Effect of Blending Sequence on the Morphology and Properties of Polyamide 6/EPDM-*g*-MA/Epoxy Blends

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ABSTRACT: The ternary blends of polyamide 6/ maleated ethylene-propylene-diene rubber/epoxy (PA6/ EPDM-*g*-MA/EP) were prepared by a twin-screw extruder with four different blending sequences. With the variation of blending sequence, the ternary blends presented distinct morphology and mechanical properties because of different interactions induced by various reactive orders. The addition of epoxy could increase the viscosity of the PA6 matrix, but a considerably larger size of the dispersed rubber phase was observed while first preblending PA6 with epoxy followed by blending a premix of PA6/EP with EDPM-*g*-MA, which was attested by rheological behaviors and SEM observations. It was probably ascribed to the fact that the great increase of the interfacial tension between the matrix and rubber phase aroused a great coalescence of rubber particles. The presence of epoxy in the rubber phase reduced the rubber's ability to cavitate so that the toughening efficiency of the EPDM-*g*-MA was decreased. The results of mechanical testing revealed that the optimum blending sequence to achieve balanced mechanical properties is blending PA6, EPDM-*g*-MA, and epoxy simultaneously in which the detrimental reactions might be effectively suppressed. In addition, thermal properties were investigated by TG and DSC, and the results showed that there was no distinct difference. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 5064–5070, 2012

Key words: polyamides; blending; morphology; mechanical properties; interfacial tension

INTRODUCTION

As an excellent engineering plastic, polyamide 6 (PA6) has good processability, excellent wear resistance, and solvent resistance,[1] but it exhibits low impact strength under the conditions of the dry-state and low-temperature. Blending is a well-known method to modify the properties of polyamide-based materials. Most of the previous work on PA6 was focused on the improvement of mechanical properties such as notched impact strength by adding a functionalized elastomeric phase.[2–14] In general, PA6 and unmodified rubber are thermodynamically immiscible; thus, large-sized aggregates of rubber particles will form during the melt processing.[15,16] Functionalization of rubber is always a good choice to improve the compatibility between the rubber phase and polymer matrix. The functionalized rubber contains a reactive group like maleic anhydride (MA), which can react *in situ* with the terminal amide group of nylons so as to improve the interfacial compatibility because of the formation of graft copolymers. Therefore, MA-grafted ethylene-propylene elastomers, like EPR-*g*-MA or EPDM-*g*-MA, are frequently used for toughening polyamides.

Certainly, the incorporation of rubber or elastomer into polymer matrix could achieve satisfied toughness yet give rise to a reduction of modulus and tensile strength of blends. Therefore, to improve the interfacial interplays between the host polymer and dispersed phase, the introduction of the third component is expected to enhance the modulus and strength of the blends or reduce the loss in strength to the minimum extent. To obtain balanced mechanical properties, ternary blends have been of great interest in both academic and industry research fields.

However, there is an interesting and noteworthy problem. Generally speaking, blending sequence in process can influence the morphology and performance of the ternary blends. The earlier investigations[17] have shown that the blending sequence in the ABS/SMA/PA6 blend determined different dynamic mechanical and rheological properties and morphology. In (ABS/SMA)/PA6 blends, SMA-*g*-PA6 seemed to locate at the interface when blending

ABS/SMA with PA6, and this copolymer worked as an effective compatibilizer, but in ABS/(SMA/PA6) blends, the formed SMA-*g*-PA6 seemed to lie preferentially in PA6 domain. Park et al.[18] have studied the effect of blending sequence on the microstructure and mechanical properties of PBT/EVA-*g*-MAH/organoclay ternary composites, and the results showed that the optimum to achieve the best tensile and impact strength of blends was blending a premixture (EVA-*g*-MAH/organoclay) with PBT in which a fine morphology and good dispersion could be obtained. Ohlsson et al.[19] found that compatibilized polypropylene/polyamide blends prepared with various blending sequences exhibited visibly different morphology and mechanical properties. All above reveals that the mixing sequence influences the order of chemical reactions and the location of graft copolymer formed *in situ* which closely relates to the final morphology and toughness of the composites. In recent years, blending sequence has surely been designed to prepare ternary blends with good mechanical performances, especially in ternary nanocomposites. However, there was an interesting phenomenon in polyamide/maleated elastomer/organoclay composites. The addition of OMMT could obviously decrease the viscosity of the matrix and weaken the interfacial interactions between PA6 and EPDM-*g*-MA when blending EPDM-*g*-MA with a premixture of PA6/OMMT nanocomposites, resulting in the increase of rubber particles size,[14] whereas, some other literature[13,20] reported that blending sequence had little or not much influence on the mechanical properties in the PA6/EPDM-*g*-MA/organoclay ternary blends. Presumably, the different results were attributed to various dispersion states of organoclay and interfacial interaction between the dispersion phases in the matrix, largely aroused by the chemical treatmented organoclay.

