# Reactive Blending of Modified Polypropylene and Polyamide 12: Effects of Compatibilizer Content on Crystallization and Blend Morphology

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**ABSTRACT:** The crystallization behavior and morphology of nonreactive and reactive melt-mixed blends of polypropylene (PP) and polyamide (PA12; as the dispersed phase) were investigated. It was found that the crystallization behavior and the size of the PA12 particles were dependent on the content of the compatibilizer (maleic anhydride–modified polypropylene) because an *in situ* reaction occurred between the maleic anhydride groups of the compatibilizer and the amide end groups of PA12. When the amount of compatibilizer was more than 4%, the PA12 did not crystallize at temperatures typical for bulk crystallization. These finely dispersed PA12 particles crystallized coincidently with the PP phase. The changes in domain size with compatibilizer content were consistent with Wu's theory. These investigations showed that crystallization of the dispersed phase could not be explained solely by the size of the dispersion. The interfacial tension between the polymeric components in the blends may yield information on the fractionation of crystallization. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3187–3192, 2006

**Key words:** reactive processing; blends; compatibilization; crystallization; morphology

## INTRODUCTION

Blending polymers is an effective way to manufacture materials with the desired macroscopic properties.[1] However, because of the inherent thermodynamic incompatibility of mixtures of long-chain molecules, the interfacial tension between the components in a blend is relatively high. Consequently, the adhesion between these components is quite weak, and the material can exhibit poor mechanical properties. To enhance structural integrity, compatibilizers such as block or graft copolymers are commonly added to the blends. These additives lower the interfacial tension and drive the incompatible polymers to form small, well-dispersed domains.[2–4] As a result, the degree of intermixing between the components and the mechanical properties of the material is greatly improved. However, the effectiveness of these interfacial agents can be limited by the formation of copolymer micelles in one of the polymeric domains.[5,6] To alleviate this problem, researchers have utilized interfacially active chains that react to form copolymers *in situ* at the interfaces between the polymer phases. Thus, a procedure called "reactive blending" has been developed.[6–10] As an example, functional groups are commonly attached to *A* and *B* blocks, and these chains react to form diblock copolymers at the interface between the immiscible *A* and *B* homopolymers.[8] Although this approach has been highly effective, a complete understanding of the properties at the reactive interfaces is still lacking.

Polyamides are a family of engineering thermoplastics whose wet affinity limits their application. Their combination with lower-module but hydrophobic polymer–like polyolefins has therefore become a matter of interest for both their ultimate and their thermal and morphological properties.[11–14]

The reactions of maleic anhydride groups with the amine end groups of PA6 and PA66 have been well documented. However, PA12 has not been studied as extensively, and information about its crystallization and morphology is still scarce. Tang et al.[15] investigated the crystallization of blends between maleic anhydride–modified polypropylene and PA12. They considered heterogeneous nucleation to be a surface behavior. Therefore, nucleation of polypropylene (PP) by polyamide (PA12) only occurred in the interfacial zone. Because the PP showed epitaxial crystallization

on the PA12 surface, the heterogeneous nucleation by PA12 reduced the undercooling of PP crystallization, so the $T_c$ of PP increased. On the addition of compatibilizer, the decreased size of the dispersed phase (PA12) brought about an increased interface area, which promoted the nucleation of PP crystallization by PA12. The segments of the compatibilizers diffused into the corresponding miscible bulk polymer, behavior that was unfavorable to the growth of crystallization in the bulk polymer. However, the method used by Tang et al.[15] for preparing the blends had low efficiency, which must have had some effects on the blend structure and morphology.

This work investigated two important issues: (1) What is the effect of the interfacial reaction on crystalline properties and morphology in polymer reaction blends of PP and PA12 with various compatibilizer (maleic anhydride–modified polypropylene) contents? (2) What is the correlation of crystallization and blend morphology for the blends?

## EXPERIMENTAL

### Material and blend preparation

The neat PP used for the investigations was F401 (Pan Jing Petrochemical Co, Liaoyang, China); its melt index (MI) was 2.4 g/10 min (230°C/2.16 kg). Polypropylene modified with 0.6% maleic anhydride (PPs), supplied by the Aldrich Co., was used as compatibilizer. The PPs had an MI of 115 g/10 min (230°C/2.16 kg) and mass-average and number-average molar masses of $3.04 \times 10^4$ and $10.35 \times 10^4$ g/mol, respectively. PA12, also supplied by the Aldrich Co., was used as the blend partner; it had a density of 1.01 g/cm$^3$, a melt index of 13 g/10 min (230°C/2.16 kg), and a viscosity-average molar mass of $3.25 \times 10^4$ g/mol, as determined by a viscometer.

