Heterogeneous Dispersion of the Compatibilizer in the Injection Molding of Polyamide 6/Polypropylene Blends

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ABSTRACT: Four kinds of ethylene–proplene–diene/maleic anhydride compatibilized polyamide 6/polypropylene samples were prepared with different mixing sequences and showed significant differences in the Izod impact strength. The morphological features of these samples were characterized with scanning electron microscopy, and a heterogeneous dispersion of the compatibilizer in the injection-molded samples was observed; this was related to the shear field in the skin and subskin layers during injection. A parameter, the transfer energy, is put forward to interpret the dispersion of the compatibilizer in the injection-molded blends, and the results show that the transfer energy is a key factor in determining the transfer of the compatibilizer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 299–305, 2009

Key words: blends; compatibilization; diffusion; dispersions

INTRODUCTION

Polymer blending is an economical route for obtaining new polymer materials with combined performances of the corresponding neat polymers at a low cost.[1–4] However, most polymers are thermodynamically immiscible, so the desired properties cannot be obtained by a simple combination of two incompatible polymers. Conventionally, a third constituent, a compatibilizer, which is a premade block or graft copolymer showing chemical affinity to the two immiscible homopolymers, is added to the blending system to improve the compatibility of the two polymers.[5–8] For these systems, the dispersion of the compatibilizer is very important to the final properties, so the knowledge of the transfer of the compatibilizer in processing procedures will be helpful for obtaining desired performances.[9–11] Cimmino et al.[9]

studied ternary polyamide 6 (PA6)/rubber/modified rubber blends and found that when a premixed ethylene–propylene random copolymer (EPM) and an ethylene–propylene random copolymer functionalized by the insertion onto its backbone of maleic anhydride (MAH) groups (EPM-g-SA) were mixed with PA6, EPM-g-SA dispersed into the matrix better than in the blend prepared by the simultaneous mixing of PA6, EPM, and EPM-g-SA. Wills[10] found the same phenomenon in a polyamide/polypropylene (PP) blend system compatibilized by an ionomer compatibilizer. When Tremblay et al.[11] studied the location of the interfacial modifier dimethylamino ethanol in a polymer blend by electron energy-loss spectroscopy, they found that in the single-step mixing process (all constituents were mixed simultaneously), the modifier was well distributed in the blend, whereas in the two-step mixing process (dimethylamino ethanol was premixed into the dispersed phase initially and subsequently mixed with the matrix), the modifier was trapped within the dispersed phase to a large degree. At the same time, these researchers mainly focused on blends prepared by extrusion or compression molding, whereas to the best of our knowledge, related investigations on injection-molded blends have not been publicly reported. Therefore, further research, especially on injection-molded blend systems, is needed.

For a better understanding of the dispersion of the compatibilizer in an injection-molded blend system, ethylene–proplene–diene (EPDM)-MAH was used as

a compatibilizer in a PA6/PP blend system in this study. In this system, the anhydride of EPDM–MAH can react with PA6,[12,13] and this results in a strong interaction between PA6 and EPDM–MAH. PP and EPDM have similar molecular chains,[14] and this results in some extensive interactions between PP and EPDM–MAH. PP and PA6 are noncompatible,[15] and their interaction is feeble. Four kinds of mixing sequences were used to analyze the transfer of the compatibilizer; at the same time, an interesting structure was observed in the injection-molded sample. The formation mechanism of this structure and the resultant properties were also analyzed.

EXPERIMENTAL

Materials

The PA6 resin used here, with the trade mark M2800, was a commercial product of Xinhui Meida-DSM Nylon Slice Co., Ltd. (Jiangmen, China), and was supplied as pellets. The melt flow rate of the resin was 4.09 g (10 min)$^{-1}$ at 275°C, exerting a force of 325 g. The resin was dried for 12 h *in vacuo* at 100°C before processing to prevent its hydrolytic degradation. Isotactic polypropylene (iPP), with the trademark F401, was obtained from Lanzhou Petro-chemical Co., Ltd. (Lanzhou, China). Certain proper-ties of the resin, provided by the manufacturer, were as follows: a melt flow rate of 2.5 g/10 min accord-ing to ASTM D 1238.79, a density of 0.91 g/cm^3 according to ASTM D 1505-68, and a tacticity of 98%. EPDM-*g*-MAH, with the trade mark CMG9802, was obtained from Shanghai Rizhisheng Co., Ltd. (Shanghai, China); its grating degree was 0.8%.

