

Effects of Bulk Morphology on the Mechanical Properties of Melt-Blended PP/PS Blends

Kazuhiro Yoshida,^{1,2} Takanobu Kawamura,² Minoru Terano,³ Koh-hei Nitta²

¹Tokyo Printing Ink Manufacturing Company Ltd., Yoshinohara, Kitaku, Saitama 331-0811, Japan

²Department of Chemical Engineering, Kanazawa University, Kanazawa 920-1192, Japan

³School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Tatunokuchi, Ishikawa 923-1292, Japan

Received 11 January 2007; accepted 27 March 2007

DOI 10.1002/app.28014

Published online 27 March 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We investigated the relationship between morphology and mechanical properties in binary blends of isotactic polypropylene (PP) and atactic polystyrene (PS) showing completely phase-separated morphology. The domain size and crystallinity in PP phase were controlled by the comp-molding conditions such as holding time in the hot-press and quenching temperature to prepare the sheets. The phase-inversion took place at 62.5 wt % of PS content and this leads to ductile-brittle transition at the blend composition. It was found that the

mechanical properties of PP-rich blends are dominantly affected by the nature of the PP matrix and independent of the domain size of PS phase. This is associated with the interfacial separation between rigid PS droplets and PP matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 211–217, 2008

Key words: isotactic polypropylene; atactic polystyrene; blends; morphology; mechanical properties; polyolefins; polystyrene

INTRODUCTION

There has been much commercial interest in the development of polymer blends of commodity plastics to improve the mechanical properties and overall physical behavior of the homopolymers.^{1–10} In addition, study of blends is very important for their possible re-use because mixtures of such commodity polymers often occur in plastic scrap and waste. In this work, we deal with the mechanical properties and gross morphology in the melt-mixed blends composed of polypropylene (PP) and polystyrene (PS), which are typically the two of the most used plastics in the world.

The binary blends of PP and PS are immiscible due to differences in their polarity and chemical nature and they show macroscopically phase-separated morphology.^{11–13} With regard to further modification of the phase-separated morphology, many researchers have examined the addition of the third component as compatibilizers. The commercial triblock copolymers such as SBS and SEBS have been used as a compatibilizer for PP/PS blends.^{14–21} However, little has been done to investigate the additional effects

of PS on the overall mechanical properties of PP without compatibilizers. This will be due to the morphological instability and reproducibility in the immiscible blends during preparation process.

The morphological and structural mechanisms underlying the deformation process of the immiscible PP/PS blends are not well clarified yet. Essentially, mechanical properties of these materials are controlled by morphological variables such as crystalline morphology of PP phase, the domain size of dispersed phase, and the composition. The diversity and interdependencies of these variables make it difficult to provide a morphological interpretation for tensile behavior of the immiscible blends. To obtain precise understanding, the interrelation between the phase-separated morphology and the tensile properties in PP/PS blends, these variables should be isolated and their individual roles assessed. So far, however, it has been hard to control the molecular and gross morphologies of immiscible blends and this leads to the diversity and interdependency of these morphological variables.

Recently, we have succeeded to control the macroscopically phase-separated state in binary PP/PS blends using a mixing technique. This enables to prepare a series of PP/PS blends with various sizes of the dispersed domains without compatibilities. The purposes of this study are two-fold: one is to show the fundamental data on tensile properties of binary immiscible PP/PS blends and the other is to

Correspondence to: K.-H. Nitta (nitta@t.kanazawa-u.ac.jp).

Contract grant sponsor: Tokyo Printing Ink Manufacturing Company.

