Rheological, Thermal, and Morphological Properties of ABS–PA1010 Blends

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ABSTRACT: Noncompatibilized and compatibilized ABS–nylon1010 blends were prepared by melt mixing. Polystyrene and glycidyl methacrylate (SG) copolymer was used as a compatibilizer to enhance the interfacial adhesion and to control the morphology. This SG copolymer contains reactive glycidyl groups that are able to react with PA1010 end groups ($—NH_2$ or $—COOH$) under melt conditions to form SG-g-Nylon copolymer. Effects of the compatibilizer SG on the rheological, thermal, and morphological properties were investigated by capillary rheometer, DSC, and SEM techniques. The compatibilized ABS–PA1010 blend has higher viscosity, lower crystallinity, and smaller phase domain compared to the corresponding noncompatibilized blend. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 683–688, 1999

Key words: ABS; PA1010; blend; compatibilizer

INTRODUCTION

Few polymers form truly miscible blends characterized by a single T_g and homogeneity at a 5–10-nm scale.[1] The majority of blends are immiscible; that is, they possess a phase-separated morphology. Immiscible polymer blends often have poor mechanical properties relative to their components because of the unfavorable interaction between molecular segments at the interface between the phases, namely, a large interfacial tension, which leads to poor control of morphology during melt mixing and poor interfacial adhesion or stress transfer in the solid state. An effective way to gain control of the morphology and to strengthen the interfacial zone is to form block or graft copolymers *in situ* during blend preparation via interfacial reaction of added functionalized polymeric components.[2–5]

Recently, *in-situ* compatibilized polymer blends based on copolymers containing glycidyl methacrylate (GMA) monomer have attracted much attention because of potentially broad applications. Chung and Carter[6] patented a polymer, claimed to have excellent low-temperature impact properties, based on PC, PET, ABS, and styrene–acrylonitrile–glycidyl methacrylate copolymer. Akkapeddi et al.[7] reported that polyethylene-g-GMA acted as a good compatibilizer of blends of PC with PET and various polyolefins. J. H. Yin and his coworkers[8–12] have reported a series of reactive compatibilizations of many blending systems based on GMA-containing copolymers.

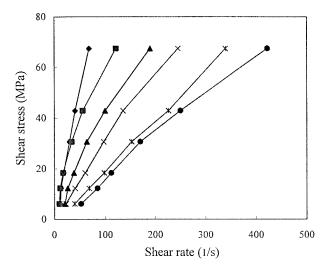In the present work, PS-co-GMA was used as a compatibilizer for ABS and nylon1010 blends.

Figure 1 Shear stress versus shear rate of the AB-S–PA system: (–◆–) ABS; (–■–) ABS–PA = 8/2; (–▲–) ABS–PA = 6/4; (–×–) ABS–PA = 4/6; (–*–) ABS–PA = 2/8; (–●–) PA.

The aim of this study was to investigate the rheological, thermal, and morphological properties of ABS–nylon1010 blends with or without compatibilizer.

EXPERIMENTAL

Materials

PA1010 was supplied by Jilin Shijinggou Union Chemical Corp., and its relative viscosity was 2.1.
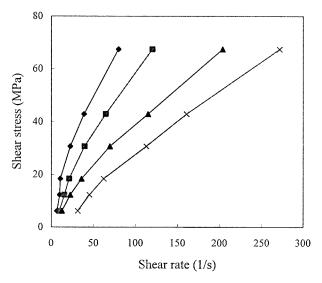

Figure 2 Shear stress versus shear rate of ABS–PA–SG system: (–◆–) ABS–PA–SG = 8/2/1; (–■–) ABS–PA–SG = 6/4/1; (–▲–) ABS–PA–SG = 4/6/1; (–×–) ABS–PA–SG = 2/8/1.
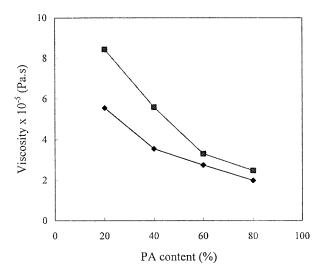

Figure 3 Viscosity versus PA content: (–◆–) ABS–PA; (–■–) ABS–PA–SG.

