Impact-Modified Blends of Compatibilized Polyamide-6 with Liquid Crystalline Copolyester

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ABSTRACT: Compatibilized blends of polyamide-6 (PA6) and thermotropic liquid crystalline polymer (LCP) modified with various high-impact polypropylene (HIPP) contents were injection-molded. These blends were compatibilized with maleic anhydride-grafted polypropylene (MAP). The effects of impact modification on the morphology, impact, static, and dynamic mechanical properties were investigated. The results showed that the HIPP addition leads to an improvement of the Izod impact strength of the blends significantly while it reduced the tensile strength and stiffness properties. An attempt was made to correlate the structure of the PA6(MAP)/HIPP/LCP blends from the scanning electron microscopic observations with the measured mechanical properties. This work provides a way to produce a tough *in situ* composite. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1611–1619, 1998

Key words: impact modifier; tensile property; liquid crystalline polymer; polyamides; maleic anhydride; electron microscopy

INTRODUCTION

Recently, there has been considerable interest in blends of commercial thermoplastics with liquid crystalline polymers (LCPs).^{1–6} The main benefits of using LCPs as blend components are that (1)the low viscosity of the LCPs can reduce the overall viscosity of the blend, with consequent improvement of processability, and (2) the LCPs can form a fibrillar structure in the thermoplastic matrix at proper compositions and under elongational flow. In the latter case, the LCP as a minor component is spontaneously oriented in the flow direction and forms in situ fibrils that reinforce the thermoplastic matrix. The spontaneous ordering of LCP molecules can be preserved upon solidification from the melt. This class of polyblends is termed in situ composites. Not all LCP blends with commercial thermoplastics can produce in

Journal of Applied Polymer Science, Vol. 70, 1611–1619 (1998) © 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/081611-09 *situ* composites. It is generally known that the mechanism of forming LCP fibrils is controlled by factors such as flow mode, viscosity ratio, blend composition, and interfacial tension.

The melt of the LCP/thermoplastic blends are considered to be incompatible. The incompatibility between the LCP domains and the thermoplastic matrix leads to poor interfacial adhesion. Consequently, the reinforcing effect is considerably lower than that obtained from the compatible system. The interfacial adhesion between the blends can be enhanced through the addition of suitable compatibilizers. Baird and coworkers^{7,8} used maleic anhydride-functionalized polypropylene (MAP) to compatibilize the blend of polypropylene (PP) with an LCP. They observed that the tensile modulus and strength of PP/LCP blends are improved significantly by adding a small amount of MAP. This is due to the functional groups of MAP that react with the amide end groups of the LCP, thereby giving rise to the formation of hydrogen bonds between them.⁸

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Compatibilized blends of polyamide (PA) with PP can offer a wide range of useful characteristics such as low water adsorption, good chemical resistance, and reduced cost.⁹ The mechanical properties of compatibilized PA/PP blends depend significantly on the ratio of PA to PP, and the higher mechanical properties for these blends are obtained when the PA6 is the continuous phase.¹⁰ Generally, the PA/PP blends exhibit a low notched impact strength. Gonzalez-Montiel et al. reported that an MA-grafted random copolymer of ethylene and propylene (EPR) acts as an effective compatibilizer and impact modifier for the PA6/PP blends.⁹ These maleated rubber particles lower the ductile-brittle transition temperatures significantly.

In a previous study,¹¹ we investigated the effect of compatibilization of MAP on the mechanical properties of PA6/LCP blends. The results showed that the tensile strain-at-break and critical strain energy release rate (G_{IC}) are dependent on the MAP concentration. The 80% PA6(MAP) (86/14)-20% LCP blend was found to exhibit the highest strain-at-break and $G_{\rm IC}$ values. Further increasing MAP content led to a sharp decrease in the $G_{\rm IC}$ value. Moreover, we also reported that one-step direct injection molding of PA6/MAP and LCP pellets results in the formation of an *in situ* composite associated with the fibrillation of LCP domains in the PA6(MAP)/ LCP blends.¹² Tensile measurements revealed that the tensile strength and modulus increase with increasing LCP content, and the static mechanical properties are above predictions from the rule of mixtures. The LCP content has a marked influence on the tensile ductility and impact toughness of the PA6(MAP)/LCP blends. The $G_{\rm IC}$ value of PA6(MAP) blend is 10 kJ/m² and it decreases to ~ 3.4 kJ/m² with the incorporation of 20% LCP in the blend.¹² To improve the tensile ductility and impact strength of the PA6(MAP) (86/14)/LCP blend, we attempt to incorporate an impact-modified PP, that is, high-impact polypropylene (HIPP) into the matrix of this blend. The morphology, tensile, and impact properties of the 80% PA6(MAP) (86/14)-20% LCP blend containing various HIPP contents were investigated.