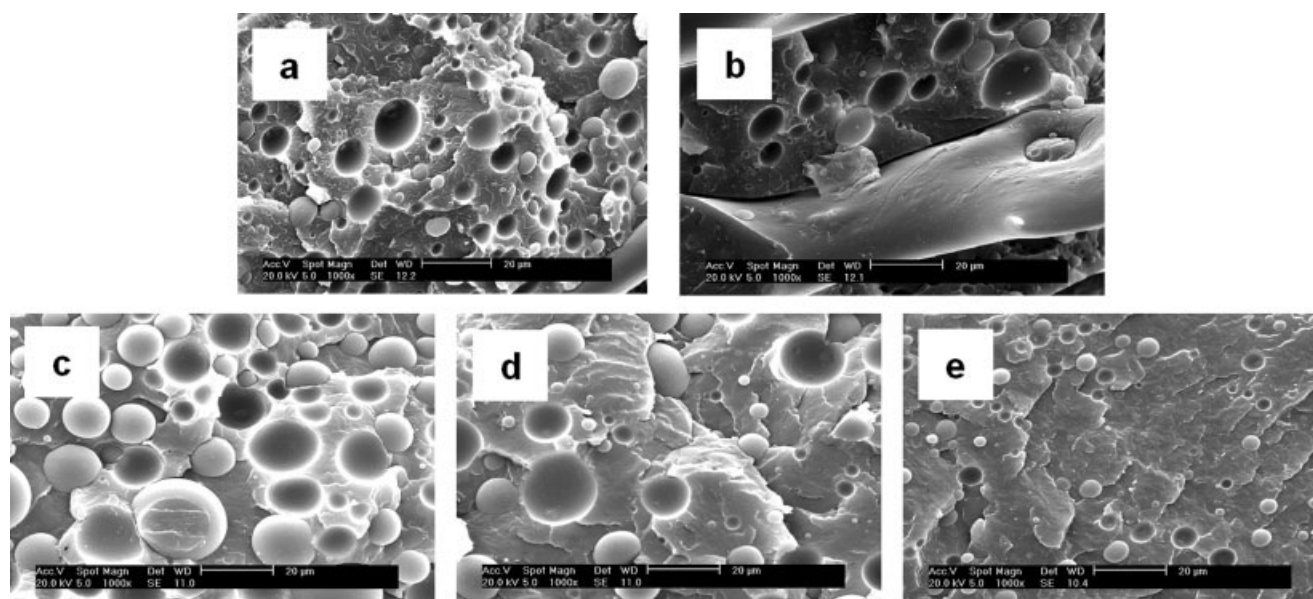


Figure 1 SEM micrographs of binary PP/PS blends with the PP contents of (a) 10 wt %, (b) PP: 30 wt %, (c) 50 wt %, (d) 70 wt %, and (e) 90 wt %.

better understand the relationship between the morphology and mechanical properties in phase-separated immiscible blends by controlling the molecular aggregation state in the ductile matrix and the size of dispersed phase. We expect that the mechanical and morphological data of the binary PP/PS blends thus prepared will be basic data in polymer recycling for re-use.

EXPERIMENTAL

Materials and blend preparation

Two commercial grades of isotactic PP and atactic PS supplied by Japan Polychem, Japan were used in this work. The number and weight-average molecular weights of the PP was $M_n = 8.0 \times 10^4$ and $M_w = 3.8 \times 10^5$, respectively. The number- and weight-average molecular weights of the PS was $M_n = 9.0 \times 10^4$ and $M_w = 2.2 \times 10^5$, respectively.

Both pellets of 40 g were melt-blended with a wide range of blend ratio using a laboratory rotary mixer (Tokyo-Printing) with small agitating blades at 5100 rpm. The internal temperature in the vessel rapidly rose above melting temperature of PP and we found the optimum condition for mixing of PP and PS by controlling the resident time under the high rotation speed.

The samples were melt-pressed in a hot press at 503 K and 10 MPa for various times and then quenched at various temperatures to control the crystal morphology of PP phase and the domain size in the phase-separated morphology. The compression-molded samples were prepared to be about 200 μm thickness.

Measurements

Tensile tests were performed using a tensile machine (Abecks). The notch-shape specimens with the gauge length of 2 mm were cut out from the comp-molded sheets. The tensile strain was calculated from the ratio of the increment of the length between clamps to the initial gauge length. The tensile stress was determined by dividing the tensile load by the initial cross section. The stress-strain behavior was measured at room temperature and at a crosshead speed of 3.2 mm/min.