Sample preparation

Samples were prepared with four different mixing sequences. Except for the mixing sequence, the other techniques of the sample preparation were the same. The detailed mixing sequences were as follows.

Sample A

PA6 and EPDM–MAH were premixed in a single-screw extruder (Shanghai Light Machine and Models Co., Shanghai, China) with a screw diameter of 20 mm and a length/diameter ratio of 25. The screw speed was maintained at 60 rpm, and the tempera-tures from the hopper to the die were 210, 235, 250, and 245°C. The extruded thread was quenched in water and pelletized and then was mixed with PP in a single-screw extruder, with the temperatures from the hopper to the die being 175, 185, 190, and 185°C. The screw speed was maintained at 60 rpm.

Sample B

PA6 and PP were premixed in a single-screw ex-truder. The screw speed was maintained at 60 rpm, and the temperatures from the hopper to the die were 210, 235, 250, and 245°C. The extruded thread was quenched in water and pelletized and was then mixed with EPDM–MAH in a single-screw extruder, with the temperatures from the hopper to the die being 210, 235, 250, and 245°C. The screw speed was maintained at 60 rpm.

Sample C

PA6, PP, and EPDM–MAH were mixed simultane-ously in a single-screw extruder. The screw speed was maintained at 60 rpm, and the temperatures from the hopper to the die were 210, 235, 250, and 245°C.

Sample D

PP and EPDM–MAH were premixed in a single-screw extruder. The screw speed was maintained at 60 rpm, and the temperatures from the hopper to the die were 175, 185, 190, and 185°C. The extruded thread was quenched in water and pelletized and was then mixed with PA6 in a single-screw extruder, with the temperatures from the hopper to the die being 210, 235, 250, and 245°C. The screw speed was maintained at 60 rpm.

The weight ratio of PA6, PP, and EPDM–MAH was 6 : 3 : 1. After drying to remove the attached moisture, the obtained pellets were injection-molded into impact samples on a PS40E5ASE precise injec-tion-molding machine (Nissei, Japan) with a temper-ature profile of 220, 230, 240, and 235°C from the feeding zone to the nozzle. Both the injection pres-sure and the holding pressure were 37.4 MPa.

Test

Izod impact test

The Izod impact measurements were carried out with a UJ-40 Izod impact tester made by Chengde Jinjian Test Instruments Co. (Chengde, China) at 23 ± 2°C with injection-molded rectangular specimens (10 mm wide). At least five specimens of each sam-ple were tested, and the average value was reported.

Scanning electron microscopy (SEM) test

The phase morphology was observed with a JEOL JSM-5900LV scanning electron microscope (JEOL Pte Ltd., Tokyo, Japan). The samples were frozen in liq-uid nitrogen for 30 min and then impact-fractured for SEM analysis. The freshly fractured surface was
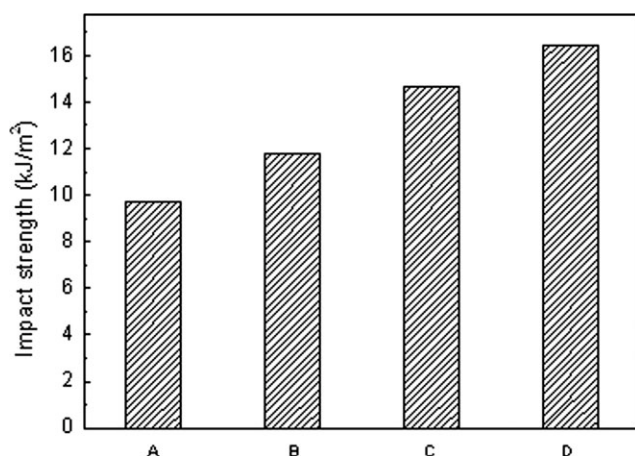
Figure 1 Impact strength of the PA6/PP blending system compatibilized by EPDM–MAH with different mixing sequences.

gold-sputtered before SEM observation. The acceleration voltage was 20 kV.

