends during the mixing process. But the studies on how morphology evolves are limited.[3–8] As polymers experience complex deformation history of both shear and extension during mixing, it is difficult to have a clear understanding of the mechanism of mixing. Favis[4] investigated the effect of mixing time on morphology. He observed morphology by changing mixing time from 2 to 20 min and reported that there was no significant reduction in domain size over the observed time periods. It is expected that the morphology change had already occurred before observation because torque had already significantly reduced in just 2 min. Scott et al.[5] studied morphology development in an intensive mixer, and Sundararaj et al.[6] compared it with that in an extruder. The Macosko group[5,6] reported major reduction in domain size occurs in conjunction with the melting or softening of the component, and that the initial mechanism of morphology development involves the formation of the sheet or ribbon structure of the dispersed phase. However, some particular morphology like a sheet or ribbon was unstable due to the flow and interfacial tension. Hence, it was difficult to maintain the particular morphology in the matrix during the mixing process. Min et al.[7] reported the formation of a fibril structure during capillary flow, but the fibril structure easily turned into small drops. The fibril structure as an intermediary during morphology evolution quickly changes into thermodynamically stable droplets.[7–13] However, as the blend with a fibril structure was found to have good mechanical properties, researches have been directed to maintaining the fibril structure using various methods.[8–11] Evstatiev et al.[8,9] applied cold and hot drawing and annealing after melt blending to maintain the microfibrillar structure in the PBT/PA6 blend, for example.

In the previous studies, extrusion temperature was normally set at sufficiently higher temperature than

Correspondence to: K. H. Ahn (ahnnet@snu.ac.kr).

	First run	Second run	Rotor speed
Condition	Temperature (°C)[a]	Temperature (°C)[a]	(rpm)
A	170/210/210/210	x	25
B	170/220/220/220	x	25
C	170/230/230/230	x	25
1	170/190/220/210	x	25
2	170/190/220/210	130/150/160/150	25
3	170/190/220/210	150/170/190/180	25
4	170/190/220/210	170/190/220/210	25

[a] Temperature profile at feeding, transition, metering, and die zone, sequentially.

the melting temperature of the constituent polymer, where it is difficult to maintain the particular morphology formed at an early stage of mixing.[5,6] Even though an intermediate structure may be maintained up to the die of an extruder, the dispersed phase quickly turns into a thermodynamically stable structure like a droplet during solidification. When a polymer blend comes out of a die, the flexible polymer relaxes and retracts against stress depending on the viscoelasticity of each component, and the blend further develops its morphology by the heterogeneous stress distribution around the dispersed phase induced by interfacial tension.[14] As this process is fast and spontaneous, it is difficult to fix the intermediate morphology such as sheet or film within the blend of a final product. However, as it is evident that the morphology depends on thermal and deformation history, and we understand the spontaneous process of morphology development, we can design experiments to obtain the intermediate morphology in a final product.

This study focuses on getting the blend with particular morphology that can be observed during the process of extrusion. We designed the experiments to obtain the blends with intermediate morphology by controlling thermal and deformation history through a second run at different processing conditions. Schematically, at a first run, we supplied minimum energy to induce deformation of rigid PBT, but as much as to prevent further morphology development into droplet structures, and then the deformed blend was forced to pass through the extruder once again at different conditions (see Table I). Furthermore, we investigated the interrelationship between its morphology and rheological properties. For these purposes, we selected two polymers (PE and PBT) having a large difference in melting temperature, and extrusion was performed at various processing conditions to maintain the specific morphology in the final product without further processing, such as drawing or cooling. Then we investigated the development of the morphology of our concern as well as the relationship between morphology and the rheological properties.