The density of the samples was measured by a Mettler AG104 balance. By assuming that both phases are completely separated, the degree of crystallinity of the PP phase in PP/PS blends was deter-

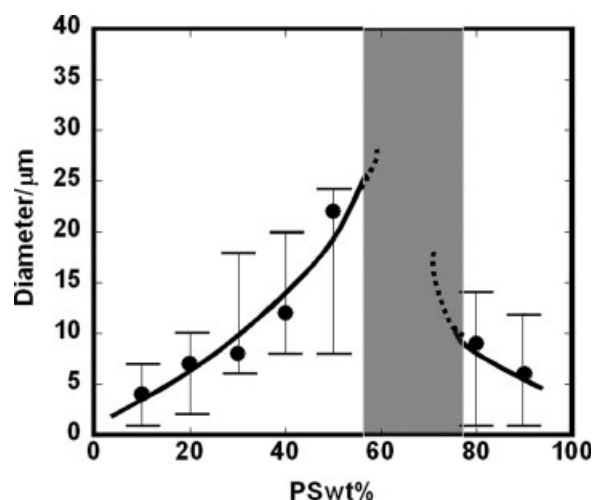


Figure 2 Diameter of dispersed domains in PP/PS blends plotted against the PS content.

TABLE I
Characteristics of PP/PS Blends

PP/PS (wt %/wt %)	0/100	10/90	20/80	30/70	40/60	50/50	60/40	70/30	80/20	90/10	100/0
Density (kg/m ³)	1045	1023	995	957	977	965	952	937	925	915	906
Crystallinity (wt %) of PP phase	–	–	–	–	–	42	45	43	46	50	54
Strength (MPa)	53	33	25	9	9	12	16	22	27	36	38
Strain at break	0.20	0.13	0.10	0.06	0.42	2.01	3.23	5.62	5.62	8.73	13.12

mined using following equation:

$$\chi_w = \frac{\rho^{-1} - \rho_{PS}^{-1}}{w_{PP}(\rho_c^{-1} - \rho_a^{-1})} + \frac{\rho_{PS}^{-1} - \rho_a^{-1}}{\rho_c^{-1} - \rho_a^{-1}} \quad (1)$$

where χ_w is the degree of crystallinity in weight fraction of PP phase, ρ is the overall density of PP/PS blends, ρ_c is the density of PP crystalline phase (936 kg/m³), ρ_a is the density of PP amorphous phase (854 kg/m³), ρ_{PS} is the density of PS phase (1045 kg/m³), and w_{PP} is the weight fraction of PP in PP/PS blends.

Scanning electron microscopy (SEM) images were taken to observe the morphology of PP/PS blends. The samples were cryogenically fractured in liquid nitrogen. The fractured surfaces of the samples were then sputter-coated with a gold thin layer, and investigated in a SEM instrument, Shimadzu-Super Scan 20, operating at 20 kV.

The morphological changes in drawn PP/PS blends were examined by means of polarized optical microscope (Olympus B201) equipped with a CCD camera.

RESULTS AND DISCUSSION

Figure 1 shows the examples of SEM morphologies of the PP/PS blends with a wide range of PS compo-

sition from 10 to 90 wt %. The samples were melt-pressed in a hot press at 503 K and under 10 MPa for 5 min and then quenched in the ice-water bath. The SEM pictures show that the blend morphologies are composed of spherical droplets of the minor component dispersed in the matrix component. The average size of dispersed droplets, estimated from the SEM pictures, linearly increases from 4 to 30 μ m when the PS content increases from 10 to 50 wt % whereas the droplet size of PP slightly decreases from 10 to 5 μ m at higher PS content above 80 wt % as shown in Figure 2. However, there are no clear droplet domains in the PP/PS blends with the range of around 70 wt % of PS content. The average droplet size of the blends with 60–70 wt % PS content has a wide distribution and their shape is ellipsoidal and distorted, suggesting that the phase inversion takes place at around 60–70 wt % of PS content. The region of the phase inversion was almost in agreement with that predicted by Jordhamo's model²² from the melt viscosity data of PP and PS employed here.

The densities of the PP/PS blends and the crystallinities of PP phase calculated from the density data using eq. (1) are summarized in Table I. The crystallinity of PP phase in the PP-matrix samples tends to decrease with increasing the PS content and reaches an approximately constant value of 43%. On the

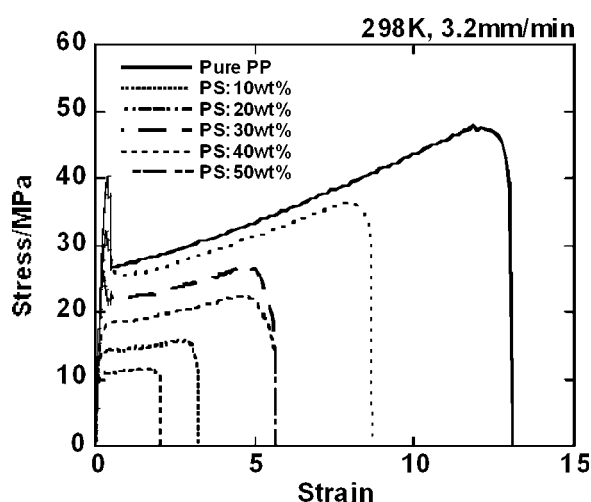


Figure 3 Stress-strain curves of PP-rich PP/PS blends.