Fourier transform infrared (FTIR) analysis

The injection sample was cut, and the fracture surface was used for FTIR analysis. FTIR spectra were determined on a Nicolet Magna-IR 560 (Madison, WI).

RESULTS

Impact strength

Figure 1 shows the impact strength of the PA6/PP blending system compatibilized by EPDM–MAH with different mixing sequences. The mixing sequence shows a notable influence on the impact properties. When PP and EPDM–MAH were premixed and then mixed with PA6, sample D showed the highest impact strength, about 80% higher than that of sample A. However, when PA6 and EPDM–MAH were premixed and then mixed with PP, the sample showed the lowest impact strength. The impact strength of the other two samples was between the two extreme values. Therefore, it cannot be simply stated that two-step processing is better than one-step processing for achieving high impact performance by a polymer blend via compatibilization. The performance still has something to do with the properties of the materials, especially with the interactions between the polymer components and compatibilizer.

SEM analysis

Figures 2–4 show the morphology in the skin, subskin, and core layers of the injection-molded PA6/PP blends compatibilized by EPDM–MAH (samples A–D), respectively. The dispersed phase, iPP, mainly existed in the form of a fiber, except in the core layer of sample A, the impact strength of which was the lowest, and the dispersed iPP phase was mainly spherical. Conventionally, in the process of injection molding, a polymer melt is subjected to a complex thermodynamic environment characterized by high cooling rates and severe stress fields. As a result, an injection-molded sample usually shows an intrinsic heterogeneous microstructure, which is generally called the skin–core microstructure. The dispersed phase in the core layer is mainly spherical, but it is in the form of a fiber in the skin and subskin layers.[16–19] In our study, just sample A showed the typical skin–core structure, and in the SEM photographs, a large number of droplets, several hundred nanometers in size, were found [Figs. 2(D) and 3(C,D)].

FTIR analysis

To reveal the components of the droplet shown in the SEM photographs, an FTIR test was carried out. The FTIR scanning surface was the same as that used for the SEM test. Figure 5 shows the FTIR spectra of samples A and D. The characteristic peaks for PA6 absorption are as follows: C=O stretching vibrations at a wave number of 1640 cm^{-1}, N—H bending vibrations at 1560 cm^{-1}, and N—H stretching vibrations at 3300 cm^{-1},[20] all of which can be found in the FTIR spectra of samples A and D. The most remarkable difference between the two samples is that sample A shows a small peak at 1660 cm^{-1}, which belongs to the region of the characteristic peak of the carbonyl group of amide. Figure 6 shows the reaction between the anhydride group of MAH and the PA6 amine terminal group; it can be seen that an amide group was generated when the reaction between the anhydride group of MAH and the PA6 amine terminal group occurred. The characteristic peak of this carbonyl shows a deviation versus that of the carbonyl group in PA6, so it can be safely concluded that the droplet shown in Figures 2(D) and 3(C,D) was EPDM–MAH.

DISCUSSION

On the basis of these results, it can be seen that the mixing sequence has a distinct effect on the impact strength, and this results from the different morphologies achieved and the dispersion of the compatibilizer. In this study, the compatibilizer was not homogeneously dispersed in the injection-molded samples and conglomerated significantly in the skin layer. In our opinion, this may be related to the transfer of the compatibilizer.

