Studies on Blends of LLDPE and Polar Polymers Compatibilized by a Random Copolymer

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ABSTRACT: Compatibilization of blends of linear low-density polyethylene (LLDPE)–poly(methyl methacrylate) (PMMA) and LLDPE–copolymer of methyl methacrylate (MMA) and 4-vinylpyridine (poly(MMA-*co*-4VP) with poly(ethylene-*co*-methacrylic acid) (EMAA) have been studied. Mechanical properties of the LLDPE–PMMA blends increase upon addition of EMAA. In order to further improve interfacial adhesion of LLDPE and PMMA, 4-vinyl pyridine units are introduced into PMMA chains, or poly(MMA-*co*-4VP) is used as the polar polymer. In LLDPE–poly(MMA-*co*-4VP)–EMAA blends, interaction of MAA in EMAA with 4VP of poly(MMA-*co*-4VP) causes a band shift in the infrared (IR) spectra. Chemical shifts of N_{1s} binding energy in X-ray photoelectronic spectroscopy (XPS) experiments indicate a transfer of proton from MAA to 4VP. Scanning electron microscopy (SEM) pictures show that the morphology of the blends were improved upon addition of EMAA. Nonradiative energy transfer (NRET) fluorescence results attest that there exists interdiffusion of chromophore-labeled LLDPE chains and chromophore-labeled poly(MMA-*co*-4VP) chains in the interface. Based on experimental results, the mechanism of compatibilization is studied in detail. Compatibilization is realized through the interaction between MAA in EMAA with 4VP in poly(MMA-*co*-4VP). © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 967–973, 1999

Key words: poly(ethylene-*co*-methacrylic acid); LLDPE; compatibilization; poly(MMA-*co*-4VP)

INTRODUCTION

Polyolefins are the most widely used polymers. Development of ways for compatibilizing blends of polyolefins and polar polymers for recycling purposes is very important. Blends of polyolefins and polar polymers exhibit poor mechanical properties because of poor interfacial adhesion. Use of appropriate interfacial agents is a way to improve properties of blend materials.[1]

The compatibilizers in the present case may be block or graft copolymers with each part chemically identical to or miscible with the immiscible polar polymers,[2–4] or they may also be formed *in situ* during processing through reaction between functionalized polymeric components.[5,6] It is widely known that block and graft copolymers as compatibilizers preferentially locate at the interface between the two phases, thus reducing the interfacial tension.[1] However, block and graft copolymers do not meet some of the other criteria for being preferred compatibilizers. They are relatively expensive and may form low-energy states in blends, such as micelles, which lower the ability of block copolymer to diffuse to interfaces for strengthening.

Random copolymers also can segregate at the interface of homopolymer blends and thus can be used as interfacial agents.[7] Kramer and coworkers used the asymmetric double cantilever beam (ADCB) or crack-opening test and found that a compositionally symmetric random copolymer of styrene and 2-vinylpyridine strongly reinforces the interface between polystyrene and poly(2-vinylpyridine) homopolymers.[8] Random copolymers without strong specific interaction cannot find practical use in compatibilization of immiscible polymer blends because of poor mechanical properties. The reason is that random copolymer chains as the compatibilizer will segregate at the interface between two phases; thus a large loss of conformational entropy of copolymer chains arises. However, if strong specific interactions are introduced into the blends, enthalpy achieved by specific interaction will outweigh the loss of conformational entropy.

Fairley and Prud'Homme reported that addition of poly(ethylene-co-methacrylic acid) (EMAA) can improve the mechanical properties of blends of polyethylene (PE) and polyamide-6.[9] The role of EMAA as a compatibilizer in the ternary blends are due to interaction of the PE segments of EMAA with polyethylene in the amorphous phase and interaction between COOH groups of EMAA and NH$_2$ terminal groups of polyamide-6.

In this article, addition of EMAA to LLDPE–poly(methyl methacrylate) (PMMA) blends and LLDPE–poly(MMA-co-4VP) blends with the purpose of improving the adhesion across the phase boundary and the accompanying change in morphology of the blends have been studied. Interaction between anions on one polymer chain with cations on another can lead to compatibilization of two incompatible polymers.[10–13] In the present study, 4VP units were introduced into PMMA chains, or poly(MMA-co-4VP) were used as polar polymers. In this way, interaction between pyridine units of the copolymer, poly(MMA-co-4VP), and carboxyl groups of EMAA should prompt miscibility.