ABS was P757 from Taiwan Chimei Corp. Ltd. GMA was obtained from Suzhou Anli Chemical Plant and was purified using vacuum distillation. PS-*co*-GMA was synthesized via free-radical polymerization using 0.5% by weight of benzoyl peroxide based on monomer. The GMA content of the copolymer was determined by chemical titration method, which involves epoxide ring opening.[13]

Preparation of ABS–PA1010 Blends

A Brabender-like apparatus was used to prepare ABS–PA1010 blends at 220°C with a roller speed of 32 rpm for 5 min. ABS and PA1010 were dried
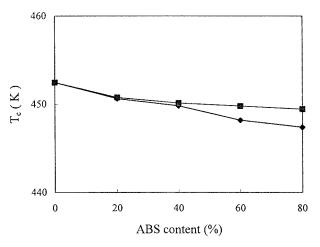

Figure 4 T_c versus ABS content: (–◆–) ABS–PA; (–■–) ABS–PA–SG.
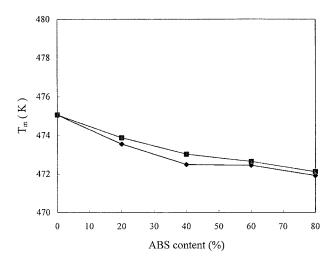
Figure 5 T_m versus ABS content: (–◆–) ABS–PA; (–■–) ABS–PA–SG.

Figure 7 Crystallinity versus ABS content: (–◆–) ABS–PA; (–■–) ABS–PA–SG.

in a vacuum oven at 80°C for 12 h before melt mixing.

Characterization

Rheological parameters were measured using a capillary rheometer (model XYL-II). The diameter of capillary is 0.5 mm, and the ratio of length to diameter is 40. The thermal behavior of blending samples was determined on a Perkin–Elmer DSC II. The fusion thermograms were obtained in a rang from 50 to 250°C at a heating rate of 10°C/min. All measurements were performed under a nitrogen atmosphere. Morphological observation was carried out by a scanning electron
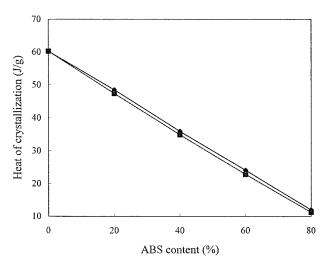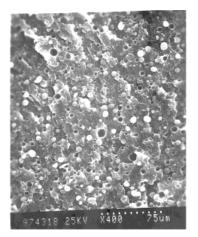
microscopy (JXA-840). The specimen were sharply cracked after immersion in liquid nitrogen.
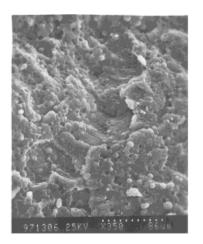
RESULTS AND DISCUSSION

Rheological measurements have been used successfully to obtain qualitative information about chemical reactivity and the extent of reaction in blends. Shear stress of ABS–PA1010, ABS–PA1010–PS-*co*-GMA blends as a function of shear rates at 240°C is shown in Figures 1 and 2. It is clear that both blend systems show pseudoplastic behavior; that is to say, the shear stress increases with increasing shear rate less than proportionately. These two flow phenotypes can be described by an equation (Power law)
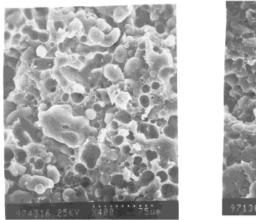
$$\tau = k \cdot \gamma^n$$

where n is the power law index, and k is a function of temperature. With the addition of compatibilizer, it doesn't change the rheological properties of the ABS–PA1010 blend. The relationship of viscosity with PA content in blends is given in Figure 3. The viscosities are decreased with the increase of PA content in blend, and the viscosities of ABS–PA1010–PS-*co*-GMA system are larger than these of ABS–PA1010 system in all the composition range. The increase of viscosity of compatibilized system can be thought of as causing some reactions to occur between PS-*co*-GMA copolymer and PA1010:
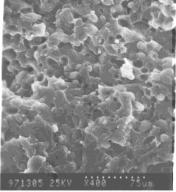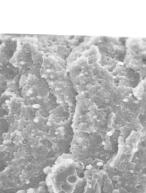

Figure 6 Heat of crystallization versus ABS content: (–◆–) ABS–PA; (–■–) ABA–PA–SG.
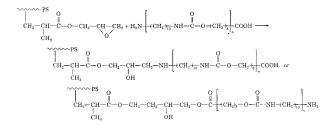
(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