EXPERIMENTAL

Materials

High density polyethylene (PE, Mw: 151K) used in this study was supplied by Honam Petrochemical Corp. PBT (Mn: 30K, Mw: 53K) was purchased from Sigma-Aldrich Co. PE as a matrix has a melt index of 0.9g/10min (ASTM D1238, 190°C/2.16kg). Thermal properties were measured by using Differential Scanning Calorimetry (a DSC 2010, TA instrument) under nitrogen atmosphere after the following procedure: first heating run at 10°C/min scanning rate up to 250°C and maintaining this temperature for 10min, cooling to room temperature at 10°C/min, and then second heating run at 10°C/min up to 250°C. It can be observed from Figure 1(a) that PBT starts phase transition near 210°C, and shows a maximum endothermic peak (melting) at 227°C, and crystallizes at 197°C. PE has a melting temperature of 128°C and crystallizes at 118°C (not shown here). Figure 1(b) shows storage moduli of PBT at four temperatures, and the phase transition of PBT is well reflected on the rheological behavior. PBT shows a solid-like behavior until 225°C, and there is a considerable reduction of modulus at around 227°C, after which it shows a liquid-like behavior. As crystallization can be induced by flow at temperatures close to 227°C, the frequency sweep test was carried out in a short measuring time, less than 200 s. Prior to extrusion, it was dried under vacuum at 80°C for at least 12 h to remove moisture. We did not use any kind of chemicals to modify the interface between the polymers.

Blend preparation

PBT/PE blends were prepared using a counter-rotating conical twin screw extruder (L/D = 16, D = 4/3 in., Haake). The extruder barrel is divided into 3 zones
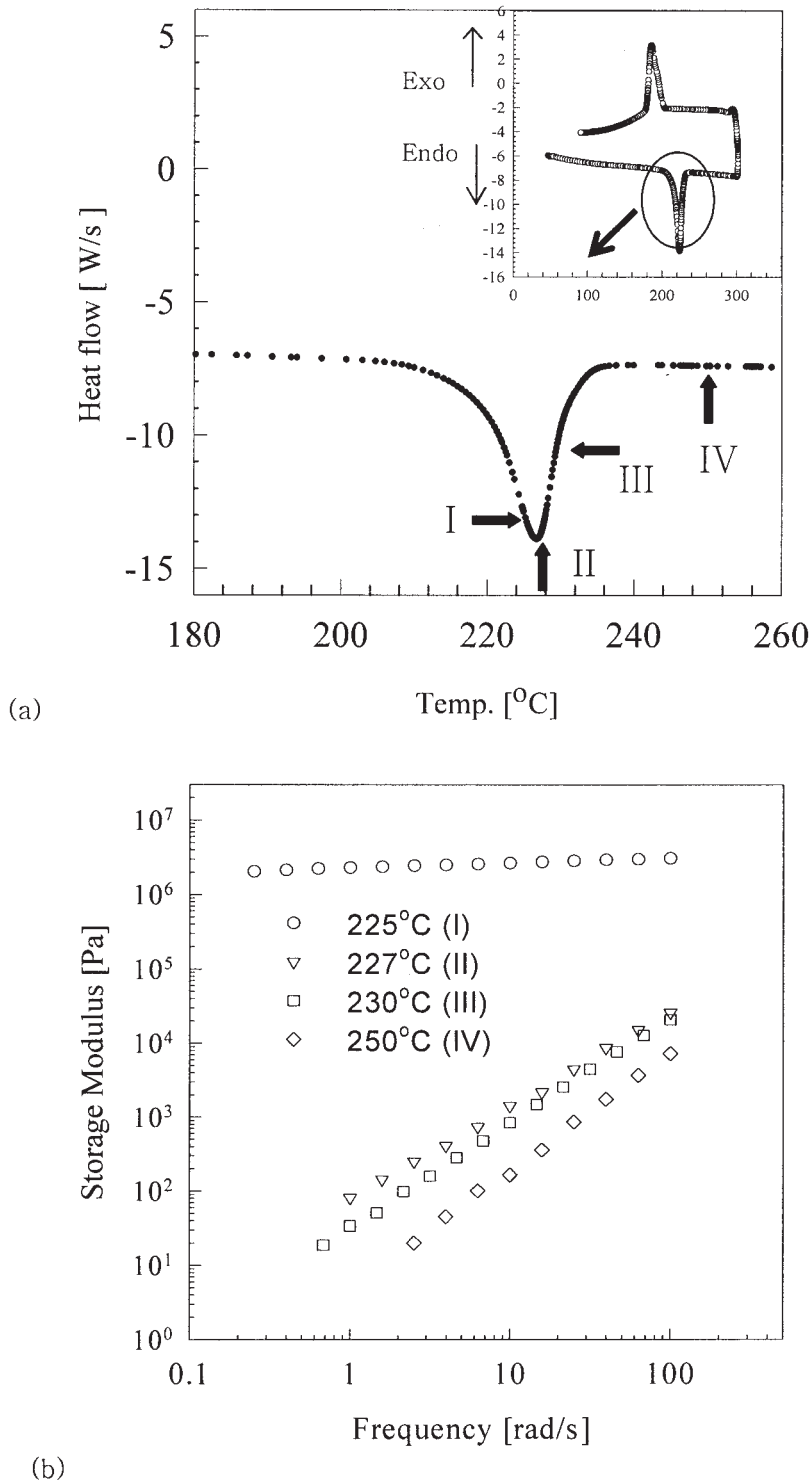
Figure 1 DSC heating thermogram of PBT (a) and the storage moduli of PBT at four temperatures from 225 to 250°C (b), which correspond to the positions (I, II, III, and IV) marked on DSC thermogram.

