

Properties of Ethylene–Propylene Copolymer/PA-1010 Blends Using Ethylene–Propylene Copolymer-*graft*-Acrylic Acid as a Compatibilizing Agent

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SYNOPSIS

The modification of ethylene–propylene copolymer (EP) has been accomplished by radical initiators. The resulting EP-*graft*-acrylic acid (EP-*g*-AA) has been used to obtain ternary PA/EP/EP-*g*-AA blends by melt mixing. Different blend morphologies were observed by scanning electron microscopy; the domain size of the EP-dispersed phase in the polyamide 1010 matrix of compatibilized blends decreased compared with that of uncompatibilized blends. It is found that EP-*g*-AA used as the third component has a profound effect on the mechanical properties of the resulting blends. This behavior has been attributed to serious chemical interactions taking place between the two components. Thermal analysis shows that some thermal properties of PA in compatibilized PA/EP/EP-*g*-AA changed because of chemical reactions taken place during the blending process. Wide angle x-ray diffraction measurements also confirmed this result. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

There are many interrelated variables that affect the mechanical/physical properties of the heterogeneous polymer blends. 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 phase, a large interfacial tension leading to poor control of morphology during melt mixing, and poor interfacial adhesion or stress transfer in the solid state. Several authors^{1–5} report that the presence of a block or graft copolymer of appropriate chemical structure can provide a lowering of the interfacial energy and an improvement of the interfacial adhesion between the two phases. When incompatible polymers are mixed, the interfacial adhesion is weak, which results in inferior mechanical properties and poor dispersion of the components. The blends require a compatibilizing agent to achieve satisfactory interfacial adhesion and in-

terfacial stress transfer between two phases. Previous studies show PP-*g*-MA to be an effective compatibilizer for polypropylene/polyamide 6 blends.^{6–9} Compatibilization is considered to occur through chemical linkage of anhydride on the compatibilizer chain and polyamide end groups.

The present study was aimed at understanding the relationship between the compatibilizer and the resulting blend properties. In particular, PA-rich PA/ethylene–propylene (EP) blends were investigated using EP copolymer grafted with acrylic acid (EP-*g*-AA) as the compatibilizer.

EXPERIMENTAL

Materials

The polyamide-1010 (PA1010) was purchased from JiLin ShiJingGou Union Chemical Co. (China). Its relative viscosity is 2.1, and melting index is 10 g/10 min. EP was supplied by LiaoNing PanJin Gas Chemical Co. (China) with melting index 1.0 g/10 min; C₂-content of this EP sample is 10.0% (in mol).

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EP-*g*-AA was prepared by reaction extruding initiated by dicumylperoxide as reported previously.¹⁰ The content of AA in EP-*g*-AA used in this work was 1.02% (in weight).

Preparation of PA1010/EP/EP-*g*-AA and PA1010/EP Blends

Ternary PA1010/EP/EP-*g*-AA and PA/EP blends were prepared by melt mixing the polymers in a bra-bender single-screw extruder ($L/D = 20$) at a temperature of 195–210°C, residence time of 2.5 min at 32 rpm. PA/EP/EP-*g*-AA were prepared in weight ratio of 75/25/0, 75/24/1, 75/23/2, 75/21/4, 75/19/6, 75/17/8, 75/15/10, 75/10/15, and 75/5/20. The melt-blended pellets were used to prepare test specimens for the measurement of mechanical properties by using a JSWF17SA injector with a barrel temperature of 195–210°C and an injection pressure of 60 MPa.

Measurements of Mechanical Properties

Dumbbell-shaped specimens of 3-mm thickness were prepared for tensile property measurements. Tests were carried out on an Instron 1121 at room temperature with a cross-head speed of 50 mm/min. Measurements of flexural modulus and strength were also performed with an Instron 1121 on the basis of ISO178-1975E. Izod impact strength measurements were carried out with an XJU-22 impact testing machine made in China on the basis of ISO/R180-1961. All dried specimens were obtained in a vacuum oven at 80°C for 12 h.

Morphological Observation

A scanning electron microscope, JXA-840, was used to observe the morphologies of the blends. Before observation, the observed sections of samples were etched with xylene for 6 h to dissolve the EP out of the blends to increase the contrast.