EXPERIMENTAL

Materials

LLDPE was purchased from Daqing Petrochem. Co. with a molecular weight of 1.67×10^5 [$\overline{M_w}$, measured by gel permeation chromatography (GPC) on PS standards].

Surlyn was purchased from Du Pont Co. The content of methacrylic acid (MAA) is 15.2 wt %, 18.04% of which in the form of zinc salt, as determined by elementary analysis and atomic spectroscopy. Its molecular weight is 2.52×10^4 ($\overline{M_w}$, measured by GPC). EMAA was obtained by adding sulfuric acid in THF to Surlyn in xylene solution at 55°C.

PMMA was synthesized by anionic polymerization with a molecular weight of 4.05×10^4 and the polydispersity of 1.2.

Poly(MMA-co-4VP) was synthesized in this laboratory. Copolymerization was initiated by azo-bis-isobutylnitrile (AIBN) in toluene at 60°C under an argon atmosphere. The conversion of the monomer was controlled below 10%. Two kinds of copolymers were synthesized, 7-poly(MMA-co-4VP) and 13-poly(MMA-co-4VP). For the two copolymers, the content of 4VP units in the copolymer were about 7 and 13.6 wt %, respectively. The average molecular weights of 13-poly(MMA-co-4VP) and 7-poly(MMA-co-4VP) were about 1.0×10^5 and 8×10^4, and the polydispersities ($\overline{M_w}/\overline{M_n}$) were about 1.8 and 1.7 (measured by GPC on PS standards). The content of 4VP units in the copolymer was measured by elemental analysis.

Anthracene-Labeled LLDPE

LLDPE was firstly grafted with maleic anhydride (MAH) in the presence of benzoyl peroxide (BPO) in xylene at 120°C. The content of MAH in LLDPE-g-MAH was about 2 wt %. LLDPE-g-MAH was reacted with aminoanthracene in toluene at 110°C under argon atmosphere for 2 h; the content of anthracene on the LLDPE chains was about 1 mol % [measured by ^{1}H nuclear magnetic resonance (^{1}H-NMR)].

Naphthalene-Labeled Poly(MMA-co-4VP)

Vinylnaphthalene was copolymerized with MMA and 4VP in toluene at 60°C with AIBN as an initiator under an argon atmosphere. The reaction was allowed to proceed until conversion of the monomers reached about 10%. The contents of 4VP and vinyl naphthalene in the copolymer were 13 and 1.6 wt %, respectively. The average molecular weight was about 1.2×10^5, and the polydispersity ($\overline{M_w};\overline{M_n}$) was about 2.0 (measured by GPC on PS standards).

All labeled polymers were purified by repeated dissolving and precipitation cycles (5 times) using a system of xylene–alcohol (solvent and precipi-

tating agent for labeled LLDPE, respectively) or THF–alcohol [solvent and precipitating agent for labeled poly(MMA-*co*-4VP)].

Blending

Blends of LLDPE–PMMA and LLDPE–poly(MMA-*co*-4VP) (2 : 1 by weight) with varying amounts of EMAA were prepared by dissolving the components in xylene at 120°C under an argon atmosphere to yield dilute solutions (2 g of polymers in 100 mL of solvent); the blends were then precipitated from alcohol, filtered, and dried in vacuo for a week at 70°C.

Measurements and Observations

The infrared studies were performed on a BIO-RAD FTS-7 Fourier transform infrared (FTIR) spectrometer at a resolution of 1 cm^{-1} with samples molded at 150–170°C.

X-ray photoelectronic spectroscopy (XPS) measurements recorded on an ESCALAB-MKII spectrometer with a monochromatized MgKα X-ray source at working conditions of a voltage of 13 kV and currents of 20 mA under an operating pressure of 5×10^{-8} mbar.

The fracture surface for scanning electron microscopy (SEM) observation was prepared by fracturing the sample frozen in liquid nitrogen for 5 min. The morphology of the fractured surface was observed on a JEOL-MAX-840 scanning electronic microscope after being coated with gold.

