Morphology and Rheological Behavior of Amorphous Polyamide/(Styrene–Acrylonitrile/Styrene Maleic Anhydride) Reactive Blends

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ABSTRACT: The effects of styrene maleic anhydride (SMA) random copolymer on the morphology and rheological behavior of amorphous polyamide/styrene–acrylonitrile (SAN) copolymer blends have been investigated. The anhydride group in SMA can react with the amine group in polyamide to form *in situ* graft copolymers at the polyamide/SAN interfaces during the melt blending. The extent of reaction was assessed by the torque change with time in the mixer. The torque obtained from a torque rheometer was compensated using a reference temperature since the actual temperature in the mixer was higher than the setting temperature due to viscous heating and exothermic reaction. The compensated torque data were found to be very useful to study the extent of reaction between functional groups during melt blending of reactive blend system, especially in the case of small concentration of functional groups available to reaction. Morphological observation showed that the finer dispersion of the SAN domains with rather narrow distribution was obtained when SMA was added to the blend.

KEY WORDS Reactive Compatibilization / Morphology / Rheology / Torque Compensation / Styrene Maleic Anhydride Copolymer /

Much attention has been paid to the use of reactive compatibilizer for immiscible polymer blends since the reactive compatibilization method has been proved to be effective for controlling morphology and improving mechanical properties in a variety of blend systems.^{1–5} The reactive compatibilizer has specific functional groups and it can generate *in situ* formation of block or graft copolymers at the interface during the blend preparation through the reaction of functional groups incorporated onto the blend components.^{6–8} The *in situ* formed copolymer at the interface provides a fine morphology and increases the interfacial adhesion strength between the phases.

In reactive compatibilization, the extent of reaction during blend preparation affects the morphology and mechanical properties of polymer blend. Therefore, it is of importance to determine the extent of reaction in reactive blends. The extent of reaction is dependent on the amount of reactive groups and the reactivity between functional groups. However, the conventional methods to check the reaction such as infrared spectroscopy can hardly be applied to the reactive compatibilization due to very low concentration of functional groups. Many studies have used the torque rheometer to check the reactivity between functional groups in reactive polymer blends^{9–11} because the *in situ* formed copolymers have high melt viscosities due to high molecular weight. However, the temperature of mixer increases with time due to the viscous heating and exothermic heat from the reaction, which results in lower torque values as compared with those at initial setting temperature. Therefore, the torque data obtained from the torque rheometer must be compensated using a reference temperature in order to study the extent of reaction quantitatively. Recently, Kim and Lee¹¹ have reported the rheological properties, modified by torque compensation,

of poly(butylene terephthalate)/polystyrene blends using glycidyl methacrylate grafted polystyrene as a reactive compatibilizer. They found that the compensated torque data were more useful in finding a relationship between the degree of the reaction and the amount of graft copolymer formed.

In this study, we performed immiscible amorphous polyamide/styrene–acrylonitrile (SAN) melt blends using styrene maleic anhydride (SMA), which is miscible with SAN, as a reactive compatibilizer. The amorphous polyamide/SAN interface was reinforced by the *in situ* formed graft copolymers between the terminal amine group in polyamide and anhydride group in SMA. The effects of functional group concentration on the morphology and rheological behavior of the blends were examined. The rheological behavior was studied using a torque compensation method.

EXPERIMENTAL

Materials

The amorphous polyamide used in this study was CX-3000 obtained from Unitika Company. The SAN containing 24 wt% acrylonitrile was a commercial molding grade, obtained from Cheil Industry, and has a weight average molecular weight of 155000 g mol⁻¹ ($\bar{M}_w/\bar{M}_n = 2.16$). The SMA, used as a reactive compatibilizer in this study, was supplied by DSM and has a weight average molecular weight of 110000 g mol⁻¹. The SMA has 28 wt% maleic anhydride content, which is miscible with SAN containing 24 wt% acrylonitrile.^{12,13}