Thermal Analysis

Thermal analysis was performed on a Perkin-Elmer DSC II apparatus. The fusion thermogram was obtained by heating from 50 to 250°C at a heating rate of 10 K/min. All measurements were performed under nitrogen atmosphere.

Wide-Angle X-Ray Diffraction (WAXD) Measurements

WAXD measurements were performed by means of a Philips PW1700 diffractometer (Ni-filtered $\text{CuK}\alpha$ radiation). The high voltage was 50 kV and tube current was 30 mA.

RESULTS AND DISCUSSION

Morphology

The scanning electron micrographs of the uncompatibilized blend of PA/EP (75/25) shows the typical morphology of an incompatible blend [Fig. 1(a)]. The large particle size, with no evidence of adhesion between the matrix and dispersed phase, confirmed the incompatibility of the two components. In compatibilized blends, the EP was dispersed in the PA as spherical particles. It was found that the average size of the second component decreased compared with that of the uncompatibilized blend in the same compositions. It was evident that small grafted contents of AA have a very large effect on particle size and the concentration of compatibilizers affect the EP particle size differently. The EP particles in the blend appeared to be more deeply embedded in the matrix. The EP particle size initially decreased with increasing amount of compatibilizer and then reached a constant value of about 4 μm when increasing compatibilizer had no further effect on particle size. The plot in Figure 2 shows that the particle size correlated better with the amount of compatibilizer. Small concentrations of AA had a profound effect on particle size, e.g., 0.20% AA decreased the average particle size from over 10–15 μm to less than 5 μm .

Mechanical Properties

The tensile and flexural properties for the dried sample are listed in Table I. For the uncompatibilized blend, mechanical properties are not as good as that of the compatibilized blend in the same compositions, indicating that the components are incompatible with almost no mutual adhesion in the case of the PA/EP blend. In the process of PA/EP/EP-*g*-AA blends, some chemical reaction occurred, and certain graft polymers formed between AA in EP-*g*-AA and terminal amino groups of PA. It improved the interfacial adhesion that caused the increase of tensile and flexural strength of PA and EP alloys.