that are heated individually. They consist of solid conveying, melting, and metering zones, and the latter is connected to a capillary die (D = 3.5mm). The processing conditions are listed in Table I. Polymers were put together into the extruder after dry mixing and blended according to the conditions of Table I.

Melt temperature of condition 1 (170/190/220/210°C) was about 210°C when measured at die. As the screw rotor speed was controlled at a very low level of 25rpm and the matrix viscosity is not high, there is no significant effect of viscous dissipation. All extrudates were solidified in the air without drawing. The max-

imum composition of PBT in the blend was restricted to 5 wt %.

Measurement of rheological properties

A Rheometrics Mechanical Spectrometer (RMS800, Rheometric Scientific) with a parallel plate fixture of 25mm diameter was used to perform the small amplitude oscillatory shear experiment. The complex viscosity (η^*[Pas]), storage modulus (G′[Pa]), and loss modulus (G″[Pa]) were measured as a function of frequency (ω). To observe the extensional behavior of materials, the Meissner-type extensional rheometer (RME, Rhoemetric Scientific) was used. All measurements were conducted under a nitrogen environment to reduce any possible degradation occurring at high temperature.

Observation of morphology

Morphology observation was conducted by using a scanning electron microscope (SEM; JSM 840A, JEOL) and a polarized optical microscope (POM; BX51, Olympus) coupled with a hot stage (Linkam CSS-450). POM was used to probe the blend morphology with a relatively low magnification lens. With this shearing system equipped on POM, we could observe the morphology evolution *in situ* under shear flow. At 180°C, we could easily discriminate the PBT phase from the PE matrix because the PE matrix is completely melted, whereas PBT is still in solid state at that temperature. We also used SEM to observe the blend morphology. The two phases were easily distinguished without extraction of the dispersed phase because of the polar functional groups of PBT.

RESULTS AND DISCUSSION

We first carried out a preliminary test by changing the extrusion temperature from 210°C (170/210/210/210°C, condition A) to 230°C (170/230/230/230°C, condition C) to find the optimum processing condition that minimizes the interfacial tension effect on morphology development. Blend morphology varied significantly in this temperature range because PBT shows a dramatic change of rheological properties near the melting temperature (227°C), as can be seen in Figure 1. The PBT phase shows a droplet morphology typically observed in polymer blends, as seen in Figure 2(b). Above 227°C (condition C), the viscosity ratio ($\lambda_{PBT}/\lambda_{PE}$) becomes less than one as the viscosity of PBT becomes very low after melting (see Table II). In this condition C, the flow as well as interfacial tension becomes an important factor for morphology development. On the other hand, at 220°C (170/220/220/220°C, condition B), which is slightly lower than the melting temperature of PBT, rigid PBT becomes

(a)