It is well known that thermodynamic miscibility is possible only if the free energy of mixing (ΔG_{mix}) is
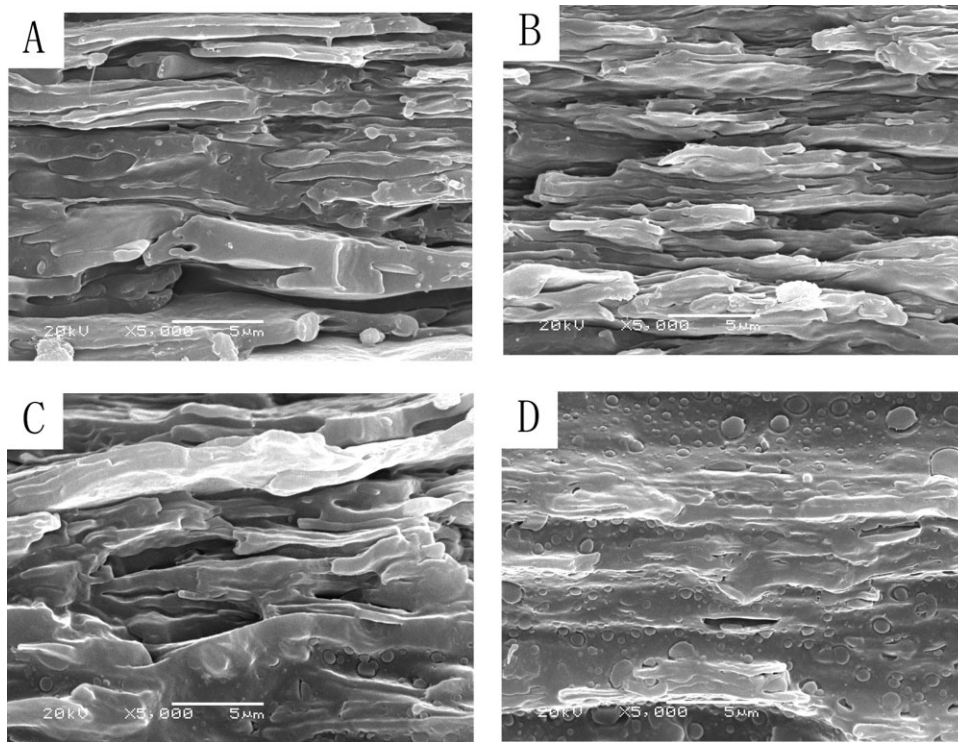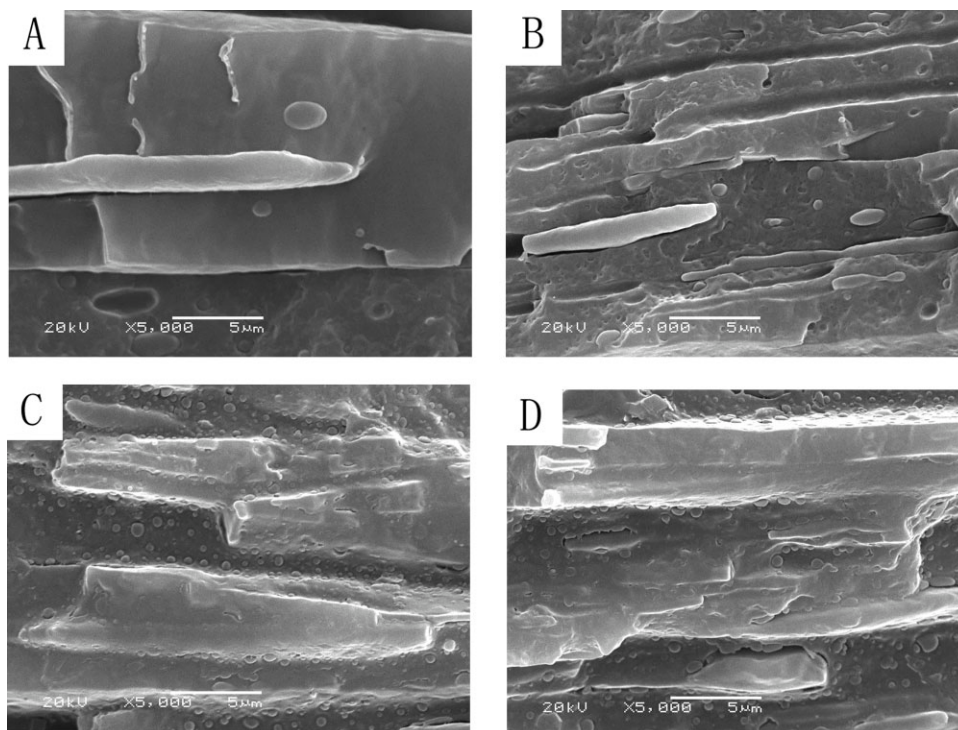
Figure 2 SEM micrographs of the injection-molded PA6/PP blend system compatibilized by EPDM–MAH samples in the skin layer: (A) sample A, (B) sample B, (C) sample C, and (D) sample D.