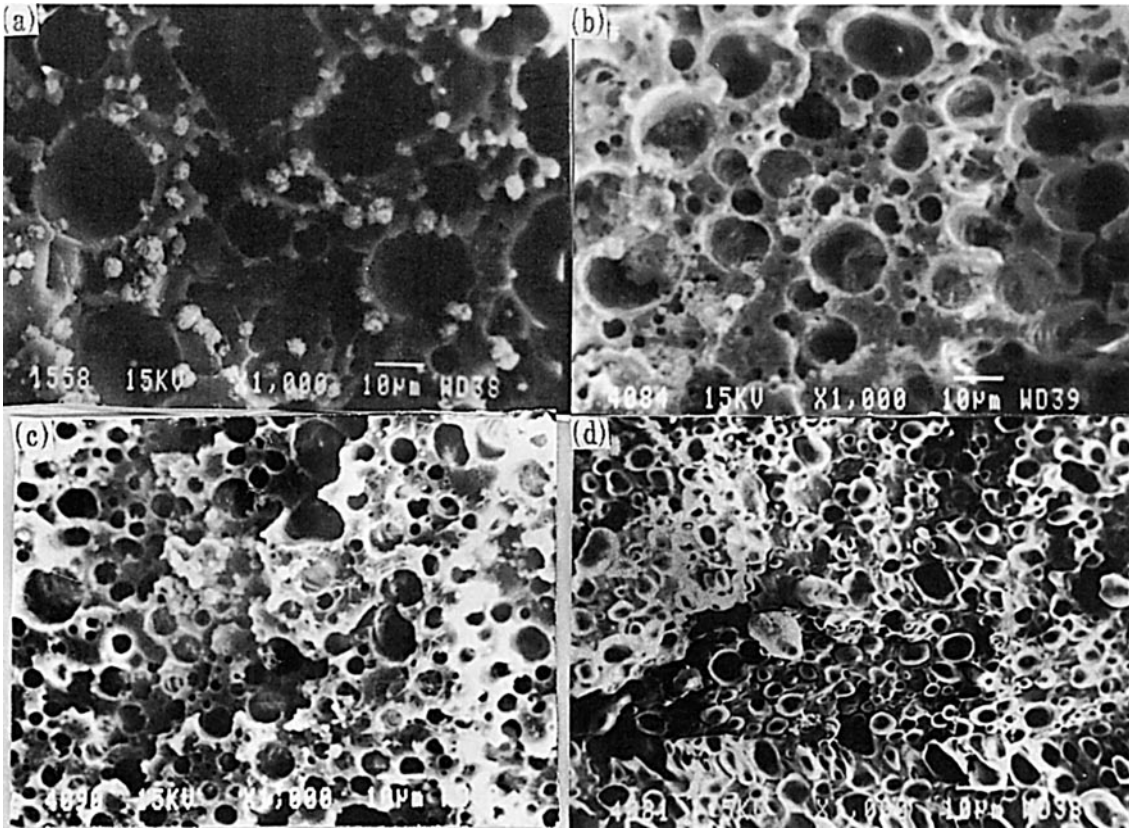


Figure 1 SEM pictures for (a) PA/EP (75/25 wt/wt); (b) PA/EP/EP-g-AA (75/20/5 wt/wt); (c) PA/EP/EP-g-AA (75/15/10 wt/wt); (d) PA/EP/EP-g-AA (75/10/15 wt/wt).

The notched Izod impact strength of blend samples are plotted against compatibilizer concentration in Figure 3. It shows that the blend of PA/EP/EP-g-AA is tougher than that of the PA/EP blend in

the same compositions; the improvement on the impact strength of the ternary blends was obvious. At the highest AA content, the impact strengths of ternary blends were not as significantly improved as

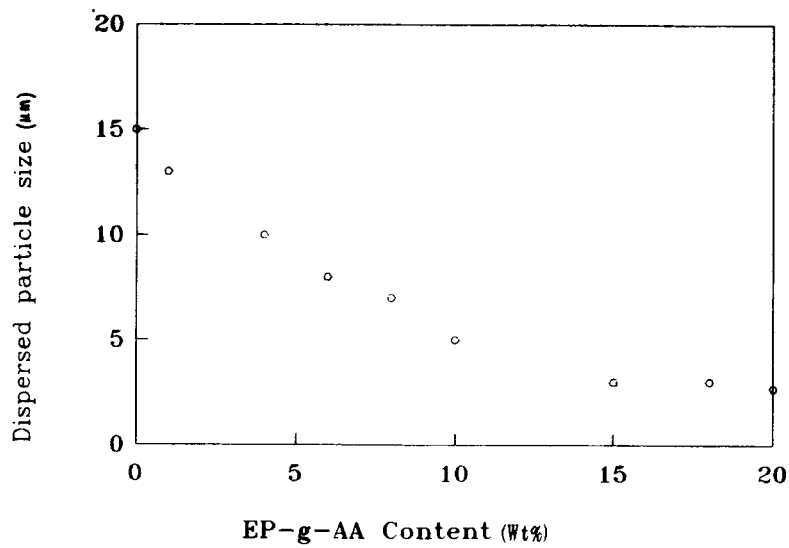


Figure 2 Dispersed particle size as a function of the AA concentration in the blend.

Table I Tensile Strength σ_b , Young's Modulus E_y , Elongation at Break ϵ_b , Flexural Strength σ_f , and Flexural Modulus E_f of Dried Samples of PA/EP and PA/EP/EP-*g*-AA Blends

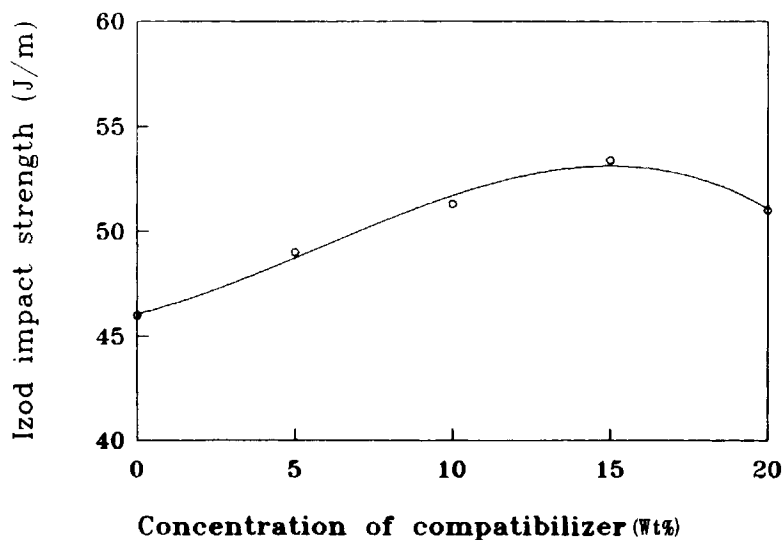
Composition (PA/EP/EP- <i>g</i> -AA in wt %)	σ_b (MPa)	E_y (MPa)	ϵ_b (%)	σ_f (MPa)	E_f (MPa)
75/25/0	37	784	22	33	612
75/20/5	40	807	31	60	1130
75/15/10	43	811	33	63	1128
75/10/15	44	801	34	62	1001
75/5/20	40	800	31	59	907