(b)
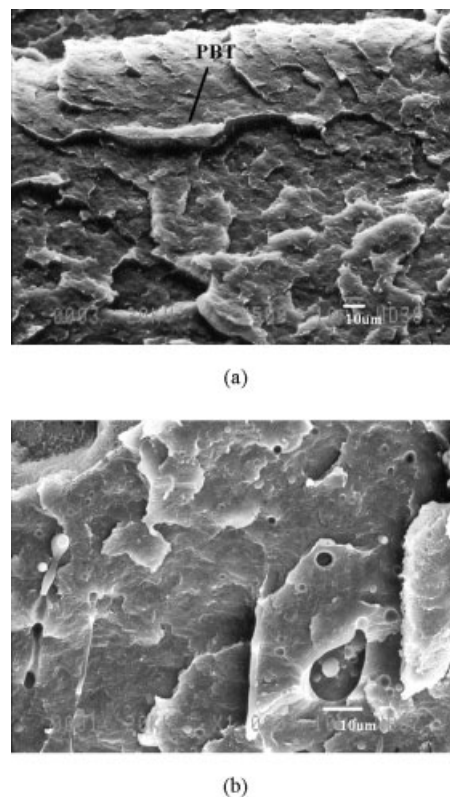
Figure 2 SEM photographs of 1 wt % PBT/PE under conditions B (a) and C (b).

soft enough to deform by mechanical abrasion, and the deformed PBT phase becomes irregularly shaped fragments of micron scale, as can be seen in Figure 2(a). However, it hardly develops into a droplet structure because PBT is not viscous enough to be influenced by interfacial tension to form droplets at this condition ($\lambda_{PBT}/\lambda_{PE} = 500$).[15] When PBT/PE was extruded at 210°C (condition A), PBT pellets come out of the extruder without melting. PBT is too rigid to deform by mechanical force. Therefore, we decided that the processing temperature should be at around 220°C to induce deformation of PBT and to maintain the deformed state of PBT at the rotor speed of 25rpm.

To get the blend with an intermediate morphology, experiments were conducted at conditions 1–4 listed in Table I. In the first run (condition 1), we set the temperature of the metering zone at 220°C (170/190/220/210°C) to delay morphology development. Since the temperature is lower than the melting temperature of PBT and high pressure is applied in the metering zone, the drag is a dominating factor for morphology development in this condition. When the extrudate is processed again, the extrusion temperature was severely lowered (conditions 2 and 3) to prevent morphology development, and in condition 4 the extrusion condition of the second run was kept the same as in the previous one. Figure 3 presents the micrographs

TABLE II
Viscosity Ratio and Melting Temperature

|	Viscosity [kPas] (1[rad/sec], 225°C)	Viscosity [kPas] (1[rad/sec], 230°C)	Melting temperature (°C)
PBT	2300	0.9	227
PE	4.6	4.5	126
Viscosity ratio	500	0.2	

of the PBT/PE blend under condition 1. In this condition, the PBT pellet is dragged and stretched out into a curved film, as can be seen in Figure 3. The film structure that can be observed at an early stage of morphology development[5,6] does not develop further and maintains its structure up to solidification since the interfacial tension effect on morphology development was minimized. In this article, we define the film as the morphology of about $1 \mu m$ in thickness and much over $100 \mu m$ in width. The film structure, though distinct in SEM photographs, does not cause a defect in the sense that the blend does not lose its transparency. It is meaningful that the film structure can be maintained and obtained as a final product by controlling the processing conditions. According to conditions 2, 3, and 4, PBT/PE blended under condition 1 was subjected to extrusion once again to observe the next stage of morphology development as more shear is applied.

At condition 2, the morphology evolution from the film structure is mainly caused by drag because the temperature for the second run was set at much lower than 220°C. During the second run, many holes in the film were formed by drag, and it was broken up by mechanical force. It is observed in Figure 4 that the film structure turns into a bundle of fibrils and has split into many strands. In the case of condition 3, the morphology is the same as in condition 2 because the PBT is still rigid, even though the temperature is increased up to 190°C.

When PBT/PE blended under condition 1 was extruded again at the same condition (condition 4), the film structure formed during the first run develops into many small spherical particles with average diameter of 1.35 μm (see Fig. 5). Although the extrusion temperature is lower than the melting temperature of PBT, it forms a droplet structure mostly by drag. Based on these results, we understand that morphology development requires more extrusion time (or equivalently more heat and shear) when a high viscosity ratio is maintained, and it gives us the possibility to control the morphology development. It is possible to keep a film or fibril structure in the final product if the dispersed phase is rigid enough to avoid the relaxation process that is related with instability originating from interfacial tension.