In this work, epoxy resin is introduced into PA6/EPDM-*g*-MA blending system as a compatibilizer to enhance the strength and stiffness of blends for its rigid molecular chain and high reactivity. The location of epoxy in the polymer blend could sharply influence interfacial property, which determines the final mechanical properties of ternary blends. Our focus is to investigate the effect of blending sequence on the morphology and properties of PA6/EPDM-*g*-MA/epoxy ternary blends and elucidate the relationship between the morphology and mechanical properties with an emphasis on the blending sequence.

EXPERIMENTAL

Materials and preparation of specimens

Polyamide 6, (YH800, density 1.156 g/cm^3, MFI 28 g/10 min at 230°C and 2.16 kg load), was purchased from Baling Petrochemical Company (Yueyang, China). The ethylene-propylene-diene rubber (EPDM, DOW 4725) was supplied by Dow Chemical Company. EPDM-MA (CMG9802, glass transition temperature ca. −30°C) with a 0.8% MA content was produced by Shanghai Sunny New Technology Development. The solid epoxy resin (NPES-903) was supplied by Nanya Plastics of Taiwan and had an epoxide equivalent weight of 730 g/equiv.

Before extrusion, PA6 was dried in a vacuum oven at 90°C for 24 h, whereas EPDM and EPDM-*g*-MA at 60°C for 5 h. All the specimens were prepared in a corotating twin-screw extruder. In the extrusion processes, all settings were maintained the same with a temperature profile of 230, 235, 240, and 240°C at 120 rpm. The extrudates were subsequently pelletized and dried at 80°C for 15 h. The resulting pellets were injected into dumbbell-shaped tensile bars with the aid of a PS40E5ASE injection machine (Nissei, Tokyo, Japan) with barrel temperature 240–250°C and injection pressure of 900 kg/cm^2.

Blending sequence and reactions

To find the effect of blending sequence on mechanical properties of ternary blends, four different blending sequences were shortly defined in Figure 1. The weight percentages of EPDM-*g*-MA and epoxy were 10 and 0.5, respectively. In comparison, pure PA6, PA6/EP, PA6/EPDM (90/10), and PA6/EPDM/EP (90/10/0.5) were prepared under the same melt-processing condition. For N4, in the first-step blending process, a half amount of total PA6 was adopted. On the basis of our analysis, reactions involved in this three-component system are complex, and the coupling reactions between PA6 and EPDM-*g*-MA, together with PA6 and epoxy, are shown in Figure 2.
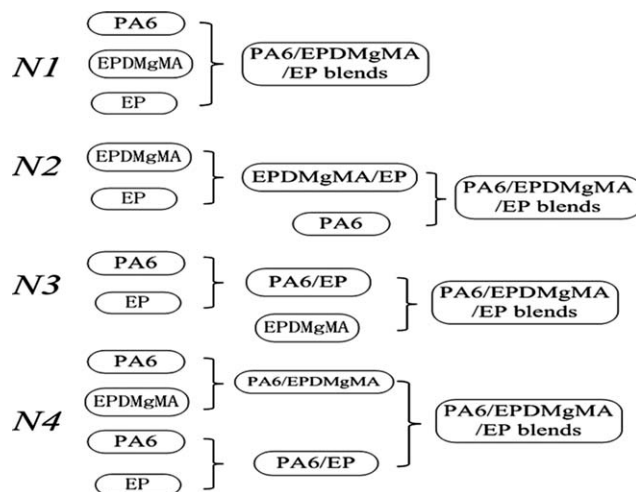
Figure 1 Schematic diagram of blending sequences for the blends of PA6/EPDM-*g*-MA/EP.
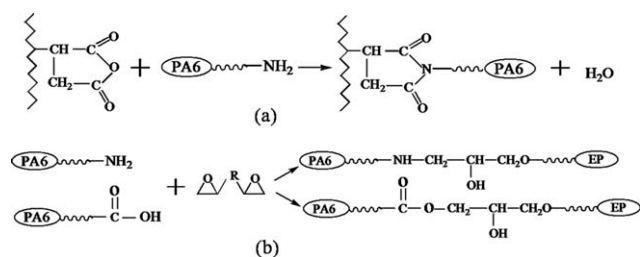
Figure 2 Schematic representation of reactions involved in this blending system: (a) EPDM-*g*-MA and PA6 and (b) PA6 and epoxy.