Melt Blending

All polymers used in this study were dried under vacuum at 80°C for 24 h before melt blending. Amorphous polyamide/(SAN/SMA) blends were prepared in

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two steps. First, SAN/SMA blends with different blend ratio were made by melt mixing in an internal mixer with capacity of 30 cm³ driven by Brabender Plasticorder at speed of 50 rev min⁻¹. The mixer temperature was set at 200°C. The resulting SAN/SMA blends and amorphous polyamide were melt blended with an internal mixer at the same condition. The final composition ratio of amorphous polyamide/(SAN/SMA) blend was 80/20 wt/wt. The SMA content in SAN/SMA blend was varied from 0 to 30 wt%. The temperature of the mixer reached 206–210°C due to the viscous heating and exothermic reaction with time.

Characterization

The complex viscosities of blends were measured using a Rheometrics Mechanical Spectrometer (RMS) with 25 mm circular discs under dynamic mode at 200°C. In order to compensate the torque data using a reference temperature, the complex viscosities of blends were also measured at angular frequency of 17.5 rad s⁻¹, which is apparent shear rate inside the Brabender internal mixer used in this study,⁹ with respect to temperature between 200–230°C.

Morphology of the melt blend was examined with a JEOL JSM-840A scanning electron microscope. The specimen was frozen in liquid nitrogen and immediately fractured.

RESULTS AND DISCUSSION

Rheological Behavior

Figure 1 shows the steady state torque and actual temperature of the melt blending of amorphous polyamide/(SAN/SMA) blends in the internal mixer as a function of SMA content in SAN/SMA blend. The torque and temperature reached the steady state within the first 5 min or so after input of the cold pellets into the heated chamber. As shown in Figure 1, the steady state torque and actual temperature in the mixer were found to increase with the amount of SMA in SAN/SMA blend. The increase of the torque resulted from the viscosity increase of blends due to the grafting reaction between anhydride groups in SMA and amine groups in polyamide. The increase of molecular weight through the grafting reaction is believed to be the major reason for the viscosity increase of blends. Furthermore, the graft copolymers formed at the interface raise the interfacial friction under shear stress. It is another reason for the higher viscosity.

The increase of the melt viscosity by the addition of SMA was verified by measuring complex viscosity of the blend using RMS. The melt viscosities of several blends with differing in SMA content *versus* shear rate at 200°C are shown in Figure 2. As shown in Figure 2, the melt viscosity of the blend increased as increasing amount of SMA in SAN/SMA blend due to graft copolymer formation. It should be also noted that the melt viscosity of the blend containing SMA was higher than that of neat amorphous polyamide which has the highest melt viscosity among blend components at this experimental condition. As a result, the main reason for the increase of melt viscosity of the blend with reactive compatibilizer, *i.e.*, SMA, was *in situ* formation of graft copolymers.

Figure 1. Torque (●) and temperature (■) in the internal mixer, measured at steady state, as a function of SMA content in SAN/SMA blend for 80/20 polyamide/(SAN/SMA) blends.

Figure 2. Complex viscosity as a function of angular frequency for four different blends varying ratio of SNA/SMA at 200°C: (●) 100/0; (■) 98/2; (▲) 90/10; (▼) 82/18 wt/wt SAN/SMA for polyamide/(SAN/SMA) blend.

The temperature in the mixer was also increased with increasing content of SMA in SAN/SMA blend. Usually, the mixer temperature is higher than the setting temperature due to viscous heating of polymers. As can be seen in Figure 1, the temperature of the blend without SMA reached at 203°C, which is higher than the setting temperature, even though there was no chemical reaction. This is mainly due to the viscous heating of the polymers. However, in the case of reactive compatibilization, the exothermic heat of reaction must be considered because it can also increase the mixer temperature in addition to the viscous heating. Since the reaction between anhydride group and amine group is exothermic, the temperature of the blend with SMA was higher than that of the blend without SMA. As the amount of SMA increased the steady state temperature in the mixer increased, as shown in Figure 1, because the extent of reaction was proportional to the concentration of functional groups, *i.e.*, the content of SMA. The increases of actual temperature and torque in the mixer indicate that graft

Figure 3. Torque change with mixing time for three different blends varying ratio of SAN/SMA at the setting temperature of 200°C: (●) 100/0; (■) 94/6; (▲) 70/30 wt/wt SAN/SMA.

copolymers were formed at interfaces during melt blending.