The melting peak temperature (T_m) and crystallizing peak temperature (T_c) measured from the DSC thermogram for the ABS–PA and ABS–PA–PS-*co*-GMA blends are shown in Figures 4 and 5. Melting points depression of about 3–5°C occurs as the ABS content decreases. The T_c of ABS–PA–PS-*co*-GMA blend is a little higher than that of ABS–PA blend. In the case of T_m, the situation is the same. Probably the adding of compatibilizer PS-*co*-GMA to the ABS–PA blends has a detrimental effect on the crystallization of PA; furthermore, polymers crystallizing in the low temperature have always a lower melting points because the structures of crystallites are not in the same order as those crystallizing in the high temperature. The heat of crystallization (Fig. 6) is almost a linear function of blend composition, although some values deviate slightly low from linearity. The crystallinity (X_c) of the PA phase was calculated by means of the following equation:

$$X_c = 100\Delta H_{blend}/(\Delta H^\circ_{PA} \times \text{weight fraction of PA})$$

where ΔH_{blend} is the heat of crystallization per gram of the blend, and ΔH°_{PA} is the equilibrium heat of fusion per gram of 100% crystalline PA 1010 (from Feng et al.[14]; $\Delta H^\circ_{PA} = 244.0$ J g). The crystallinities of these two blending systems are independent of the composition of blends (see Fig. 7), but the crystallinities of compatibilized system are slightly lower than these of noncompatibilized system. The reduction in the crystallinity may be due to the formation of graft copolymers by the reactions of amide end groups of nylon with glycidyl groups of GMA.

Figure 8 shows the micrographs of the blends of ABS–PA with or without compatibilizer. It is clear that below 40% ABS, the ABS phase is dispersed, and the PA is continuous. At about 60% ABS, the ABS phase is continuous, and the PA is dispersed. In the intermediate range, it is not clear which is continuous or dispersed because the phase contrast is not very clear; but it seems that PA and ABS are co-continuous. The phase inversion may occur between ABS–PA = 40/60 ~ 60/40. For noncompatibilized blends [Fig. 8(b) and (d)], we noted that large phases domains of ABS in PA matrix and no adhesion between the two phases. For compatibilized blends [Fig. 8(a) and (c)], the morphologies are largely modified. We can see smaller phase domains and total blurring of the phase boundaries. The compatibilizing effect leads to a decrease in the size of phases and an increase of the interface adhesion. The morphologies clearly demonstrate the improvement of miscibility of ABS–PA blends due to the presence of PS-*co*-GMA compatibilizer.

CONCLUSIONS

ABS and PA1010 are immiscible and incompatible with poor interfacial adhesion and large domains. This incompatible blend can be converted into a compatible one by incorporating PS-*co*-GMA copolymer, which itself does not function as a compatibilizer but will become one after reacting with PA1010 end groups during melt blending. With addition of PS-*co*-GMA, the rheological behavior of the blending system does not change too much, but the viscosity is increasing compared to the noncompatibilized system. The crystallinity of compatibilized system is a little lower than the one of noncompatibilized system due to the reactions between glycidyl groups with PA1010 end groups. The morphological studies show that PS-*co*-GMA copolymer behaves as an effective interfacial agent by improving the adhesion between ABS and PA and decreasing the dimensions of dispersed phase.

Figure 8 Scanning electron microscopy micrographs of ABS–PA1010 and ABS–PA1010–SG blends with compositions of (a) ABS–PA1010 (20/80), (b) ABS–PA1010–SG (20/80/10), (c) ABS–PA1010 (40/60), (d) ABS–PA1010–SG (40/60/10), (e) ABS–PA1010 (60/40), (f) ABS–PA1010–SG (60/40/10), (g) ABS–PA1010 (80/20), (h) ABS–PA1010–SG (80/20/10).

REFERENCES

1. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum Press: New York, 1976.
2. Gan, P. P.; Paul, D. R. Polymer 1994, 35, 3513.
3. Lee, P. C.; Kuo, W. F.; Chang, F. C. Polymer 1994, 35, 5641.
4. Zhang, X. M.; Yin, Z. H.; Li, L. X.; Yin, J. H. J Appl Polym Sci 1996, 61, 2253.
5. Kim, J. K.; Lee, H. Y. Polymer 1996, 37, 305.
6. Chung, J. Y. J.; Carter, R. P. U.S. Pat. 4,554,315, 1985.
7. Akkapeddi, M. K.; Mason, C. D.; VanBuskirk, B. Polym Prepr 1993, 34, 848.
8. Zhang, X. M.; Yin, Z. H.; Yin, J. H. J Appl Polym Sci 1996, 62, 893.
9. Zhang, X. M.; Yin, Z. H.; Yin, J. H. J Appl Polym Sci 1996, 62, 1993.
10. Yin, Z. H.; Zhang, X. M.; Yin, J. H. J Appl Polym Sci 1997, 63, 1857.
11. Zhang, X. M.; Yin, Z. H.; Yin, J. H. J Appl Polym Sci 1997, 64, 1489.
12. Zhang, X. M.; Yin, Z. H.; Yin, J. H. Polymer 1997, 38, 5905.
13. Dobinson, B.; Hofmann, W.; Stark, B. P. Determination of Epoxide Groups; Pergamon: London, 1969.
14. Feng, J. H.; Mo, Z. C.; Chen, D. L. Chin J Polym Sci 1990, 8, 61.