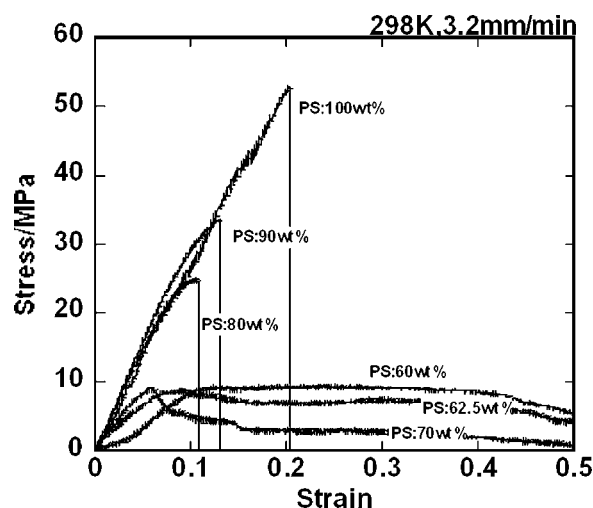


Figure 4 Stress-strain curves of PS-rich PP/PS blends.

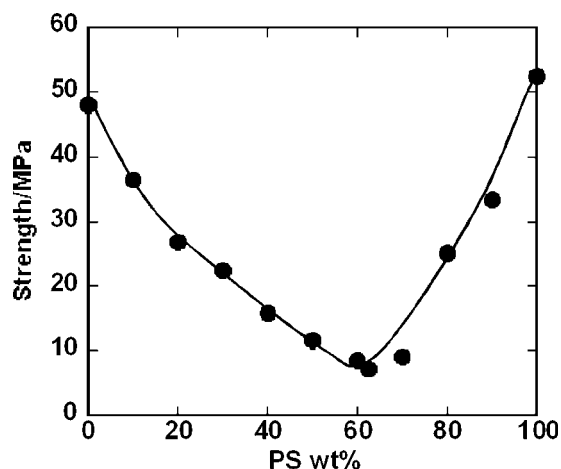


Figure 5 Strength estimated from the stress–strain curves plotted against the PS content in the PP/PS blends.

other hand, the PS-matrix samples showed considerable lower densities so that the crystallinity of the PP phase in the PS-rich samples failed to be determined from the density data. In this case, PP is organized in a spherical morphology as seen in Figure 1 and the PP droplets are placed in a state of negative pressure on cooling from the liquid state because the thermal expansion coefficient of PP is higher than that of PS,²³ as demonstrated for PS/polybutadiene blends by Bates et al.²⁴ The stress that is induced by the thermal expansion mismatch has possibly caused the cavitation or void-opening in the interfacial zone between PS matrix and PP droplets, which plays a central role in the craze initiation under tensile elongation.

Figures 3 and 4 compare the stress–strain curves measured at room temperature in PP-rich and PS-rich blends, respectively. The data of elongation at break and the tensile strength were listed in Table I. It was found that tensile behaviors of PP-rich and PS-rich blends are quite different from each other. The addition of PS in the PP-rich blends reduces the

overall stress level and markedly lowers the elongation at break. This is likely because PP and PS are completely immiscible and their blends exhibit a poor interfacial adhesion. On the other hands, PS-rich blends with 60–70 wt % of PS content showing no strict phase-separated morphology show a lower stress level and a higher drawability as compared with other PS-rich blends with PS content larger than 80 wt %. Considering that the PS is extremely brittle and the PP is highly ductile with a high ultimate elongation at room temperature, this result also demonstrates that the PS component forms a matrix in the blends with PS content from 70 to 100 wt % whereas the PP component becomes matrix in the blends with PS content up to 60 wt %.