other series of blends. Hence, a significant improvement on the impact strength of the blend could be obtained only if the blend consisted of an optimal concentration of the compatibilizer. Figure 4 indicates the relationship of compositions and impact strength at fixed compatibilizer concentrations of 10 wt %. The impact strength of PA/EP/EP-*g*-AA blends were all higher than plain PA. PA1010, as other polyamides, shows a poor impact resistance, especially at temperatures below T_g and in the dry state. As morphology analysis, the degree of dispersion, adhesion between two phases of PA and EP, are remarkably improved after EP-*g*-AA was added. EP domains dispersed in rigid PA1010 matrix stop the craze growth, which can yield the formation and development of failure cracks during impact, and act as stress concentrators forming a barrier to the extension of crazing at the same time. Strong interactions between two phases resulted in good adhesion and efficient stress transfer from contin-

uous to the dispersed polymer phase, and it should be responsible for the increase of impact strength.

Thermal and WAXD Analysis

The fusion thermograms of all the materials tested are shown in Figure 5. Both of the components of the blends are semicrystalline, and they produce two distinct melting peaks of the pure components. PA1010 is known to have one crystalline structure, the monoclinic α -modification. In the fusion thermogram of PA1010, two distinct melting peaks have been detected. The one at higher temperatures has been attributed to the α -crystalline modification, the other one may be produced by thermal history. The samples of compatibilized blends show a main peak with no or less pronounced shoulder at 463 K. This behavior can be attributed to the presence of EP-*g*-AA and its reaction products with PA in these blend systems.

**Figure 3** Dependence of impact strength of PA/EP/EP-*g*-AA blends on the compatibilizer concentration

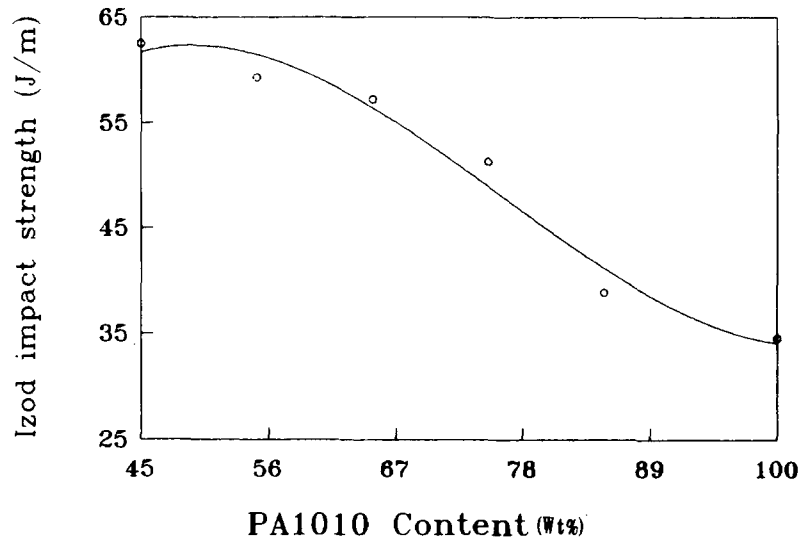


Figure 4 The relationship of compositions and impact strength at fixed compatibilizer concentration 10 wt %.