Before blending, all materials were dried under vacuum for 12 h at a temperature of 80°C to minimize the effect of moisture. Pellets of the components were mixed before blending. Blends were prepared in a Rheomix 600 mixer (Haake) equipped with a mixing head (50 cm$^3$) at 200°C. The rotation speed was fixed at 50 rpm; at that rotor speed, the maximum shear rate in the mixer was 65 S$^{-1}$. The mixing proceeded for 7 min. Compression-molded sheets about 1 mm thick were obtained using a self-made press at 200°C/50 kgf/cm$^3$ for 5 min and then cooled to ambient temperature in air. To investigate the effects of the compatibilizer content on crystallization and blend morphology, different weight percents of compatibilizer (PPs), 0, 2.4, 4, 8, 12, 15, 25, and 40 wt %, in the 80:20 (PP/PPs)/PA12 blend were investigated.

### Thermal analysis

Differential scanning calorimetry (DSC) measurements were conducted with a Perkin-Elmer DSC 7 at a scan rate of ±10 K/min under an N$_2$ atmosphere in a temperature range of 60°C–220°C. Automatic calibration was carried out using indium and zinc as standards. The sample mass used was 5–7 mg. The first heating scans showed the effects of different thermal histories as a consequence of nonidentical conditions during blend processing. Therefore, for characterization of the thermal properties, the cooling and the second heating scans were used. The heat of fusion and crystallization calculated for PP and PA12 were normalized to their content. The statistical error, which was estimated from the repeated measurements, was less than ±1 K for temperature and about 5% for the transition heats. Crystallinity was calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline samples: $\Delta H_{PP} = 137.9$ J/g[14] and $\Delta H_{PA12} = 95$ J/g.[16]

### Microscopy

To visualize the particles in the blends, the cryofractured surface was etched in m-cresol at ambient temperature for 12 h to remove the unreacted PA12. After drying, the etched surfaces were gold-sputtered and analyzed by a JEOL JXA-840 scanning electron microscope (Japan) or an XL-30-ESEM-FEG Field Emission scanning electron microscope (FEI; Philips) using an acceleration voltage of 20 kV. The micrographs for the quantitative analysis were acquired under comparable conditions.
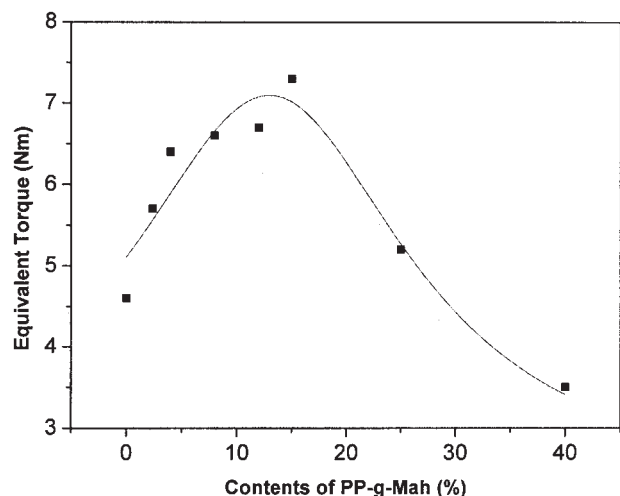
## RESULTS AND DISCUSSION

### Asymptotic mixing torque

During blending, the torque first rose quickly as the cold material was fed to the mixer. As the material was heated by shear and conduction, it softened, and the torque fell. The torque then leveled off to an asymptotic value for the rest of the mixing time.[17]

The asymptotic mixing torque versus the compatibilizer content of various blends is presented in Figure 1, which shows that the asymptotic mixing torque initially increased with the compatibilizer content and then decreased when the compatibilizer content was more than 12%. Because torque is an indication of melting viscosity, the increased asymptotic torque may be accounted for by the formation of high-molecular-weight species from the reaction between the maleic anhydride (MA) groups of the compatibilizer and the NH$_2$ end groups of PA12. It can be safely assumed that, under the experimental conditions, the maximum reaction occurred in blends with a compatibilizer content of about 12%.