EXPERIMENTAL

Materials

The LCP used in this work was Vectra A950 produced by the Hoechst Celanese Co. (Chatham, NJ). This LCP is based on 2,6-hydroxynaphthoic acid (HNA) and *p*-hydroxybenzoic acid (HBA). Russian-made PA6 pellets (PA6-120/321) and PP supplied by Himont (Wilmington, DE; Profax 6331) were used as the matrix material. The maleic anhydride (MA) supplied by Fluka Chemie (Buch, Switzerland) and dicumyl peroxide (DCP) produced by the Aldrich Chemical Co. (Milwaukee, WI) were used for the maleation of PP. The HIPP was received from Himont (KS-059P). The HIPP was an ethylene–propylene copolymer with a melt flow index of 10 g min⁻¹, yield strength of 5.5 MPa, and flexural modulus of 130 MPa.

Blend Compounding

The PA6 and LCP pellets were dried at 100°C in an oven for 24 h prior to blending. The maleated PP designated as MAP was prepared in a twinscrew Brabender plasticorder at 220°C and 15 rpm by a one-step reaction of PP with MA in the presence of DCP. The weight concentration ratio of PP, MA, and DCP was fixed at 94 : 6 : 0.3. The extrudate was cut into pellets by a pelletizer. Subsequently, 86 wt % PA6 and 14 wt % MAP were mixed in the Brabender at 260°C and at 35 rpm. The extrudate was also pelletized and it is designated as PA6(MAP) in this article. The PA6(MAP) pellets were mixed with 5, 10, 20, 30, and 40 wt % HIPP, respectively, in the Brabender at 260°C and 35 rpm. These blends were also pelletized.

Finally, the PA6(MAP)/HIPP granulated compounds containing various proportions of HIPP and LCP pellets were injection-molded using a Chen-Hsong machine. Both plaques with a thickness of 6 mm and tensile bars according to ASTM D-638 were produced. Only one composition level of LCP was prepared based on the relative weight of PA6(MAP)/ HIPP, that is, 20%. A typical representative designation for the injection-molded blend containing 5 wt % HIPP is 80%[95%PA6(MAP)– 5%HIPP]–20%LCP. The injection-molding parameters are summarized in Table I.

Scanning Electron Microscopy

The morphology of the fracture surfaces of the injection-molded blends was observed in a scanning electron microscope (JEOL JSM 820). The specimens were fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of gold before observation.

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Parameter	Nozzle	Zone 1	Zone 2	Nozzle
Temperature (°C)	285	290	285	40
	Injection I		olding	
Pressure (kg/mm ²)	11		9	

Table IInjection-Molding Parametersfor PA6(MAP)/HIPP/LCP System

Mechanical Properties

The tensile behavior of the specimens was determined using an Instron tensile tester (Model 4206) at 23°C. A cross-head speed of 1 mm min⁻¹ was used in the test. Five specimens of each composition were tested and the average values reported.

Notched Izod impact specimens with dimensions of $65 \times 12.7 \times 6$ mm were prepared from the injection-molded plaques. The length direction of the impact specimens was parallel to the mold filling direction. Five specimens were tested and the average values reported.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) of the injection-molded specimens was conducted with a DuPont dynamic mechanical analyzer (Model 983) at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm. The temperature range studied was from -50 to 160° C with a heating rate of 2°C min⁻¹.

Molecular Weight Determination

The molecular weight of the PA6(MAP) matrix was determined using an Ubbelohde viscometer at a concentration of 0.5 g/dL in formic acid at 25°C.

RESULTS AND DISCUSSION

Grafting Efficiency

Figure 1 shows the percentage grafting efficiency (Ge) versus the reaction time for the MAP specimen. The grafting content in maleated PP was determined by the chemical titration method. The percentage grafting efficiency of MA grafted onto

PP was calculated according to the following equation:

Ge = Gm/(mmol of charge MA per 100 g PP)

$$\times 100\%$$
 (1)

where Gm is the millimolecules of MA grafted onto 100 g of PP. From Figure 1, it is evident that the grafting efficiency approaches a plateau value of about 25% after a 5-min reaction time. This implies that the efficiency of grafting is relatively low. In this case, a large amount of unreacted MA is present in the MAP specimen.