The significant lower strength in the PS-rich blends led us to conclude that the brittle PS component is matrix phase and the ductile PP is the dispersed one in the PS-rich blends.²² The ductile–brittle transition takes place at around the 62.5 wt % PS content at which phase inversion occurs. Furthermore, as shown in Figure 4, the stress–strain curve of PP/PS blend with 62.5 wt % PS content is much different from those of other PS-rich blends and shows a relatively higher drawability and lower stress level, suggesting that the ductile PP forms a continuous phase in the blends.

The tensile strength is plotted against the composition for all the blend samples in Figure 5. The value of tensile strength monotonously decreases with increasing of PS content up to 62.5 wt % in which the minimum of tensile strength appears. Then, the strength inversely increases with increasing the PS content. Thus, the phase inversion occurs at the minimum of tensile strength as also demonstrated by Wang et al.²¹ This is consistent with the SEM results that PP component changes from the matrix phase to the dispersed phase at around 60–70 wt %.

The tensile deformation in the immiscible blends causes the interfacial detachment between domains

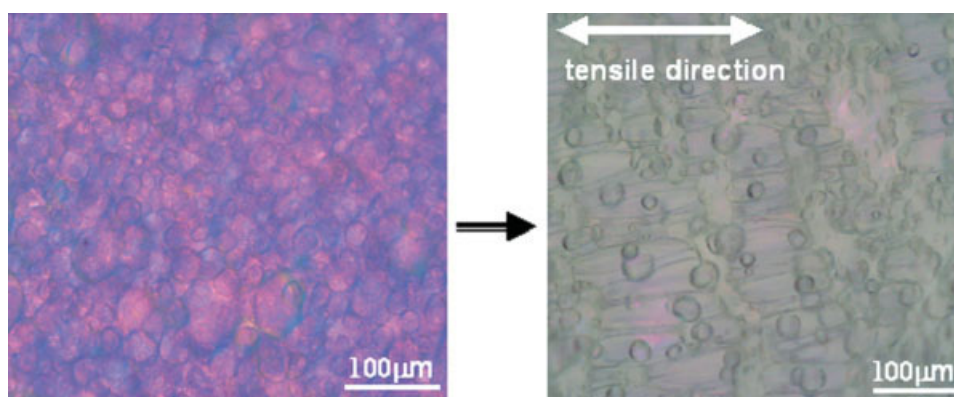


Figure 6 Polarized optical micrographs of undrawn and drawn PP/PS (50 wt %/50 wt %) blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