negative, and ΔG_{mix} can be given by[21]

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (1)$$

where the enthalpy and entropy of mixing, ΔH_{mix} and ΔS_{mix}, are both functions of the composition, temperature (T), and molecular weight. A negative

Figure 3 SEM micrographs of the injection-molded PA6/PP blend system compatibilized by EPDM–MAH samples in the subskin layer (the distance to the surface was 500 μm): (A) sample A, (B) sample B, (C) sample C, and (D) sample D.

Figure 4 SEM micrographs of the injection-molded PA6/PP blend system compatibilized by EPDM–MAH samples in the core layer: (A) sample A, (B) sample B, (C) sample C, and (D) sample D.
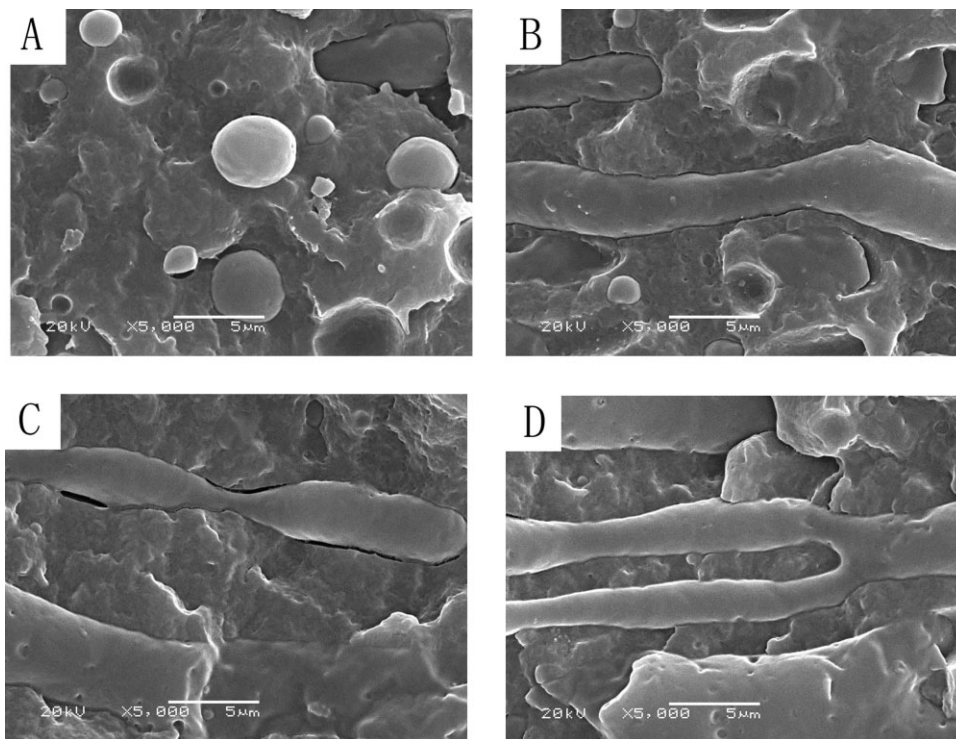
ΔG_{mix} value is a necessary but insufficient condition for miscibility. To obtain phase stability, additional requirements have to be satisfied:

$$\left(\frac{\partial^2 \Delta G_{mix}}{\partial w_i^2}\right)_{T,P} > 0 \qquad (2)$$

where ΔG_{mix} is the free energy of mixing, w_i is the weight fraction of component i, and P is pressure. Because ΔS_{mix} of high-molecular-weight polymers is quite small, the miscibility is ensured by a negative value of ΔH_{mix}, which corresponds to the existence of attractive interactions between the components. It
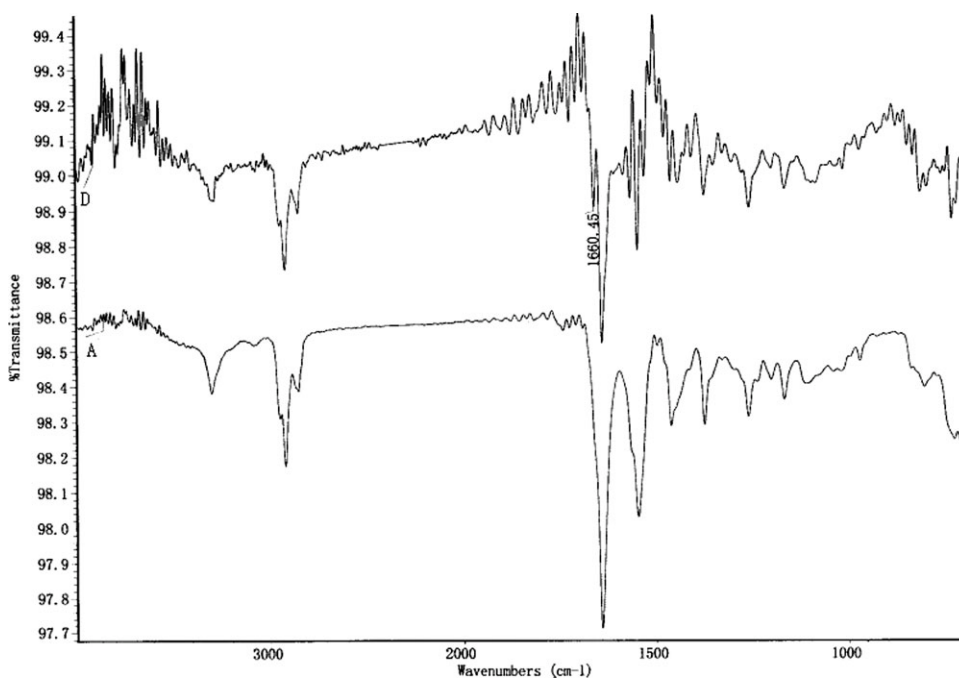
Figure 5 FTIR spectra of the surface of the injection-molded samples: (A) sample A and (D) sample D.
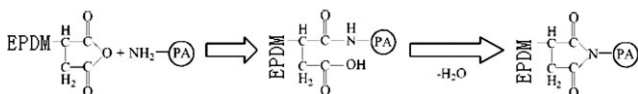
Figure 6 Reaction between an anhydride group and a PA6 amine terminal group.

is worth remembering that such specific interactions (e.g., hydrogen-bonding and dipole–dipole interactions) operate in a system in addition to dispersive interactions or London forces,[22] which act between groups not interacting specifically and are expected to contribute endothermically to the total enthalpy of mixing.

In this study, the most stable state was achieved when EPDM–MAH, the compatibilizer, was dispersed in the interface between PA6 and PP because the energy was lowest; this resulted from the following two kinds of interactions: (1) the interactions from the reaction between the anhydride group of MAH and the PA6 amine terminal group and (2) the interactions between PP and EPDM from the interaction between molecular chains. That is, if EPDM–MAH chains can move freely, EPDP–MAH will disperse in the interface between PA6 and PP; this is the ideal state and will be beneficial to the desired performance of the blend. However, such a state cannot be achieved in practice because the EPDM–MAH chains cannot move freely.