Mechanical Properties

Figures 2(a,b) show the variations of tensile strength and tensile modulus of the 80% PA6-(MAP)-20%LCP blend with HIPP content. It is evident that both the tensile strength and modulus decrease dramatically with the addition of HIPP content up to 10 wt %; thereafter, they show a steady decrease with increasing HIPP concentration. This behavior is as expected as the addition of an impact modifier generally leads to a decrease in tensile strength and stiffness of the polymer blends. Figure 3 shows the Izod impact strength as a function of the HIPP concentration. It can be seen that the impact strength increases monotonically with HIPP content up to 20 wt %. At this HIPP concentration, the impact strength is four times higher than that of the blend containing no impact-modified PP. Apparently, the



Figure 1 Efficiency of grafting versus reaction time for the MAP specimen.



Figure 2 Variations of (a) tensile strength and (b) modulus of 80%PA6(MAP)–20%LCP specimens with HIPP content.

increase in the impact toughness of the blends is obtained at the expense of stiffness and strength. From Figure 3, the impact strength shows little variation with HIPP content at and above 20 wt %, and this is likely due to the existence of HIPP domains which have poor interfacial adhesion with the polymer matrix. This implies that HIPP is incompatible with the PA6(MAP) matrix. In other words, a phase-separated morphology can be observed for the blends containing HIPP content ≥ 20 wt %.

In the present work, LCP content is fixed at 20%. Previous work has shown that the tensile and impact properties of PA6(MAP)–LCP blends depends significantly on the LCP content.¹² Both the tensile strength and modulus show an in-

crease with increasing LCP content while the impact toughness decreases sharply with increasing LCP content. Furthermore, numerous high-extended LCP fibrils are formed in the skin and core sections of the PA6(MAP)-20%LCP blend. In this respect, LCP fibrils reinforce the PA6(MAP) matrix effectively. Therefore, the addition of 20% LCP to PA6(MAP) leads to an increase in both stiffness and tensile strength but a decrease in tensile ductility and impact toughness. The improvement in mechanical strength can be attributed to that MAP acts as an effective compatibilizer for PA6/LCP blends, thereby resulting in the formation of elongated LCP fibrils.¹² It is noted that the addition of HIPP up to 20 wt % content in this work has little effect on the compatibility between LCP and PA6(MAP) as evidenced by DMA in the next section. However, addition of an HIPP content above 20 wt % results in the incompatibility between the LCP and PA6(MAP) matrix.

Interaction Energy Density

According to the Flory-Huggins theory,¹³ the Gibbs free energy per unit volume of mixing two dissimilar polymers of A and B is given by

$$\frac{\Delta G}{(V_A + V_B)} = RT \left(\frac{\rho_A \phi_A}{M_A} \ln \phi_A + \frac{\rho_B \phi_B}{M_B} \ln \phi_B \right) + \chi \phi_A \phi_B \quad (2)$$



Figure 3 Variation of Izod impact strength of 80%PA6(MAP)-20%LCP specimens with HIPP content.



Figure 4 Calculated interaction energy density versus HIPP content for blends of PA6(MAP) and HIPP. The χ values in the shaded zone were calculated from eq. (5) on the basis of the range of estimated values for solubility parameters.

where ϕ_i is the volume fraction; ρ_i , the mass density; M_i , the molecular weight of component *i*; and χ , the binary interaction energy density.

The condition for the stability in miscible blends is

$$\left(\frac{\partial^2 \Delta G}{\partial \phi_i^2}\right)_{TP} > 0 \tag{3}$$

According to Gonzalez-Montiel et al.,¹⁴ a compatible blend can be produced when χ is smaller than a critical value, χ_c ; that is,

$$\chi_C = \frac{RT_{\text{mixing}}}{2} \left\{ \sqrt{\frac{\rho_A}{M_A}} + \sqrt{\frac{\rho_B}{M_B}} \right\}^2 \tag{4}$$

Koningveld and coworkers^{15,16} reported that the weight-average molecular weight (M_w) should be used in these evaluations.