Figure 6 shows the dependence of composition on rheological properties at 150°C. 1 wt % and 5 wt % PBT/PE with both film and droplet structure were compared. The blend with droplet structure was made by condition 4, and the film structure by condition 1 of Table I. We cannot observe any increases in rheological properties when we add 1 wt % PBT nor any difference between the two structures. However, as the composition is increased to 5 wt %, large differences between the film and droplet structure are well reflected on the rheological properties.
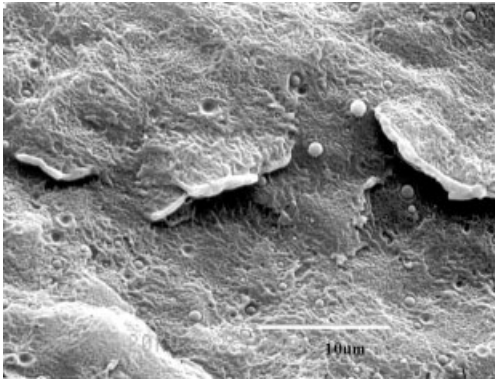
When the measuring temperature was increased to 230°C, both PBT/PE blends (with film and droplet structure) show nearly the same behavior under shear flow, as can be seen from Figure 7. At low tempera-
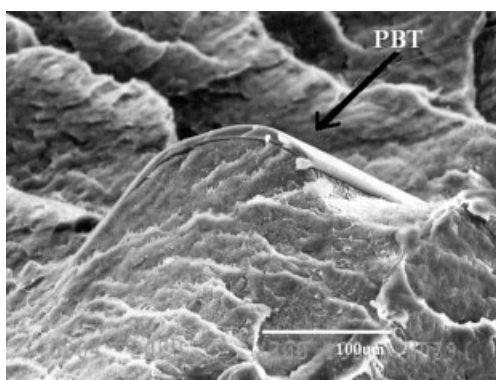
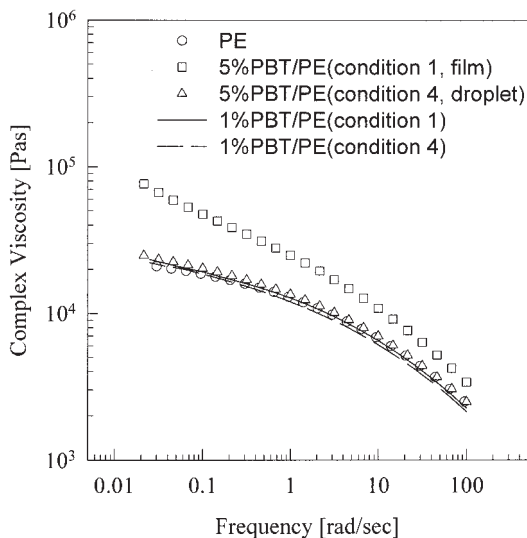**Figure 3** SEM photograph of 1 wt % PBT/PE under condition 1.

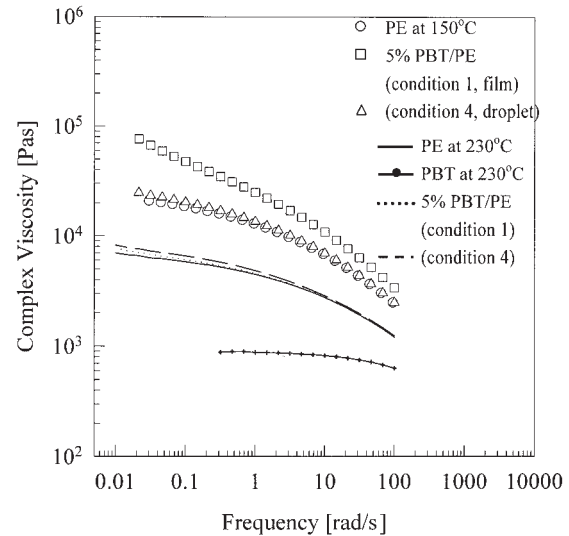**Figure 4** SEM photograph of 1 wt % PBT/PE under condition 2.

Figure 5 SEM photograph of 1 wt % PBT/PE under condition 4.