The plot of heat fusion for PA versus the concentration of EP-g-AA in Figure 6 shows a decrease in heat of fusion from about 38 to 25 J/g as the concentration of the compatibilizing agent increases from 0 to 20 Phr. This suggests that PA crystallinity in the blends decreases as the concentration of EP-g-AA increases. The decrease in ΔH_m of the PA with the increase in EP-g-AA can be explained as follows.

The decrease in crystallinity is caused by a difficulty in polymer chain arrangement, whereby movement of segments is presented by the branched chain. As the amount of EP-g-AA added to blends increases, more PA reacts with EP-g-AA and forms *in situ* PA-g-EP, which is restricted in its segmental mobilities, and hence this restriction causes the decrease in crystallinity of PA. The heat of fusion of EP in

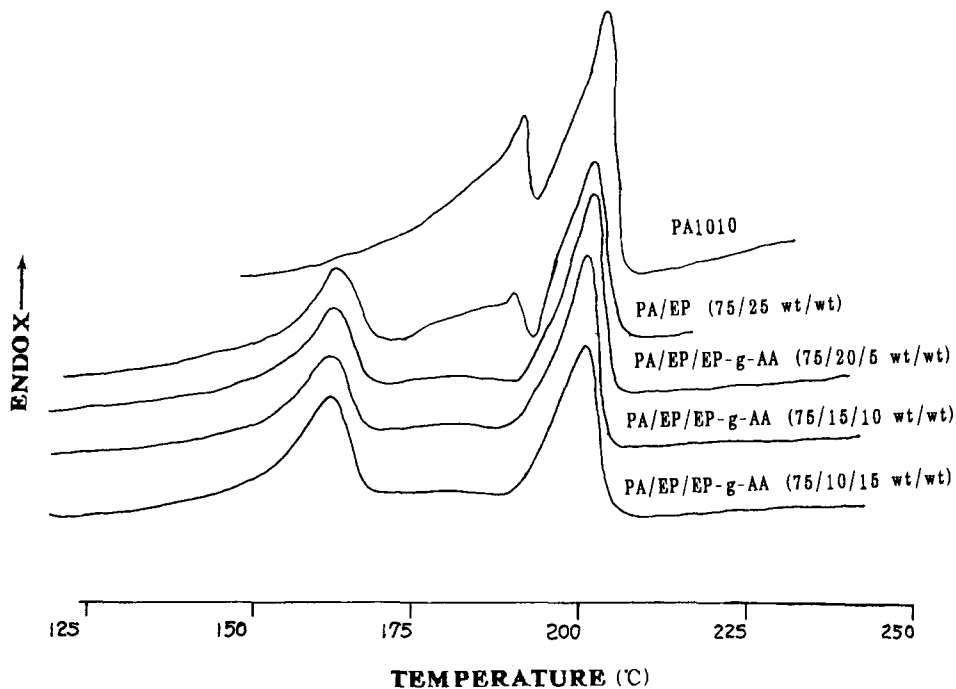


Figure 5 DSC heating thermograms of EP/PA = 25/75 blends with various amounts of EP-g-AA.

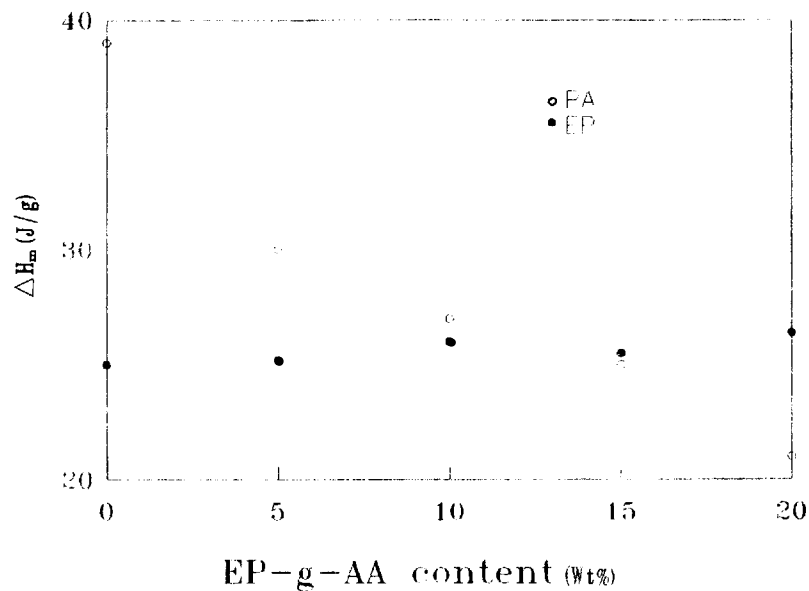


Figure 6 Plot of heat of fusion (ΔH_m) versus EP-g-AA content in EP/PA = 25/75 blends.