In this study, the M_w of PA6(MAP) and HIPP are 56,000 and 39,000 g/mol, while the density of PA6(MAP) and HIPP are 1.13 and 0.90 g cm⁻³, respectively. Using these values, χ_c is calculated to be 0.193. It should be noted that the calculated interaction energy density is used for a very approximated prediction only. From the Flory– Huggins theory, the polymer systems should be in thermodynamic equilibrium and it is applicable to a dilute solution. In combination with the binary interaction model,^{17–19} the Flory–Huggins interaction energy density can be expressed as

$$\chi = (\delta_A + \delta_B)^2 \phi_B^2 \tag{5}$$

where δ is the solubility parameter. Solubility parameters for PA6(MAP) and HIPP can be calculated using a group-contribution method.²⁰ The calculated solubility parameters for PA6(MAP) and HIPP are 19.8 and 17.8 (J/cm³)^{1/2}, respectively. Hence, the variation of χ with the HIPP content can be determined from eq. (5), and the result is shown in Figure 4. It is noted that the interaction energy is represented as a shaded zone rather than as a straight line. From this figure, it can be seen that χ $> \chi_c$ when the volume fraction of the HIPP content is above 0.22 (corresponding to 20 wt % HIPP content). In this case, phase separation is expected to occur for the blends containing an HIPP content higher that 20 wt %.

Dynamic Mechanical Properties

Figure 5 shows the variation of the storage modulus versus temperature for the PA6(MAP)/LCP system containing various HIPP contents. The storage modulus of the 80%PA6(MAP)–20%LCP blend generally decreases with increasing HIPP content. Thus, the storage modulus follows a qualitatively similar decreasing trend with that of the Young's



Figure 5 Storage modulus versus temperature for the PA6(MAP)/HIPP/LCP system containing various HIPP contents.



Figure 6 Loss modulus versus temperature for the PA6(MAP)/HIPP/LCP system containing (a) 10 and 20 wt % HIPP and (b) 30 and 40 wt % HIPP contents.

modulus. Figure 6(a) shows the loss modulus versus temperature for the 80%PA6(MAP)–20%LCP blend containing 10 and 20 wt % HIPP. A single peak can be observed in the 80%PA6(MAP)–20%LCP system containing an HIPP content up to 20 wt %, indicating that the PA6 and HIPP phases are compatible. However, an additional peak appears at $\sim -20^{\circ}$ C in the curves of loss modulus versus temperature for the 80%PA6(MAP)–20%LCP system containing an HIPP content $\geq 30 \text{ wt }$ %. This peak corresponds to the glass transition temperature of the impact modified PP.²¹ In this case, the addition of HIPP $\geq 30 \text{ wt }$ % results in incompatibility between the PA6 and HIPP phases. Similarly, the loss factor (tan δ) versus temperature plots yield a single peak located

at ~ 70°C for the 80%PA6(MAP)–20%LCP system with an HIPP content up to 20 wt % [Fig. 7(a)]. However, an additional peak located at ~ 113°C associated with the glass transition temperature of LCP can be seen in the plots of tan δ versus temperature 80%PA6(MAP)–20%LCP containing an HIPP content \geq 30 wt % [Fig. 7(b)]. This behavior implies that the phase separation between PA6(MAP) and HIPP results in the incompatibility between the LCP phase and the matrix. The incompatibility can be attributed to the dilution of MAP concentration in the matrix.

Morphology

Figure 8(a,b) shows SEM micrographs of the fracture surface of the skin and core layers of the



Figure 7 Tan δ versus temperature for the PA6(MAP)/HIPP/LCP system containing (a) 10 and 20 wt % HIPP and (b) 30 and 40 wt % HIPP contents.

(a)



(b)



Figure 8 SEM micrographs showing the fracture surfaces of (a) skin and (b) core sections of the 80%[95%PA6(MAP)-5%HIPP]-20%LCP blend.

80%[95%PA6(MAP)-5%HIPP]-20%LCP blend. LCP fibrils are evident in the skin layer and core section of this blend. It is interesting to see that the LCP fibrils can still be formed in the matrix of the PA6(MAP)-20%LCP system containing a higher HIPP content [Fig. 9(a,b)].

Figure 10(a-d) shows SEM micrographs of the PA6(MAP) (86/14) blends containing various HIPP contents without the presence of the LCP. The fracture surface of the blend with 10 wt %HIPP illustrates the distribution of HIPP particles, hence forming a two-phase system in the matrix [Fig. 10(a)]. These particles can absorb a considerable amount of energy during the impact test, thereby improving the impact toughness of the blends (Fig. 3). A similar morphology is observed for the blend containing 20 wt % HIPP [Fig. 10(b)]. However, various voids associated

with the phase separation of HIPP particles from the matrix can be observed in the PA6(MAP) (86/14) blends containing an HIPP content ≥ 30 wt %. The morphological observations for the PA6(MAP)-HIPP system are in good agreement with the results of the dynamic experimental and thermodynamic calculations as discussed above.