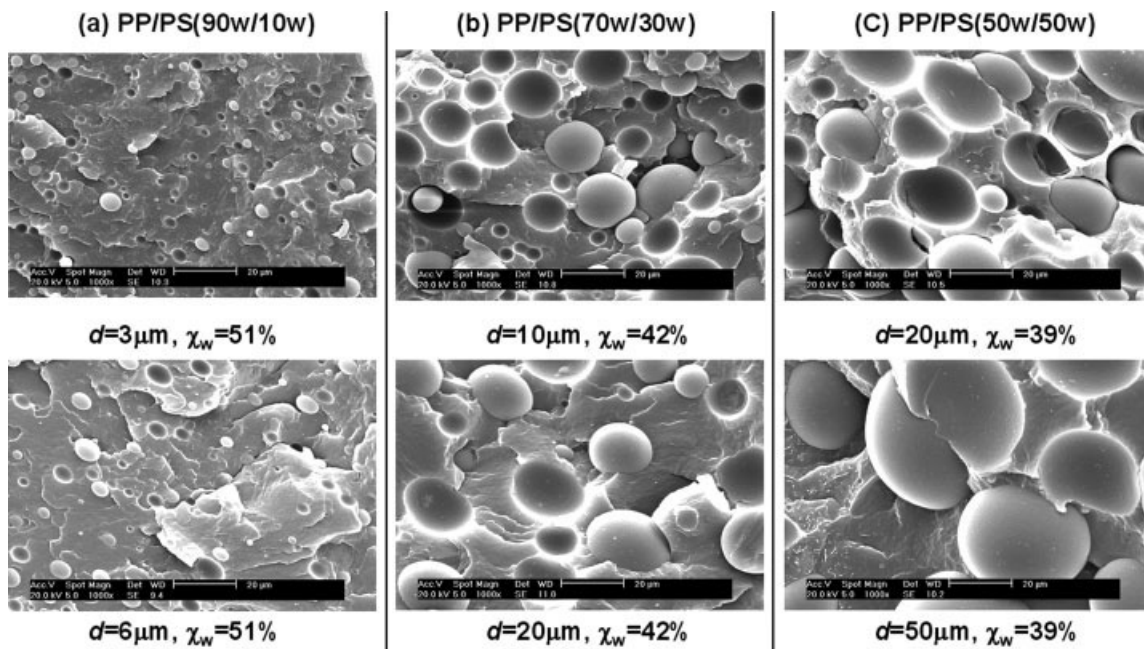


Figure 7 SEM micrographs of three PP/PS blends, (a) PP/PS (90 wt %/10 wt %); (b) PP/PS (70 wt %/30 wt %); (c) PP/PS (50 wt %/50 wt %), having a fixed crystallinity of PP phase and different sizes of PS droplets. The diameter d of PS droplets for these PP/PS samples reading off from the SEM pictures and the crystallinity χ_w of PP phase are cited below the pictures.

and matrix because of poor interfacial interaction. Figure 6 compares the POM pictures of the undrawn and drawn PP/PS (50 wt %/50 wt %) sheets with the PP matrix and dispersed PS phase. The drawn PP/PS sample was cut in planes perpendicular to the drawn direction of the sheets. One can observe the ellipsoidal void-opening around the PS droplets in the POM image of the drawn sample. The dispersed PS droplets are almost spherical and the shape of spherical droplets is unchanged by stretching. This indicates that the PS droplets are too rigid to be deformed. Thus, a part of the mechanical energy during elongation is expended in the interfacial detachment and the remainder is used for the deformation of the PP matrix. The interfacial detachment process reduces the stress level in the yielding process in the materials.

To investigate the effect of droplet size on tensile properties in the PP-rich blends, we prepared three pairs of the PP/PS samples having different compositions, each of which has a fixed crystallinity of PP matrix but different droplet sizes. The SEM pictures of morphology of three pairs of samples are shown in Figure 7. The droplet size was controlled by changing the holding time at 503 K and 10 MPa in the hot-press and the crystallinity in PP matrix was fixed for each sample by quenching them to 273K. As a result, the PP/PS (90 wt %/10 wt %) pair exhibits the PS droplet size of 3 μm and 6 μm under a fixed PP crystallinity of 0.51, the PP/PS (70 wt %/30 wt %) pair exhibits the PS droplet size of 10 μm

and 20 μm under a fixed crystallinity of 0.42, and the PP/PS (50 wt %/50 wt %) pair exhibits the PS droplet size of 20 μm and 50 μm under a fixed crystallinity of 0.39. As shown in Figure 7, the reached crystallinity in PP matrix decreases with increasing the PS content, suggesting that the addition of PS component reduces the crystallization rate of PP phase in the blends. Figure 8 compares the stress-strain curves of three pairs of the samples. It should be noted here that the overall stress level and the elongation at break decrease with increasing the PS

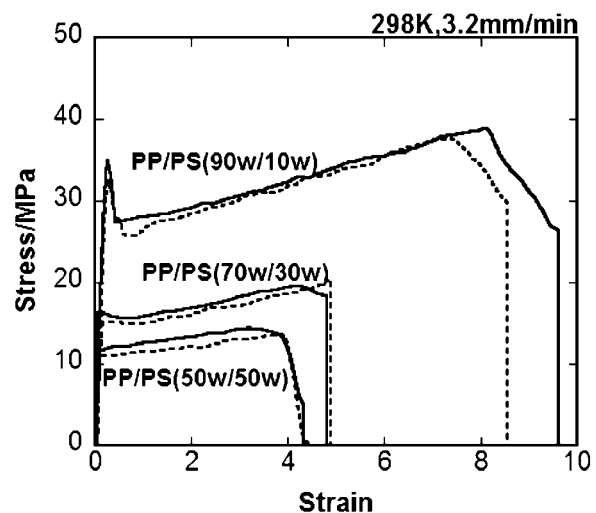


Figure 8 Stress-strain curves of the PP/PS blends shown in Figure 7.