The samples used in the fluorescence study were compression molded at 150–170°C for 5 min and then cooled slowly to room temperature. Quenching was carried out by dipping samples into liquid nitrogen from a temperature of 140°C. Emission spectra were measured on a Shimadzu RF-5000 fluorescence spectrometer at room temperature. The energy transfer efficiencies were determined by recording the reflectance fluorescence spectrum of films irradiated at 280 nm, and the ratio I_D/I_A of the fluorescence intensity of the donor at 336 nm and of the acceptor at 408 nm was characterized.

Mechanical properties of the blends were measured at room temperature on an Instron 1211 testing machine, with the drawing rate being 100 mm/min. The samples used in the measurement were also compression-molded at 150–170°C.
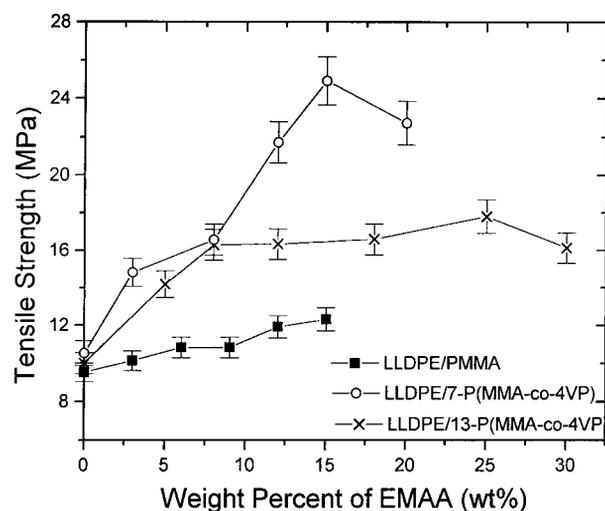

Figure 1 Tensile strength at break of blends of LLDPE and polar polymers compatibilized by EMAA versus the weight percentage of EMAA: (–■–) LLDPE–PMMA–EMAA; (–○–) LLDPE–7-poly(MMA-*co*-4VP)–EMAA; (–x–) LLDPE–13-poly(MMA-*co*-4VP)–EMAA.

RESULTS AND DISCUSSION

Mechanical properties of compatibilized blends are very important in practical use. The tensile strength of LLDPE–PMMA blends and LLDPE–poly(MMA-*co*-4VP) blends compatibilized by varying amounts of EMAA are shown in Figure 1. We can see that tensile strength of blends increase upon addition of EMAA, indicating that interfacial adhesion between LLDPE phase and polar polymer phase are enhanced by EMAA. It is noted that tensile strength of compatibilized blends LLDPE–PMMA–EMAA are lower than those of LLDPE–poly(MMA-*co*-4VP)–EMAA blends. EMAA is composed of randomly distributed ethylene and methacrylic acid units. Methacrylic acid units in EMAA are very strongly self-associated through the formation of hydrogen-bonded cyclic dimers. In the infrared spectrum of EMAA, the bond at 1700 cm^{-1} shows carboxyl groups form intermolecular dimers as a result of hydrogen bonding[14] (Fig. 2), so the interaction between EMAA and PMMA is very weak. In fact, the interaction between carboxylic acids and pyridine nitrogen is very strong. MAA units and 4VP units not only form hydrogen bonds but they also have the following complete proton transfer reaction: some of the protons shared by pyridine and neighboring carboxylic groups are captured by the heterocycle, and the resulting ions interact through coulombic interactions.[15] The incorporation of 4-vinylpyri-
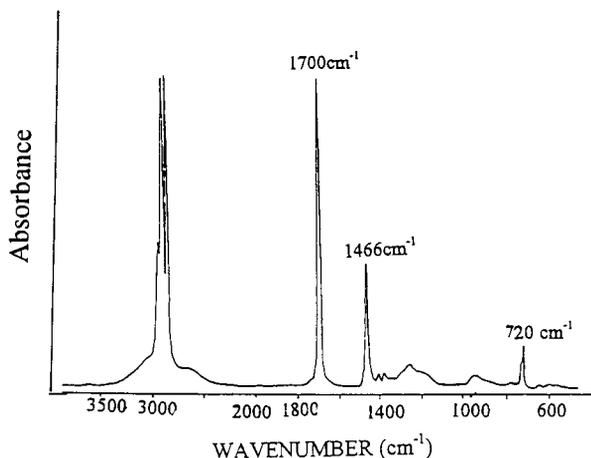
Figure 2 Infrared spectrum of EMAA.