Figure 3 shows the torque change with mixing time at the setting temperature of 200°C for several amorphous polyamide/(SAN/SMA) blends having different SAN/SMA composition. The torque of the blend with SMA showed minimum and maximum points once SMA was present, while the torque of the blend without SMA did not show such behavior. This behavior was due to the reaction between anhydride and amine groups with mixing time. As the reaction proceeded with time, the highly viscous graft copolymers formed during mixing raised the torque with time. However, the reaction was completed in a very short time and any increase of torque with mixing time was masked by the fluxing process. Furthermore, the torque decreased slightly with time by mastication of the graft copolymer formed.¹⁰ As a result, a maximum in torque appeared. Therefore, the difference between minimum and maximum in torque reflects the extent of reaction. As shown in Figure 3, the difference increased as increasing amount of SMA in the blend.

However, as mentioned early, the actual temperature in the internal mixer is higher than the setting temperature due to the viscous heating and exothermic heat of reaction. The torque is dependent on temperature because the torque is a function of melt viscosity which depends on temperature. Therefore, in order to assess the extent of reaction during melt blending quantitatively, the actual torque directly obtained from the rheometer must be compensated based on the reference temperature. In the internal mixer, the reduced torque, $M(T_{\text{ref}})$, at the reference temperature can be calculated by the following equation^{11,14,15}:

$$M(T_{\text{ref}}) = M(T) \exp[(\Delta E/R)(1/T_{\text{ref}} - 1/T)] \quad (1)$$

where ΔE is the activation energy, R is the gas constant, and T is the absolute temperature.

In order to do this calculation, an activation energy in the relation between viscosity and temperature is needed. The activation energy was calculated from Arrhenius relationship by measuring the complex viscosity of the blend with respect to temperature since

Figure 4. Torque change with mixing time for blends: (a) without SMA; (b) with SAN/SMA ratio of 94/6 wt/wt: (●) without torque compensation; (■) with torque compensation.

the viscosity can also be expressed by the Arrhenius relationship.

$$\eta(T_{\text{ref}}) = \eta(T) \exp[(\Delta E/R)(1/T_{\text{ref}} - 1/T)] \quad (2)$$

In order to use eq 2, the shear rate in the internal mixer must be fixed because the temperature dependence of shear viscosity can change with shear rate. Since the shear rate inside the internal mixer can be varied with respect to the position, we assumed apparent shear rate of 17.5 s^{-1} , which is an average value between maximum shear rate and minimum shear rate inside the Brabender internal mixer used in this study. The complex viscosity of the blend was measured as a function of temperature between 200–230°C at angular frequency of 17.5 rad s^{-1} which was equivalent to the apparent shear rate in the internal mixer.

With this activation energy calculated from eq 2, the torque data obtained directly from the rheometer were compensated based on the reference temperature of 200°C using eq 1 and the results are shown in Figure 4, coupled with the torque data obtained directly from the rheometer. Note that the calculated value of the activation energy in this case was 87.3 kJ mol^{-1} . The detailed methods in calculating activation energy and compensat-

Figure 5. Scanning electron micrographs of cryofractured surfaces for four different blends varying ratio of SAN/SMA for 80/20 amorphous polyamide/(SAN/SMA) blends: (a) 100/0; (b) 98/2; (c) 90/10; (d) 82/18 wt/wt SAN/SMA.

ing torque data were described elsewhere.^{11,14,15}

From Figure 4, it can be ascertained that the extent of reaction during melt blending is more evident after torque compensation. In the case of the blend without SMA (Figure 4a), the torque data after compensation did not show a maximum. In the first 2 min or so, the torque was dominated by fluxing of the cold polymer pellets, but thereafter the torque was leveled off. However, in the case of the blend with SMA (Figure 4b) the difference between maximum and minimum in torque after torque compensation was larger as compared to the case before torque compensation. All other blends with SMA showed the same behavior although the data were not shown in this paper. From these results we can conclude that the torque compensation method is very effective to quantify the extent of reaction during melt blending, especially in small concentration of functional groups.