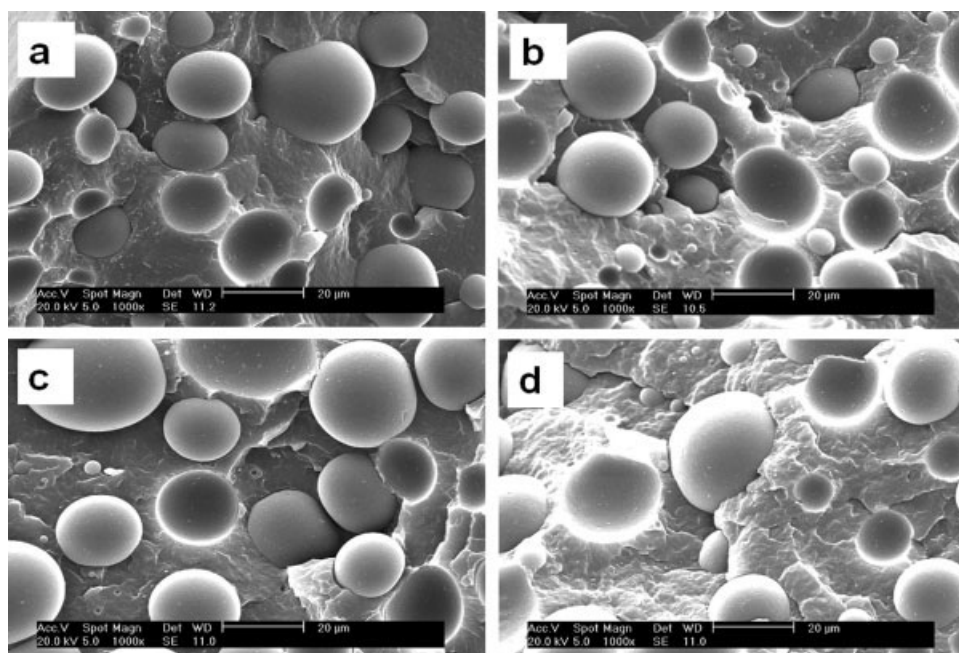


Figure 9 SEM micrographs of PP/PS(70 wt %/30 wt %) blends with various crystallinities of PP matrix: (a) 65 wt %, (b) 57 wt %, (c) 42 wt %, and (d) 34 wt %.

content but the stress–strain curves are almost same for each pair of PP/PS blends having a different size of PS droplets and a fixed crystallinity of PP phase. This demonstrates that the overall tensile behavior in the blends is essentially independent of the domain size of dispersed phase and dominantly dependent on the crystallinity of PP matrix.

To confirm the effects of crystallinity in PP matrix on tensile properties, we prepared four kinds of PP/PS (70 wt %/30 wt %) blends having different crystallinities, ranging from 0.34 to 0.65, at a fixed size (about 20 μm) of PS droplets. Figure 9 shows SEM

pictures of these PP/PS (70 wt %/30 wt %) blends having different crystallinities of PP phase. As shown in Figure 10, the increase of crystallinity in the PP matrix sharply leads to the increase of the overall stress level in stress–strain curves but to the decrease of the strain at break. Table II summarizes the strength and elongation at break. The crystallinity of PP matrix was confirmed to strongly affect the tensile properties in the PP/PS blends. The crystallinity of PP matrix dominates the tensile properties, suggesting that the PP matrix in the PP-rich blends is preferentially deformed under a uniaxial elongation owing to the interfacial separation between the rigid PS droplet and the ductile PP matrix.

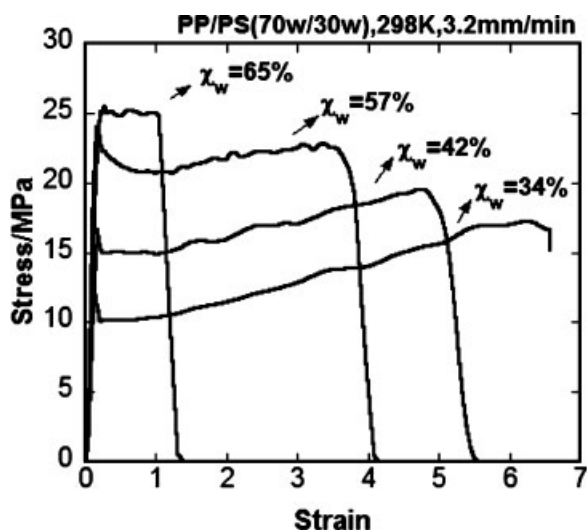


Figure 10 Stress–strain curves of the PP/PS blends shown in Figure 9.