Figure 3 Infrared spectra in the carbonyl region of blends of LLDPE and 13-poly(MMA-*co*-4VP) (2 : 1 by weight) with 6, 18, and 30 wt % of EMA.

dine into PMMA chains will greatly improve the interfacial adhesion of the phases. In Figure 1, another interesting phenomenon is that the tensile strength of LLDPE–7-poly(MMA-*co*-4VP)–EMAA blends are higher than those of LLDPE–13-poly(MMA-*co*-4VP)–EMAA blends, which indicates that too many interaction sites are not favorable for the mechanical properties of the blends. Comparing 7-poly(MMA-*co*-4VP), the loss of conformational entropy of 13-poly(MMA-*co*-4VP) is larger when 4VP units distributed at the interface. Enthalpy is determined mainly by EMAA content in blends, so too high a content of 4VP in the copolymer should be avoided.

The infrared spectrum of blends of LLDPE and 13-poly(MMA-*co*-4VP) compatibilized by EMAA are shown in Figure 3. At 6 wt % EMAA content, the infrared absorption band of EMAA at 1700 cm^{-1} shifts to 1730 cm^{-1}, indicating the dissociation of the intermolecular carboxylic acid dimers and the formation of interaction between carboxylic acid and pyridine. The formation of specific interaction sites between MAA in EMAA and 4VP of 13-poly(MMA-*co*-4VP) dictates the monomeric instead of dimeric character of the MAA units. It is noticed that when the concentration of EMAA is above 18 wt %, the peak at 1730 cm^{-1} reappears, which indicates that EMAA is in excess at this content and MAA units exist as dimeric acids.

XPS spectra of N$_{1s}$ peaks of 4VP in blends of LLDPE and 13-poly(MMA-*co*-4VP) with varying amounts of EMAA are shown in Figure 4. In binary blends of LLDPE and 13-poly(MMA-*co*-4VP), the N$_{1s}$ binding energy is about 401.8 eV. In the ternary blends with 6 and 18 wt % EMAA, the
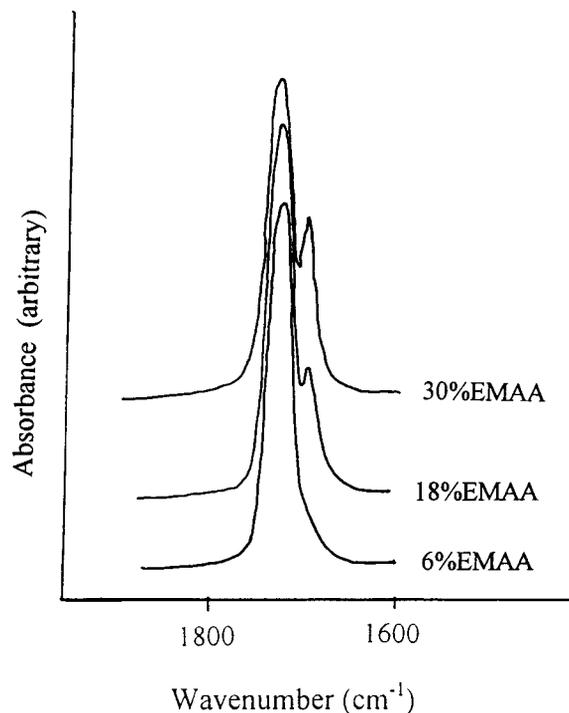
N$_{1s}$ binding energies increase to about 404.2 and 404.8 eV, respectively. However, the binding energy of the blends with 30 wt % EMAA stays almost the same as that of the blends with 18 wt
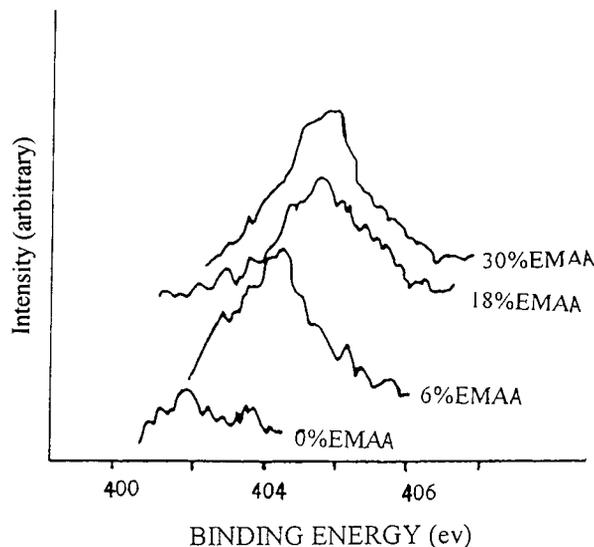