Figure 7 Complex viscosity of PE and 5 wt % PBT/PE at 150°C and 230°C.

ture, the blend maintains its structure during measurement, but the film structure is changed into a droplet structure at 230°C during the equilibration and measuring time. This morphology change is confirmed by POM, in which the film structure quickly disappears and results in droplets, as can be seen in Figure 8. The effect of morphology on the complex viscosity of 5 wt % PBT/PE is shown in Figure 9. In the case of the blend with film structure (condition 1), the complex viscosity shows a significant enhancement. The fibril structure (conditions 2 and 3) obtained in this study also enhances viscosity over the entire frequency range because PBT maintains a high aspect ratio. In the case of the droplet structure (condition 4), however, it is hard to expect any viscosity increase in contrast to the film or fibril structure.

When noninteractive spherical particles of small fraction (ϕ) are dispersed in the Newtonian matrix

(η_m), the viscosity is simply represented by the following equation:

$$\eta_s = \eta_m\left(1 + \frac{5}{2}\phi\right) \tag{1}$$

According to Eq. (1), in 1 wt % and 5 wt % PBT/PE blends with droplet structure ($\phi_{\text{vol. of 1wt\%PBT}} = 0.005$ and $\phi_{\text{vol. of 5wt\%PBT}} = 0.026$), the viscosity of each blend (η_s) can be increased by 1.25% and 6.5% over the matrix viscosity (η_m). However, as the anisotropy of the dispersed phase increases, they can be oriented by a flow field and become more dissipative than the dispersion of droplets. As can be seen in Figure 9, the film structure significantly enhances viscosity compared with droplets. The stress (σ_s) of non-Brownian suspension of rod-like particles with high aspect ratio (L/d) has another contribution from the anisotropy in addition to the stress contribution of the matrix.[16]

$$\sigma_s = \sigma_m + \sigma_d = 2\eta_m D + \nu\xi_{str}\langle uuuu\rangle{:}D \tag{2}$$

Here, D is the rate of deformation tensor, ν is the number concentration, and ξ_{str} is the viscous drag coefficient, which depends on the geometry of the dispersed phase. For fibers of high aspect ratio, the viscous drag coefficient can be estimated according to Batchelor[17] as $[\xi_{\text{str}}]_{\text{rod}} = \pi\eta_m L^3/3\ln(\pi/\phi)$. Since film structure is highly anisotropic, it is strongly energy-dissipative and leads to an increase of viscosity. Entangled solid fibrils are physically networked with each other instead of being aligned with shear flow, also resulting in strong resistance against shear.

The characteristics of morphology obtained in this study are more clearly differentiated under the uniax-

Figure 6 Complex viscosity of 1 wt % PBT/PE and 5 wt % PBT/PE at 150°C.
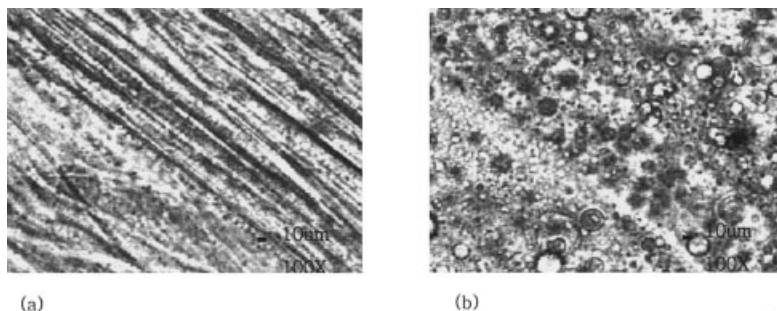
Figure 8   Polarized optical micrographs of 5 wt % PBT/PE at 230°C after 20 s (a) and 120 s (b).

ial extensional flow even with as small as 1 wt % addition of PBT because energy dissipation is maximized by the highly anisotropic films aligned along the extensional flow direction. Figure 10 shows a transient tensile force measured at the rate of 0.05[1/s] at 150°C. The blend with fibril structure shows a significant increase of tensile force, which means an increase of melt strength.[18,19] Since PBT fibrils entangle and have many physical networks, they induce significant resistance against extension, leading to the enhancement of tensile properties without losing ductility. This suggests that the melt strength can be enhanced by morphology control. In the case of the blend with PBT film, the tensile force increases very fast but fails at a much shorter time than the previous case due to the lack of extensibility. Though it shows a significant enhancement of shear viscosity, the improvement of tensile property is not effective since it fails at small strain due to the solid-like contribution of PBT. Thus, the rheological behavior of the blends is different depending on their morphology, and the morphology may affect the properties under shear and extension in

different manners. Another point to be noted is that we could observe the enhanced rheological properties in a blend of two incompatible polymer pairs, even a strain hardening behavior.