CONCLUSION

This work has demonstrated the relationship between morphology and mechanical properties in binary blends of isotactic PP and atactic PS. It was found that the drastic change in the tensile proper-

TABLE II
Crystallinity and Mechanical Properties of PP/PS
(70 wt %/30 wt %) Blends

Crystallinity (wt %) of PP phase	Strength (MPa)	Strain at break
65	25	1.2
57	22	3.9
42	19	5.3
34	16	6.6

ties of the binary PP/PS blends occurs at 62.5 wt % PS content at which phase inversion occurs in PP/PS blends.

In this work, the PS domain size and crystallinity in PP phase were controlled by the preparation parameters such as holding time in the hot-press and quenching temperature. To examine the dominant factor for tensile properties in the immiscible PP/PS blends, the PP phase in the PP-rich PP/PS blends was found to be preferentially deformed under uniaxial elongation. Consequently, the size of the dispersed PS droplets did not affect the stress-strain curves in the PP-rich blends but the crystallinity in the PP matrix has influenced dominantly on the tensile properties in the PP-rich blends. This is plausible because the PS droplets are too rigid to be deformed in room temperature and the adhesion between PS droplets and PP matrix is poor.

The authors deeply appreciate Tokyo Printing Ink Manufacturing Company for the permission of publication.

References

1. Wilkinson, A. N.; Laugel, L.; Clemens, M. L.; Harding, V. M.; Marin, M. *Polymer* 1999, 40, 4971.
2. Wilkinson, A. N.; Clemens, M. L.; Harding, V. M. *Polymer* 2004, 45, 5239.
3. Ohisson, B.; Hassander, H.; Tornell, B.; *Polymer* 1998 39, 6705.
4. Kim, G.-M.; Michler, G. H. *Polymer* 1998, 39, 5689.
5. Kim, G.-M.; Michler, G. H. *Polymer* 1998, 39, 5699.
6. Taha, M.; Frerejean, V.; *J Appl Polym Sci* 1996, 61, 969.
7. Guo, H. F.; Meier, D. *J Polymer* 1998, 39, 2495.
8. Bureau, M. N.; Dickson, J. I. *Polym Eng Sci* 1997, 37, 377.
9. Sahnoune, F.; Lopezcuesta, J. M.; Crespy, A. *Polym Eng Sci* 2003, 43, 647.
10. Hermes, H. E.; Higgins, J. S. *Polym Eng Sci* 1998, 38, 847.
11. Fortelny, I.; Michalkova, D.; Mikesova, J. *J Appl Polym Sci* 1996, 59, 155.
12. Xie, Z.; Zhang, D.; Sheng, J.; Song, K. *J Appl Polym Sci* 2002, 85, 307.
13. Inbege, J. P. F.; Hunse, P. H.; Gaymans, R. J. *Polym Eng Sci* 1999, 39, 340.
14. Macaubas, P. H. P.; Demarquette, N. R. *Polymer* 2001, 42, 2543.
15. Halimatudahliana, A.; Ismail, H.; Nasir, M. *Polym Test* 2002, 21, 263.
16. Halimatudahliana, A.; Ismail, H.; Nasir, M. *Polym Test* 2002, 21, 163.
17. Lee, S.-G.; Lee, J. H.; Choi, K.-Y.; Rhee, J. M. *Polym Bull* 1998, 40, 765.
18. Albano, C.; Reyes, J.; Ichazo, M.; Gonzalez, J.; Hernandez, M.; Rodriguez, M. *Polym Degrad Stab* 2003, 80, 251.
19. Zhang, Q.; Yang, H.; Fu, Q. *Polymer* 2004, 45, 1913.
20. Rek, V.; Grguric, T. H.; Jelcic, Z. Hace, D. *e-Polymer* 2004, 34.
21. Wang, Y.; Xiao, Y.; Zhang, Q.; Gao, X.-L.; Fu, Q. *Polymer* 2003, 44, 1469.
22. Jordhamo, G.; Manson, J.; Sperling, L. *Polym Eng Sci* 1986, 26, 517.
23. Brandrup, J.; Immergut, E. N.; *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; Vol. 27.
24. Bates, F. S.; Cohen, R. E.; Argon, A. S. *Macromolecules* 1983, 16, 1108.