Figure 4 XPS spectra of blends of LLDPE and 13-poly(MMA-*co*-4VP) (2 : 1 by weight) with different amounts of EMAA.
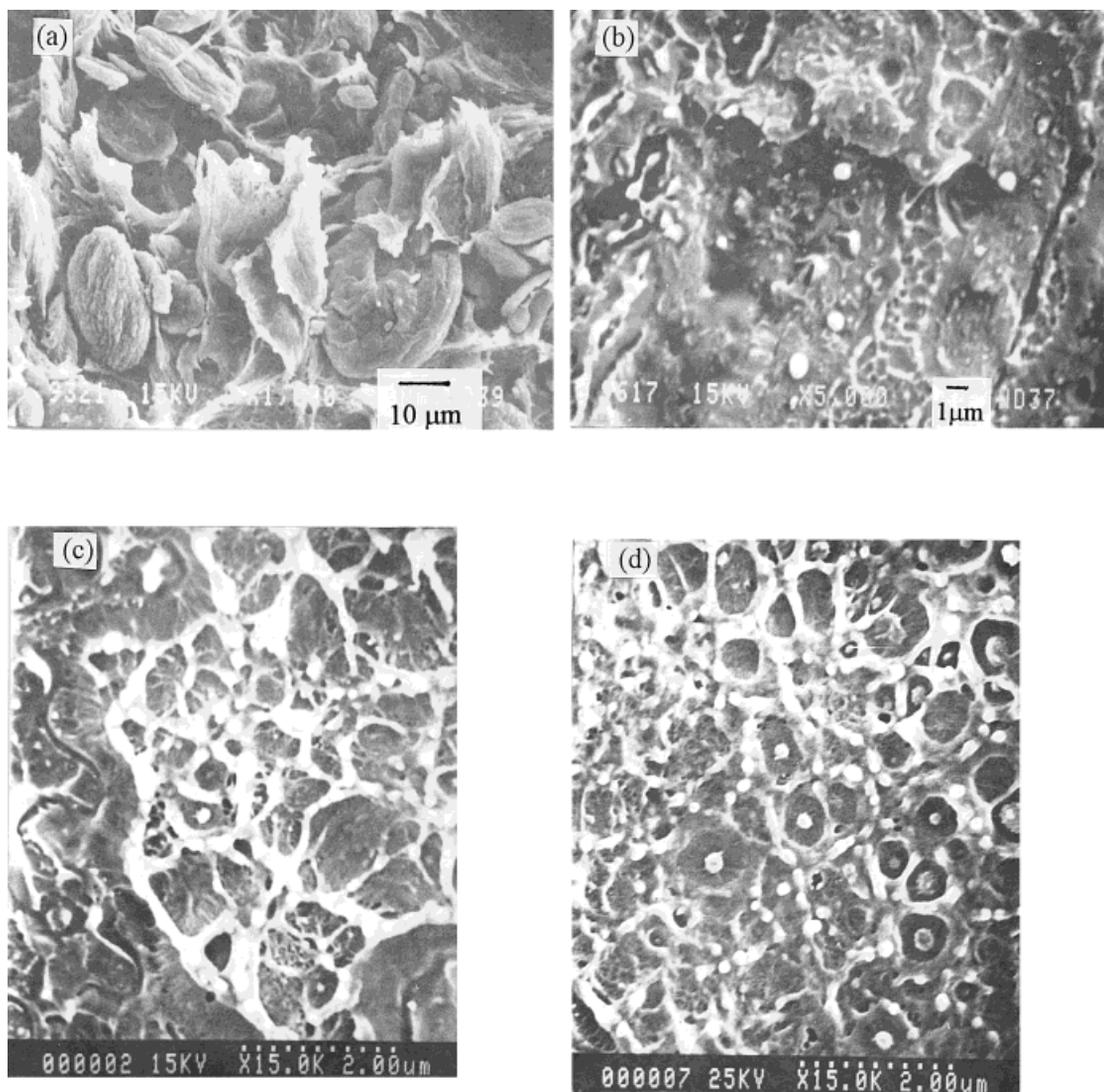
Figure 5 Scanning electron micrographs of blends of LLDPE and 13-poly(MMA-*co*-4VP) (2 : 1 by weight) compatibilized by different amount of EMAA. Weight percentages of EMAA in ternary blends are as follows: (a) 0, (b) 12, (c) 18, and (d) 25 wt %.