Similar experiments have been conducted with other polymers to determine whether these observations are valid in other blend systems as well. The morphology observed in PBT/PP or PBT/PS blends was qualitatively similar to that with a PE matrix.[20] A PBT/PP blend with film or fibril structure, however, did not show a significant enhancement of rheological properties compared with a PBT/PE blend. A small difference at interface (possibly due to their different crystallization kinetics) seems to affect the properties of the blend. Details of the comparative studies will be reported later.

CONCLUSIONS

This study shows that diverse morphology can be obtained by controlling the processing conditions, and the rheological properties can be dramatically enhanced by morphology control. When PE is blended with a small amount of PBT whose melting temperature is much higher than that of PE, we could obtain blends with film, fibril, or droplet structure depending on thermal and deformation history. Extrusion temperature has been varied widely from below to above the melting temperature of the second phase, PBT. When PE was blended with PBT slightly below the melting temperature of PBT, rigid PBT forms a film structure by drag. In this condition, the PBT phase does not evolve to droplet structure unless a significant amount of additional heat or shear is applied, and it can maintain its structure during extrusion. On the contrary, when the processing temperature is higher than the melting temperature of PBT, a thermodynamically unstable film or fibril structure observed at an early stage of morphology development easily evolves to droplet structure during extrusion. Therefore, we could maintain a film or fibril structure in the final product by keeping the dispersed phase rigid enough to avoid the relaxation process that is related with the
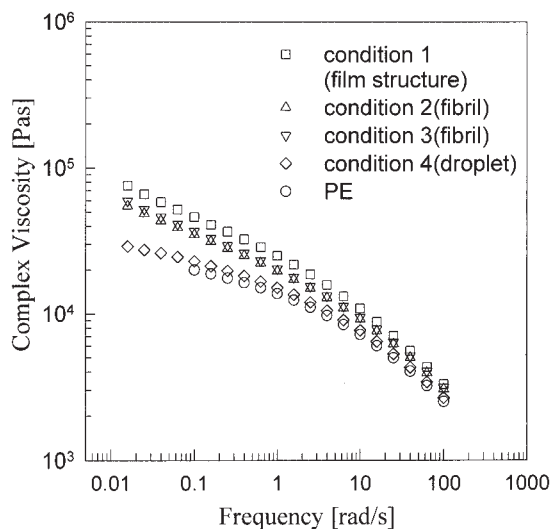
Figure 9   Complex viscosity of PE and 5 wt % PBT/PE with diverse morphology at 150°C.
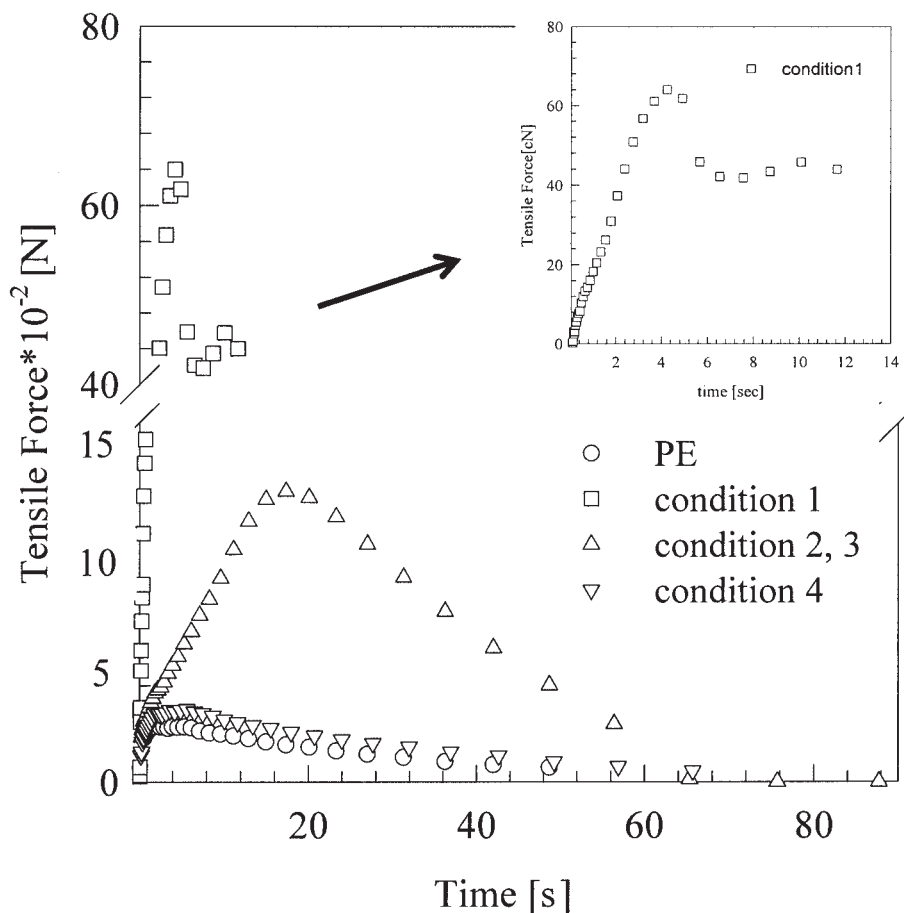
Figure 10 Transient tensile force measurement of PE and 1 wt % PBT/PE with diverse morphology, measured at 150°C and the strain rate of 0.05[1/s].