Stoichiometric calculations indicated that equilibrium for the complete reaction of all reactive groups of the polymers ([MA] = [NH$_2$]) was obtained for a

**Figure 1** Asymptotic mixing torque as a function of compatibilizer content.



**Figure 2** Second fusion thermogram for the neat homopolymers and the indicated blends.

PP/PPs/PA12 blend whose composition ratio was close to 70:10:20. Therefore, when the content of compatibilizer was more than 10%, the end $NH_2$ groups of PA12 reacted almost completely with MA. Because asymptotic torque consists of the intrinsic torque of the component and the torque induced by the increased molecular weight from the chemical reaction during blending, superfluous compatibilizer content only resulted in a decrease in asymptotic torque because of its far lower viscosity.

It was reported[15] that the PP segments of the compatibilizer cocrystallized with the bulk PP to yield partial compatibilization of the two components. The polar parts of the compatibilizer were thought to be partially compatible with the PA12 in two possible ways: (1) the $NH_2$ end groups of the PA12 would react with the MA of the compatibilizers to form a new graft copolymer, (PP-MA)–$g$–PA12, that should be a good compatibilizer for the PP/PA12 blends; (2) the unreacted MA of the compatibilizers might have a strong dipole/dipole interaction and weak H-bonding with the CONH groups of PA12. The conditions in which we prepared the blends were favorable for the formation of (PP-MA)–$g$–PA12, it was mainly the formation of (PP-MA)–$g$–PA12 by the reaction that was responsible for the compatibilizing effect, and the dipole/dipole interaction between the unreacted MA and the CONH groups of PA12 was merely secondary.

## Concurrent crystallization

In crystalline/crystalline polymer blends, there exists a mutual effect on the crystalline structures and crystallization behavior between the two components. Figure 2 shows the DSC scans for the neat polymers and the corresponding blends of PP/PA12 with various amounts of compatibilizer. It shows that the melting
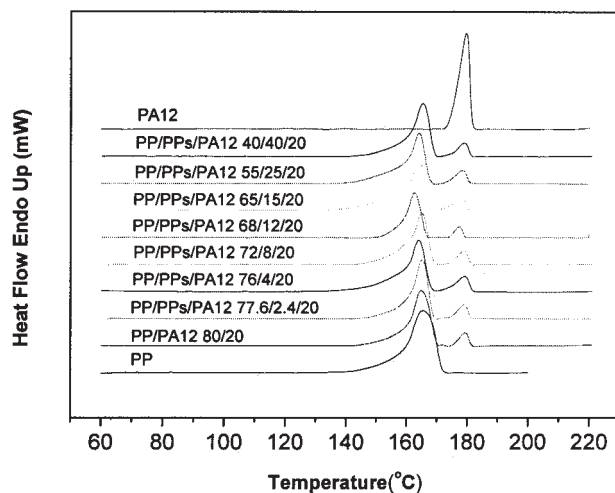
behavior of PP and PA12—as a measure of PP and PA12 crystallinity—was similar in all blends. This was predictable because the fraction of the interfacial area was small. The compatibilization effects could be observed in the corresponding cooling cycles (Fig. 3). The corresponding values of the crystallization temperature, crystallization enthalpy, and crystallinity are listed in Table I. The results of the present work show that after blending, the crystallization temperature, $T_c$, of PP increased by up to 4.9°C (Fig. 3, Table I). At the same time, the height of the crystallization peak of PP increased as well. After the compatibilizer was added, the $T_c$ of PP increased further, showing an increase in the nucleation of PP by PA12. The increasing amount of the compatibilizer caused a large decrease in the enthalpy associated with the crystallization of PA12, which completely disappeared when the amount of
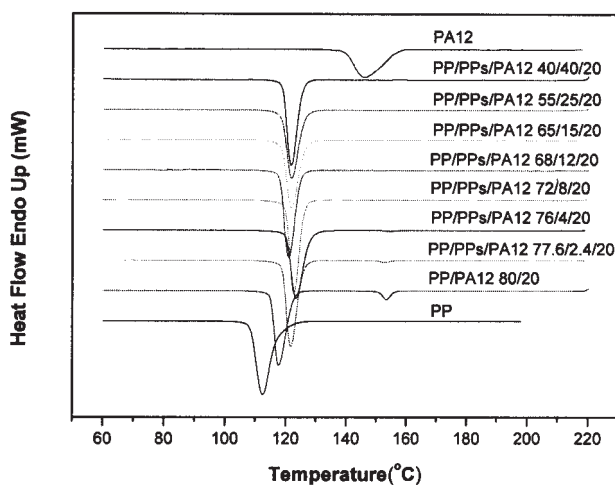