CONCLUSIONS

The morphology, impact, static, and dynamic mechanical properties of MAP-compatibilized blends of PA6 with LCP modified with HIPP were investigated. Tensile measurements show that the tensile strength and modulus of the 80%PA6(MAP)-20%LCP blend tends to decrease with increasing

(a)

(b)



X2,500 10Nm

2506 12KV X1,300 10µm WD33

Figure 9 SEM micrographs showing the fracture surfaces of (a) skin and (b) core sections of the 80%[60%PA6(MAP)-40%HIPP]-20%LCP blend.

 $(d) \qquad (d) \qquad (d)$

(c)



Figure 10 SEM micrographs showing the fracture surfaces (a) 90%PA6(MAP)-10%HIPP, (b) 80%PA6(MAP)-20%HIPP, (c) 70%PA6(MAP)-30%HIPP, and (d) 60%PA6(MAP)-40%HIPP blends.

HIPP content. However, Izod tests indicate that the impact strength of the 80%PA6(MAP)-20%LCP blend increases with increasing HIPP content. Therefore, a tough in situ composite can be produced by the incorporation of an appropriate impact-modified PP. SEM observations reveal that the incorporation of HIPP into the 80%PA6(MAP)-20%LCP blend does not affect the fibrillation of the LCP domains. A theoretical approach based on thermodynamic calculations was used to determine the compatibility between the PA6(MAP) and HIPP components. The results show that phase separation tends to occur in the PA6(MAP)/HIPP system when the HIPP content is above 20 wt %. Such theoretical calculations are in good agreement with the SEM morphological observations.

REFERENCES

- P. R. Subramanian and A. I. Isayev, *Polymer*, **32**, 196 (1991).
- H. Verhoogt, H. C. Langelaan, J. Van Dam, and A. Posthuma De Boer, *Polym. Eng. Sci.*, 33, 754 (1993).
- A. Valenza, F. P. La Mantia, L. I. Minkova, S. De Petris, M. Paci, and P. L. Magagnini, J. Appl. Polym. Sci., 52, 1653 (1994).
- S. C. Tjong, J. S. Shen, and S. L. Liu, *Polym. Eng. Sci.*, **36**, 797 (1996).
- C. Lekakou and C. E. Dickinson, *High Perform.* Polym., 8, 109 (1996).
- G. Sawhney, S. K. Gupta, and A. J. Misra, J. Appl. Polym. Sci., 62, 1395 (1996).
- A. Datta, H. H. Chen, and D. G. Baird, *Polymer*, 34, 759 (1993).

(a)

- H. J. O'Donnell and D. J. Baird, *Polymer*, **36**, 3113 (1995).
- A. Gonzalez-Montiel, H. Keskkula, and D. R. Paul, *Polymer*, 36, 4587 (1995).
- 10. S. C. Tjong, J. Mater. Sci., 32, 4613 (1997).
- S. C. Tjong and Y. Z. Meng, Polym. Int., 42, 209 (1997).
- S. C. Tjong and Y. Z. Meng, *Polymer*, 38, 4609 (1997).
- 13. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- A. Gonzalez-Montiel, H. Keskkula, and D. R. Paul, J. Polym. Sci. Polym. Phys. Ed., 33, 1751 (1995).

- 15. R. Koningsveld and H. M. Schoffeleers, *Pure Appl. Chem.*, **39**, 1 (1991).
- R. Koningsveld and L. A. Kleintjens, J. Polym. Sci. Symp., 61, 221 (1977).
- R. P. Kambour, J. T. Bendler, and R. C. Bopp, *Macromolecules*, 16, 753 (1983).
- 18. D. R. Paul and J. W. Barlow, Polymer, 25, 487 (1984).
- G. Ten-Brinks, F. E. Karasz, and W. J. MacKnight, Macromolecules, 16, 1827 (1983).
- 20. D. W. Van-Krevelen, *Properties of Polymers*, Elsevier, New York, 1976, p. 127.
- S. C. Tjong, W. D. Li, and R. K. Y. Li, *Polym. Bull.*, 38, 721 (1997).