Morphology

Typical examples of the effect of the reactive compatibilizer, *i.e.*, SMA, on the blend morphology are shown in Figure 5. As shown in Figure 5a, the blend without SMA exhibited a dispersion of spherical particles of the SAN phase and a discrete interface that indicates weak interfacial adhesion between dispersed and matrix phase. However, the presence of SMA in blends significantly reduced the size of the dispersed domain and showed good interfacial adhesion (Figures 5b–d) because graft copolymers *in situ* formed played a role as a compatibilizer in the immiscible blend. At this moment,

we have no direct evidence supporting the existence of graft copolymers at the interface. The experimental results on the characterization of the interphase by using transmission electron microscopy will be reported in the forthcoming paper.

It can be seen from Figure 5 that the domain size of the dispersed phase decreased rapidly as the contents of SMA increased. This is due to the higher amount of anhydride groups in SMA that can react with the amine end groups in polyamide. The effect of the SMA as a reactive compatibilizer on the morphology of the blends has been well demonstrated in these micrographs. Moreover, with high content of SMA a narrower distribution of the dispersed phase was obtained as compared to the uncompatibilized blend. This result coupled with the reduced domain size indicates that SMA acts efficiently as reactive compatibilizer.

Figure 6 shows the number average domain size of the amorphous polyamide/(SAN/SMA) blends as a function of the content of SMA in SAN/SMA blend. The error bars shown at each point are standard deviation for the measured sizes of the domain. Without SMA, the average size of the dispersed domain was about 1.8 μm and the distribution of domain sizes was broad. However, the average domain size decreased rapidly to the order of 0.2 μm and the narrower distribution of dispersed phase was obtained with increase of SMA in blends. It can be explained by two reasons. One is the reduced interfacial tension due to the presence of graft copolymers formed at interfaces because the size of dispersed phase is proportional to the interfacial tension.¹⁶ Many re-

Figure 6. Number average diameter of the dispersed phase in 80/20 amorphous polyamide/(SAN/SMA) blends as a function of SMA content in SAN/SMA blends.

searchers^{17,18} have reported that the interfacial tension in reactive blends decreased as observed in the addition of block copolymer to homopolymer blends.

However, the breadth of the domain size distribution cannot be explained by the reduction of interfacial tension especially in the uncompatibilized system. It means that coalescence effects may be more important factor in determining the final blend morphology in the melt blending, as already reported by many researchers.^{19,20} In the case of the uncompatibilized system, very small domain may result from the breakup process in the high shear regions, while increased coalescence due to more domain interaction will result in very large domains.²¹ However, in the case of the reactive compatibilized system, *i.e.*, the blends with SMA in this study, the coalescence process is prevented because the *in situ* formed graft copolymer at interfaces may form an interphase that must be overcome for coalescence to occur.²¹ As a result, with increasing SMA content in blends the breadth of domain size distribution became narrower, as shown in Figure 6.

CONCLUSION

This study shows that SMA is an effective reactive compatibilizer in immiscible amorphous polyamide and

SAN system. In studying the degree of reaction in reactive compatibilization, the torque compensation method based on the reference temperature using activation energy was found to be an effective method especially in small amounts of functional groups available to reaction. The smaller domain size coupled with the finely dispersed minor phase indicates that the graft copolymer *in situ* formed during melt blending played the role as a compatibilizer efficiently.

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