**Figure 3** Crystallization thermogram for the neat homopolymers and the indicated blends.

**TABLE I**
Crystallization Temperature ($T_c$) crystallization enthalpy ($\Delta H_{cr}$) and Crystallinites [$1 - \lambda \times 100$] for PP and PA12
Phases in Neat Homopolymers or Indicated Blends

| | $T_c$ (°C) | | $\Delta H_c$ (J/g)[a] | | $(1 - \lambda) \times 100$ | |
| --- | --- | --- | --- | --- | --- | --- |
| | PP | PA 12 | PP | PA 12 | PP | PA 12 |
| PP | 112.5 | | −93.6 | | 67.8 | |
| PP/PA 12 = 80/20 | 117.6 | 153.4 | −79.5 | −7.5 | 72.1 | 39.5 |
| PP/PPs/PA 12 = 77.6:2.4:20 | 121.7 | 152.7 | −84.8 | −2.4 | 76.9 | 12.8 |
| PP/PPs/PA 12 = 76:4:20 | 123.4 | 154.9 | −83.3 | −1.0 | 75.5 | 5.1 |
| PP/PPs/PA 12 = 72:8:20 | 122.7 | / | −85.9 | / | 77.8 | / |
| PP/PPs/PA 12 = 68:12:20 | 121.0 | / | −86.0 | / | 78.0 | / |
| PP/PPs/PA 12 = 65:15:20 | 120.7 | / | −85.3 | / | 77.3 | / |
| PP/PPs/PA 12 = 55:25:20 | 121.9 | / | −84.7 | / | 76.8 | / |
| PP/PPs/PA 12 = 40:40:20 | 121.7 | / | −85.2 | / | 77.2 | / |
| PA 12 | | 147.9 | | −58.6 | | 39.3 |

[a] Calculated on the basis of the crystallization enthalpy divided by the weight fraction of the respective polymer.

compatibilizer was greater than 4%. In contrast, the enthalpy associated with the crystallization of PP increased synchronously. Therefore, we concluded that the crystallization of PA12 was suppressed and transferred partially or entirely into that of PP. This can be explained in terms of the fractionated crystallization.[18,19] Nucleation was expected to be the rate-determining step of the crystallization process for the minor crystalline component in the limit of very fine dispersion. The number of droplets of the minor component could become larger than the number of main nucleating heterogeneities, and the nucleation could then be controlled by another type of heterogeneity. In this case, the addition of compatibilizer would fractionate the crystallization procedure of PA12: one at the $T_c$ of PA12 and the other that of PP in the blends. The addition of more than 4% compatibilizer was able to almost completely suppress the crystallization of PA12 at its $T_c$. The crystallization of PA12 at the $T_c$ for PP does not mean that PA12 cocrystallized with PP, because each component showed a separate melting endotherm, as shown in Figure 2. The coincident crystallization of PA12 with PP was a concurrent crystallization.[20]

## Blend morphology

The morphological characteristics of the blends are illustrated in the SEM micrographs of Figure 4(a–h), which show that when there was no compatibilizer in the blends, the average domain size (circle diameter) of the dispersed phase was about 5.0 $\mu$m and the size distribution was broad. This indicates that insufficient phase adhesion had developed [Fig. 4(a)]. When compatibilizer was added in a concentration of only 2.4%, the average domain size decreased to about 1.3 $\mu$m. With further increases in the amount of compatibilizer, the domain size decreased significantly. It was only 0.29 $\mu$m with the addition of 12% compatibilizer.

However, once the addition of compatibilizer was in excess, domain size increased again. The average domain size increased to 1.2 $\mu$m when the amount of the compatibilizer reaches 40%.