instability originating from interfacial tension. The rheological properties of blends with diverse morphology produced with the above strategy were also measured. The geometric characteristics of fibril or film structure give rise to enhanced resistance against deformation compared with the droplet structure. The film or fibril structure was found to enhance modulus as well as viscosity of the blend significantly because it is more dissipative due to its anisotropy.

References

1. Utracki, L. A. Polymer Alloys and Blends; Hanser: New York, 1990.
2. Tadmor, Z.; Gogos, C. G. Principles of Polymer Processing; John Wiley & Sons: New York, 1979.
3. David, B.; Kozlowski, M.; Tadmor, Z. Polym Eng Sci 1993, 33, 227.
4. Favis, B. D. J Appl Polym Sci 1990, 39, 285.
5. Scott, C. E.; Macosko, C. W. Polymer 1995, 36, 461.
6. Sundararaj, U.; Macosko, C. W. Polym Eng Sci 1992, 32, 1814.
7. Min, K.; White, J. L.; Fellers, J. F. Polym Eng Sci 1984, 24, 1327.
8. Evstatiev, M.; Schultz, J. M.; Petrovich, S.; Georgiev, G.; Fakirov, S.; Friedrich, K. J App Polym Sci 1998, 67, 723.
9. Evstatiev, M.; Fakirov, S.; Bechtold, G.; Friedrich, K. Adv Polym Tech 2000, 19, 249.
10. Cassagnau, P.; Michel, A. Polymer 2001, 42, 3139.
11. Monticciolo, A.; Cassagnau, P.; Michel, A. Polym Eng Sci 1998, 38, 1882.
12. Champagne, M. F.; Dumoulin, M. M.; Utracki, L. A.; Szabo, J. P. Polym Eng Sci 1996, 36, 1636.
13. Li, X.; Chen, M.; Huang, Y.; Lin, G.; Zhao, S.; Liao, B.; Wang, C.; Cong, G. Adv Polym Tech 1997, 16, 331.
14. Stone, H. A.; Bentley, B. J.; Leal, L. G. J Fluid Mech 1986, 173, 131.
15. Wu, S. Polymer Interface and Adhesion; Marcel Dekker: New York, 1982; Chapter 5.
16. Larson, R. G. The Structure and Rheology of Complex Fluids; Oxford University Press: New York, 1999; Chapter 6.
17. Batchelor, G. K. J Fluid Mech 1971, 46, 813.
18. Wagner, M. H.; Bernnat, A.; Schulze, V. J Rheol 1998, 42, 917.
19. Micic, P.; Bhattacharya, S. N.; Field, G. Int Polym Processing 1996, XI.
20. Shon, J. W.; Hong, J. S.; Ahn, K. H.; Lee, S. J. In Proceedings of PPS Conference, Taiwan, 2002, 105.