Here we introduce a parameter, the transfer energy (the energy of the compatibilizer transferred from the initial state to the interface), which is mainly controlled by the initial state and dynamics, to analyze the transfer of the compatibilizer. The transfer of EPDM–MAH from the initial state to the interface is related to two courses. First, EPDM–MAH chains must be mobile and can get rid of the restriction between molecules, which then transfer to the interface between PP and PA6, so the transfer energy should include two parts when EPDM–MAH chains move from the initial state to the interface: (1) the energy that makes the EPDM–MAH chains mobile (E_i), which is mainly related to the starting state (e.g., if EPDM–MAH is restricted heavily at first, E_i will be large), and (2) the energy that moves EPDM–MAH to the interface from the state when EPDM–MAH is movable (E_o), which is mainly related to the processing procedures. The final transfer of EPDM–MAH chains is determined by the total transfer energy (total transfer energy = $E_i + E_o$).

For sample A in our study, E_i was big because the interaction was strong, resulting from the reaction between the anhydride group of MAH and the PA6 amine terminal group, which restricted the movement of EPDM–MAH. In a practical processing procedure, the mobility of EPDM–MAH is low, so the movement of EPDM–MAH chains to the interface is

hard, and this results in a few EPDM–MAH chains dispersed in the interface; the compatibility is poor, and this results in low impact strength. For sample D, E_i was small because the interaction was weak on account of the interaction between the PP chains and EPDM chains. In a practical processing procedure, the mobility of EPDM–MAH is large, so the movement of EPDM–MAH chains to the interface is easy, and this results in many EPDM–MAH chains dispersed in the interface; the compatibility of the blend is quite good, and this results in high impact strength. The other two samples were between the two extremes. At the same time, as the compatibility increased from sample A to sample D, the stress transfer from the skin layer to the core layer was easy,[23] so the stretching of the dispersed phase in the core layer happened more easily. This is why just sample A showed the typical skin–core structure and the dispersed phase in the core layer of the other three samples was mainly in the form of a fiber.

For the interesting structure presented in Figures 2(D) and 3(C,D), the compatibilizer was not homogeneously dispersed in the injection-molded samples and conglomerated significantly in the skin layer. We think that this should be related to the shear field in the course of injection molding. The shear field decreases E_o, and this results in the reduction of the transfer energy in the skin and subskin layers versus that in the core layer, so the compatibilizer in the skin and subskin layer can move more easily to the interface than in the core layer. This process is responsible for the phenomenon in which a large amount of the compatibilizer conglomerates in the skin and subskin layers, as shown in Figures 2(D) and 3(C,D). The reason that this phenomenon was not observed in the other samples in the skin and subskin layers is that E_i was low, and the shear field was not enough to make a large amount of the compatibilizer conglomerate in the interface. In other words, the transfer ability of the compatibilizer is decided by the transfer energy. The higher the transfer energy is, the harder it is for the compatibilizer to be transferred to the interface.

CONCLUSIONS

Experimental results have shown that the mixing sequences have a significant influence on the properties of a PA6/PP blend system compatibilized with EPDM–MAH. When premixed PP and EPDM–MAH were mixed with PA6, the sample showed the highest impact strength. However, when premixed PA6 and EPDM–MAH were mixed with PP, the sample showed the lowest impact strength. A parameter, the transfer energy (the energy of the compatibilizer transferred from the initial state to the interface), has been introduced in this article to analyze the transfer

of the compatibilizer. The morphological features of the samples were characterized with SEM, and a heterogeneous dispersion of the compatibilizer in the injection-molded samples was observed, which was related to the shear field in the skin and subskin during injection. The shear field decreased the transfer energy and thus increased the transfer ability of the compatibilizer, so a large amount of the compatibilizer could be transferred to the interface.

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