The relationship between dispersed domain size and interfacial tension can be calculated by the following equation[21]:

$$\gamma \eta_m d_n / \sigma = 4(p)^{\pm 0.84} \tag{1}$$

where the result is positive when $p > 1$ and negative when $p < 1$ and where $\gamma$ is the shear rate adopted in preparing the blend, $d_n$ is the particle diameter (circle diameter), $\sigma$ is the interfacial tension, and $p = \eta_d / \eta_m$ is the viscosity ratio ($\eta_m$ is the matrix viscosity, and $\eta_d$ is the dispersed-drop viscosity). This expression was derived on the basis of the balance between the shearing force, which tends to deform the minor phase into droplets, and the interfacial tension, which tends to restore the spherical shape of the minor phase. In our blends, the same mixing process was adopted. This meant that the parameter $\gamma$ could be assumed to be constant when $\gamma = 65$ S$^{-1}$. It provides a useful approach for quantitative measurement of interfacial tension. Combining the viscosity as measured by rheometry with the average domain size (circle diameter) of the dispersed phase, we calculated the interfacial tension of various components as listed in Table II. The results showed that mean interfacial tension was about 9.5 m/Nm for the blends without compatibilizer; with an increasing concentration of compatibilizer, interfacial tension decreased gradually to the minimum, 0.43 m/Nm, reached when 12% compatibilizer was added. Increasing compatibilizer content just led to an asymptotic interfacial tension of about 0.75 m/Nm.

On the basis of the above results, we consider it probable that the dispersed phase was smaller in the reactive blends than in the nonreactive blends because
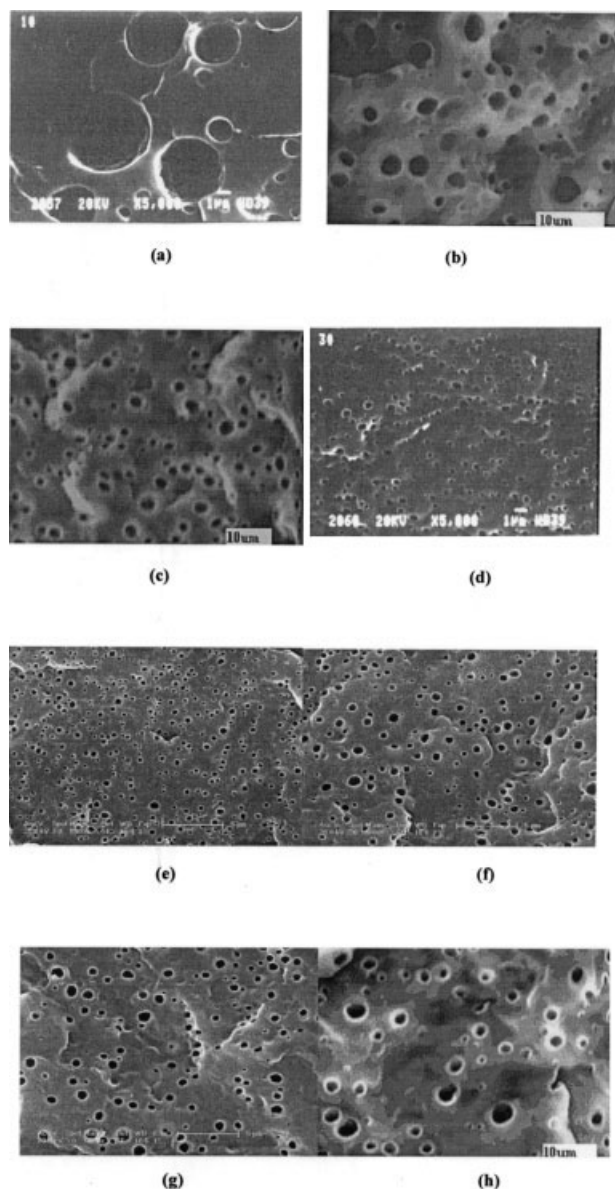
**Figure 4** SEM of cryofractured surface after etching the PA12 for blends of (a) PP/PA12 = 80:20, (b) PP/PPs/PA12 = 77.6:2.4:20, (c) PP/PPs/PA12 = 76:4:20, (d) PP/PPs/PA12 = 72:8:20, (e) PP/PPs/PA12 = 68:12:20, (f) PP/PPs/PA12 = 65:15:20, (g) PP/PPs/PA12 = 55:25:20 and (h) PP/PPs/PA12 = 40:40:20 (magnification: 5000×).

of the effects of (1) reduction of the effective interfacial tension between the phases and (2) inhibition of particle coalescence by the copolymer at the interface. This is consistent with previous conclusions.[22,23]

## Correlation of morphology and concurrent crystallization

We have shown that the *in situ* interfacial reaction between the modified blend components resulted in compatibilization connected to the blend having a more finely dispersed morphology and to the appear-

ance of fractionated crystallization. There is a critical particle size, $d_{cr}$, which explains the effect of the fractionated crystallization of the dispersed blend phase.[24,25] Crystallization in particles smaller than $d_{cr}$ did not occur at temperatures typical for bulk behavior.