% EMAA. In this system, the chemical shift of N_{1s} binding energy originates from electron transfer from an electron donor (4VP) to an electron acceptor (MAA) at the interface. Just as the infrared experiment shows, EMAA is in excess at 18 wt % content, so no incremental electron transfer between MAA and 4VP above 18 wt % EMAA content is envisaged.

One of the best methods to comprehend compatibilization is to measure directly the interfacial tension.[16] Because the size of particles of the dispersed phase in immiscible blends is directly proportional to the interfacial tension, the efficiency of a compati-

bilizer can also be determined by observing the change of particles size using SEM.

In our experiments, the morphology of blends of LLDPE and 13-poly(MMA-*co*-4VP) was examined. In binary LLDPE–13-poly(MMMA-*co*-4VP) blends, the dispersed 13-poly(MMMA-*co*-4VP) domains in the LLDPE continuous phase are almost spherical, and the average diameter is as large as approximately 15 μm (Fig. 5). The influence of added EMAA on the morphology of LLDPE–13-poly(MMA-*co*-4VP) (2 : 1) blends is obvious. With addition of EMAA, the size of the dispersed 13-poly(MMA-*co*-4VP) domains become smaller. The

average diameter of dispersed particles is reduced to approximately 1 μm on addition of 12 wt % EMAA, approximately 0.15 μm with 18 wt % EMAA. An interesting phenomenon is that when 25 wt % EMAA is added to the blend, the average diameter of the particles is about 0.2 μm with broader polydispersity.

Since nonradiative energy transfer (NRET) fluorescence displays a resolution of only 2–4 nm, in the gap between routine methods, such as differential scanning calorimetry (DSC) and dynamical mechanical analysis (DMA), it has aroused much interest since its introduction to the study of polymer blends.[17–20] In immiscible polymer blends, the energy transfer efficiencies are very low because of the long distance between the donor and the acceptor. However, if there exists interdiffusion of fluorescence-labeled homopolymers in the interface, the volume fraction of the interfacial zone increase and the distance between the donor and the acceptor gets shortened in the interface, which results in an increase in energy transfer efficiency. The emission spectra of naphthalene-labeled poly(MMA-co-4VP) overlaps the absorption spectra of anthracene-labeled LLDPE.[21] The efficiency of energy transfer is measured by the ratio of the fluorescence intensities of the donor at 336 nm and the acceptor at 408 nm (I_D/I_A). In this article, we studied the change in the ratio I_D/I_A, which reflects interdiffusion of polymer chains of matrix phases in the interface at different levels of added compatibilizer.

Curve (a) in Figure 6 shows the NRET results obtained from blends of labeled LLDPE and labeled poly(MMA-co-4VP) with varying amounts of EMAA. The efficiency of the energy transfer increases with addition of EMAA. However, I_D/I_A reaches a minimum at about 20 wt % EMAA, suggesting the attainment of a maximum volume fraction of the interfacial zone. At about 20 wt % EMAA content, the interfacial tension is the lowest, and the interdiffusion of labeled LLDPE chains and poly(MMA-co-4VP) chains is most strong at the interface. IR, XPS, and SEM experimental results all show that in LLDPE–13-poly(MMA-co-4VP)–EMAA blends, EMAA is in excess at about 18 wt %. Taking into account the different resolution and concentration interval of EMAA, the NRET result is consistent with IR, XPS, and SEM results.