blends does not change markedly with the change of the compatibilizing agent concentration. It is almost constant for the ΔH_m of EP. Because the EP in blends took no reaction during the compounding processes, its segmental mobilities did not change

appreciably, and, consequently, the heat of fusion of EP shows no significant change as the concentration of EP-g-AA increases.

Figure 7 shows WAXD spectrum of the neat PA-1010, EP, and the ternary blends of PA/EP/EP-g-

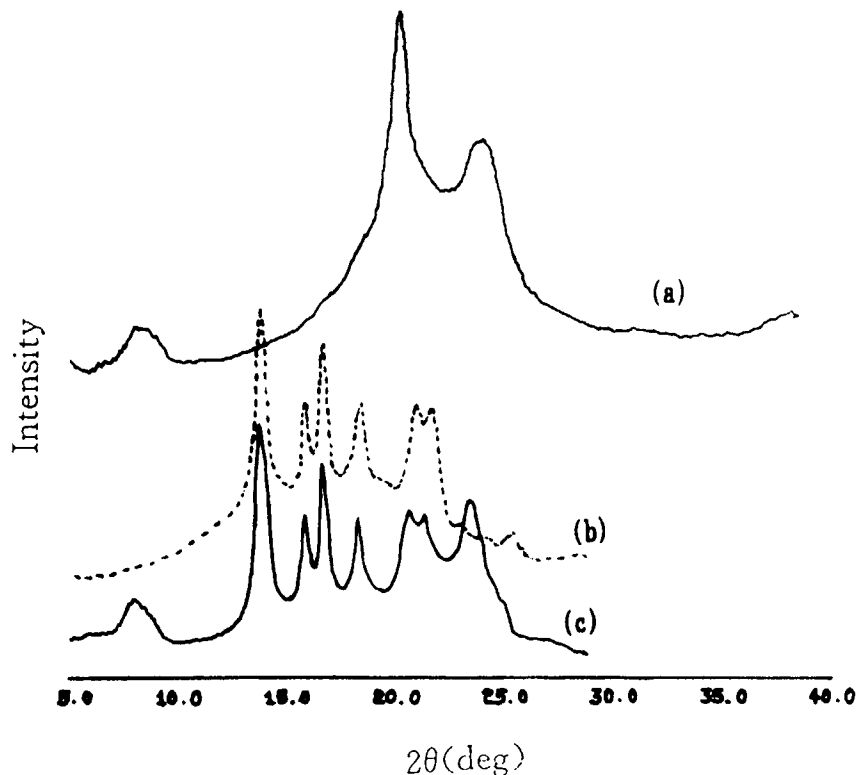


Figure 7 WAXD patterns of (a) PA1010, (b) EP, and (c) PA/EP/EP-g-AA (75/5/20).

AA. The WAXD of the neat PA showed a characteristic diffraction peak of 100, T00 and 110, 010, 0T0 crystalline structures at $2\theta = 20.29, 23.67$, respectively. The relative proportions of the two crystalline structures in compatibilized and uncompatibilized blends were significantly different. It is suggested that the introduction of the compatibilizer was favored for the formation of crystal at $2\theta = 23.67$.

CONCLUSIONS

Binary blends of PA and EP copolymer are immiscible with poor interfacial adhesion and large-phase domains. In compatibilized ternary blends, chemical reactions take place between the AA group in EP-*g*-AA and terminal amino groups of PA1010 and increases the adhesion between two phases. The compatibilized blends display a much finer dispersion of the minor phase in the matrix polymer, and reduction in polydispersity of particle size was found in compatibilized blends. The strong interaction between two phases cause compatibilized blends to have better mechanical properties than that of uncompatibilized blend. Thermal analysis confirmed the interaction between EP-*g*-AA and PA, and the heat of fusion for PA decreased as compatibilizer contractions increased.

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