In our case, when compatibilizer content was not in excess, that is, less than 12%, the average domain size (circle diameter) of the dispersed phase decreased from about 5.0 to 0.40 $\mu$m, the enthalpy associated with the crystallization of PA12 decreased from 7.5 J/g to zero and was conductive to fractionated crystallization. When the domain size of 0.40 $\mu$m equaled the critical particle size, $d_{cr}$, PA12 did not crystallize normally, and coincident crystallization of both PP and PA12 occurred. PP crystals induced the crystallization of submicroscale PA12 particles. When compatibilizer content was 12%, the average domain size of the dispersed phase reached a minimum value because the maximum reaction occurred during the blending.

It was predictable that the size of the PA12 dispersion and the interfacial tension between the blend components decreased with increasing concentration of compatibilizer in the blend, although compatibilizer content was not in excess. The more compatibilizer was added to the blends, the more (PP-MA)–*g*–PA12 copolymer was formed at the expense of PA12 in the blends. Thus, the PA12 particles became enclosed with more (PP-MA)–*g*–PA12 copolymer. As a result, the size of the PA12 particles in the blends decreased with reduction in interfacial tension between the PP and the PA12 phases. The *in situ*–formed graft copolymer, (PP-MA)–*g*–PA12, played some role in the concurrent crystallization, reducing interfacial tension and increasing the dispersiveness of PA12.

In contrast, with excess compatibilizer content, that is, above 12%, the average domain size increased. However, it did not show any crystallization of PA12 at its $T_c$. It seems that in the compatibilized blends, the

**TABLE II**
**Predicted Interfacial Tension According to Viscosity Ratio and Dispersed Particle Size**

| Blend | $\eta_m$ (Pa S)[a] | $P$[b] | $d_n$ ($\mu$m) | $\gamma$ (mN/ m) |
|---|---|---|---|---|
| PP/PA 12 = 80:20 | 217 | 2.04 | 5.0 | 9.5 |
| PP/PPs/PA 12 = 77.6:2.4:20 | 211 | 2.10 | 1.3 | 2.4 |
| PP/PPs/PA 12 = 76:4:20 | 207 | 2.14 | 1.0 | 1.8 |
| PP/PPs/PA 12 = 72:8:20 | 198 | 2.24 | 0.40 | 0.65 |
| PP/PPs/PA 12 = 68:12:20 | 188 | 2.36 | 0.29 | 0.43 |
| PP/PPs/PA 12 = 65:15:20 | 181 | 2.45 | 0.52 | 0.72 |
| PP/PPs/PA 12 = 55:25:20 | 157 | 2.82 | 0.66 | 0.71 |
| PP/PPs/PA 12 = 40:40:20 | 121 | 3.66 | 1.2 | 0.78 |

[a] Viscosity of the polymer was measured at 200°C with a rheometer.
[b] Calculated on the basis of $\eta_d$ = 443 (Pa S).

crystallization of the dispersed phase cannot be explained solely by the size of the dispersion. In line with Wu's theory,[20] interfacial tension ($\sigma$) can be thought of as asymptotic. This is predictable if the interfacial coupling reaction is definite. The thick interlayer between the two phases inhibited the nucleating activity of the dispersed PA12 phase. The results revealed that the interfacial tension between the polymeric components in the blends could yield information on the fractionation of crystallization.

## CONCLUSIONS

We investigated melt-mixed blending of nonreactive and reactive blends that used PP as the matrix component and PA12 as the dispersed phase. In the reactive blends, the maleic anhydride–modified PP apparently reacted with the amide end groups of the PA12, which was responsible for the compatibilizing effect. The asymptotic mixing torque initially increased with compatibilizer content and then decreased because of its far lower viscosity.