Compatibilization of blends of LLDPE and poly(MMA-co-4VP) by EMAA is realized through the interaction of MAA and 4VP units at the interface. The interface of LLDPE and poly(MMA-co-
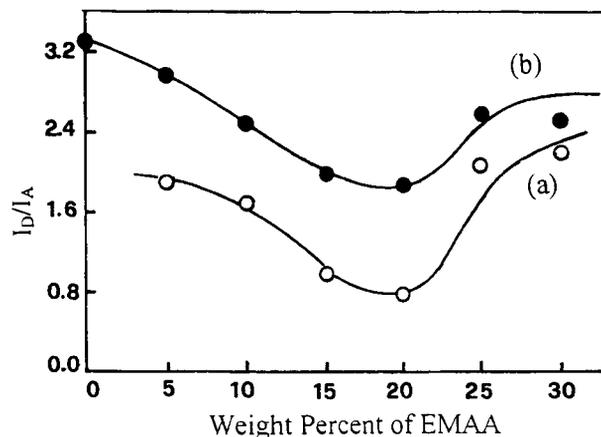

Figure 6 The energy transfer efficiency obtained from blends of anthracene-labeled LLDPE and naphthalene-labeled 13-poly(MMA-co-4VP) (2 : 1 by weight) compatibilized by EMAA as a function of the weight percentage of EMAA in ternary blends: (a) annealed from 150°C to room temperature; (b) quenched in liquid nitrogen from 140°C.

4VP) get broader with the addition of EMAA. There exists interdiffusion and interpenetration of labeled LLDPE chains (acceptor) and labeled poly(MMA-co-4VP) chains (donor) at the interface. When EMAA is in excess, EMAA will aggregate to form clusters as pairs or higher multiplets in the polyethylene phase or in the interface.[22] Clusters in the interface prevent chromophore-labeled polymers from interdiffusing, so the efficiency of the energy transfer decreases above 20 wt % EMAA content.

It is well known that quenched samples keep the same state at higher temperatures. Samples quenched from 140°C to liquid nitrogen were also used in the fluorescence study. The results shown as curve (b) in Figure 6 display almost the same trend as curve (a), reflecting the same compatibilization behavior at a high temperature. But it is noticed that the energy transfer efficiencies at a high temperature are lower than that at the room temperature.

According to Gibbs function, a decrease in entropy is unfavorable for free energy. In blends of LLDPE and poly(MMA-co-4VP) compatibilized by EMAA, the 4VP units and MAA units locate at the interface in order to interact with each other. This kind of distribution leads to a decrease in entropy. But the loss of entropy is compensated by the heat of interaction between carboxylic acids and pyridine. Because of the negative entropy, a rise of temperature is unfavorable for free en-

ergy, which results in a increase of interfacial tension and lower energy transfer efficiencies at a high temperature. EMAA as a compatibilizer is more efficient at room temperature than it is at a higher temperature.

Random copolymers with strong specific interaction can be used as an efficient compatibilizer for immiscible polymer blends. Based upon the above analysis of experimental results, a mechanism is proposed. For EMAA and poly(MMA-*co*-4VP), both MAA units and 4VP units favor random distribution in the bulk phase. Only in this way can favorable entropy be preserved. However, due to interaction with each other, most of the 4VP units of poly(MMA-*co*-4VP) and MAA units of EMAA locate at the interface. This kind of distribution leads to a decrease in entropy. But heat of neutralization is a negative value, which compensates the loss in entropy. In other words, the enthalpy term outweighs the entropy contribution.

CONCLUSIONS

EMAA is a very efficient compatibilizer for incompatible blends of LLDPE–poly(MMA-*co*-4VP). As studied by IR, XPS, SEM, NRET, and mechanical properties, for LLDPE–poly(MMA-*co*-4VP) blends, compatibilization is materialized through the interaction of MAA in EMAA with 4VP in poly(MMA-*co*-4VP) and the interaction of LLDPE with PE segments in EMAA in amorphous regions. In ternary blends, LLDPE chains and poly(MMA-*co*-4VP) chains interdiffuse in the interface, which results in a broader interface between LLDPE and polar polymers. For the ternary blends, there is an equimolar point of MAA to 4VP, above which the excess EMAA is no longer efficient as a compatibilizer.

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