The compatibilized blends showed fractionated crystallization, which depended on compatibilizer content. An increasing amount of compatibilizer caused a large decrease in enthalpy that was associated with the crystallization of PA12, which completely disappeared when the concentration of compatibilizer was more than 4%. These finely dispersed PA12 particles crystallized coincidently with the PP phase.

The chemical reaction at the interface reduced the average size of the dispersed phase. The domain size changed with the content of compatibilizer, which is consistent with Wu's theory.

The *in situ* interfacial reaction in the modified blend component resulted in compatibilization connected with a more finely dispersed blend morphology and the appearance of fractionated crystallization. The *in situ*–formed graft copolymer (PP-MA)–*g*–PA12 played a role in concurrent crystallization by reducing interfacial tension and increasing the dispersiveness of PA12. However, the crystallization of the dispersed phase cannot be explained solely by the size of the dispersion. The interfacial tension between the polymeric components in the blends may yield information on the fractionation of crystallization.

## References

1. Paul, D. R.; Newman, S. Polymer Blends; Academic: New York, 1978; Vol. 2.
2. Lyatskaya, Y.; Gersappe, D.; Gross, N. A.; Balazs, A. C. J Phys Chem 1996, 100, 1449.
3. Gersappe, D.; Irrine, D.; Balazs, A. C.; Liu, Y.; Sokolov, J.; Rafailovich, M.; Schavarz, S.; Peiffer, D. G. Science 1994, 265, 1072.
4. Macosko, C. W.; Guégan, P.; Khandpur, A. K.; Inoue, T. Macromolecules 1996, 29, 5590.
5. Dai, H. K.; Kramer, E. J.; Shull, K. R. Macromolecules 1992, 25, 220.
6. Tan, N. C. B.; Tai, S. K.; Briber, R. M. Polymer 1996, 37, 3509.
7. Marco, C.; Collar, E. P.; Areso, S.; García-Martínez. J Polym Sci B: Polym Phys 2002, 40, 1307.
8. Wu, S. Polymer 1985, 26, 1855; Koberstein, J. MRS Bull 1996, 21, 19.
9. Scott, C.; Macosko, C. W. J Polym Sci B: Polym Phys 1994, 32, 205.
10. Yin, Z.; Koulic, C.; Pagnoulle, C.; Jérôe, R. Macromolecules 2001, 34, 5132.
11. Majumdar, B.; Paul, D. R.; Oshinski, A. J. Polymer 1997, 38, 1787.
12. Charoensirisomboon, P.; Inoue, T.; Weber, M. Polymer 2000, 41, 4483.
13. Marco, C.; Ellis, G.; Gómez, M. A.; Fatou, J. G.; Arribas, J. M.; Campoy, I.; Fontecha, A. J Appl Polym Sci 1997, 65, 2665.
14. Campoy, I.; Arribas, J. M.; Zaporta, M. A. M.; Marco, C.; Gómez, M. A.; Fatou, J. G. Eur Polym J 1995, 31, 475.
15. Tang, T.; Li, H.; Huang, B. Macromol Chem Phys 1994, 195, 2931.
16. Brandrup, J.; Immergut, E. H. Polymer Handbook, 4th ed.; Interscience: New York, 1999.
17. Scott, C. E.; Macosko, C. W. Polymer 1994, 35, 5422.
18. Tang, T.; Lei, Z.; Zhang, X.; Chen, H.; Huang, B. Polymer 1995, 36, 5061.
19. Tang, T.; Lei, Z.; Huang, B. Polymer 1996, 37, 3219.
20. Moon, H. S.; Ryoo, B. K.; Park, J. K. J Polym Sci B: Polym Phys 1994, 32, 1427.
21. Wu, S. Polym Eng Sci 1987, 27, 335.
22. Liu, N. C.; Baker, W. E. in Reactive Modifiers for Polymers; Al-Maleika, S., Ed.; Chapman and Hall: London, 1997; Chapter 4.
23. Datta, S.; Lohse, D. J. Polymeric Compatibilizers—Uses and Benefits in Polymer Blends; Carl Hanser: Munich, Vienna, New York, 1996.
24. Frensch, H.; Harnischfeger, P.; Jungnickel, B. J. In Multiphase Polymers: Blends and Ionomers; Utracki, L. A.; Weiss, R. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 1989; Chapter 5.
25. Pompe, G.; Pötschke, P.; Pionteck, J. J Appl Polym Sci 2002, 86, 3445.