In addition, a crosslinking reaction may be involved in epoxy and EPDM-*g*-MA because they both have no less than two functional degree (not given here).

Scanning electron microscope (SEM) observation

The morphology of the PA6/EPDM-*g*-MA/epoxy blends was characterized by SEM (FEI INSPECT F) at an accelerating voltage of 10 kV. The injection molding specimens were broken cryogenically in liquid nitrogen, and the elastomeric phase was extracted from the surface by etching with the xylene at room temperature for 24 h. After sputter coating with a thin film of gold, the specimens were examined. The micrographs of SEM were analyzed using an image analyzer to determine the average size of dispersed phase. A minimum number of 200 dispersed particles were counted, and the average rubber particle size were calculated as the following equation

$$\bar{d}_w = \sum n_i d_i^2 / \sum n_i d_i \qquad (1)$$

where n_i is the number of particles with diameter d_i.

Dynamic rheological measurements

The melt viscoelasticity of the PA6/EPDM-*g*-MA/epoxy blends was examined in an Advanced Rheometric Expansion System (ARES, TA Instruments, USA). All the samples were compression molded under at 235°C with a constant pressure of 5 MPa for 5 min. The measurements were performed in an oscillatory shear mode with parallel-plate geometry 25 mm in diameter at 230°C with a strain of 2%, which was within the linear viscoelastic region of the samples.

Mechanical testing

Tension properties were measured according to ISO 527-1:1993 with a Shimadzu AG-10TA Universal Testing Machine (Japan). The notched Izod tests were performed at room temperature of 25°C on an

I200XJU-2.75 Impact Tester according to the ISO 180: 2000 standard. At least five specimens were tested and the average values reported.

Thermal properties

The thermal analysis was carried out using a NETZSCH 209F1 (Germany) thermogravimetry (TG) and a TA Instruments Q20 (USA) differential scanning calorimeter (DSC). All TG samples were scanned from 30 to 600°C at a heating rate of 10°C/min. Samples of 5–10 mg in weight for DSC were subjected to heating–cooling–heating cycles between 40 and 260°C with a heating rate of 10°C/min in a nitrogen atmosphere. The percentage of crystallinity (X_c) of PA6 was calculated using the following formula:

$$X_c(\%) = \frac{\Delta H_m}{(1 - \Phi)\Delta H_m^0} \times 100 \qquad (2)$$

where ΔH_m is the apparent enthalpy of crystallization of the sample, ΔH_m^0 is the extrapolated value of the enthalpy corresponding to the melting of 100% crystalline PA6, which was taken as 190 J/g,[21] and Φ is the total weight fraction of EPDM-*g*-MA and EP in the blends.

RESULTS AND DISCUSSION

SEM morphology

Figure 3 shows the morphology of PA6/EPDM-*g*-MA blend and PA6/EPDM-g-MA /epoxy ternary blends prepared by varying blending sequences. As shown in Figure 3, their microstructures were distinctly different for the various kinds of sizes of the dispersed phase. The holes and knobs on the fracture surface of the PA6 matrix reflected the dispersion of EPDM-*g*-MA phase. For PA6/EPDM-g-MA blends, the rubber particles are small and the boundaries are obscure, as shown in Figure 3(a), indicating that the PA6 matrix has a good interfacial adhesion with EPDM-*g*-MA, whereas, Figure 3(b) shows that the addition of epoxy makes a smaller particle size, that is, N1 exhibits the minimum dispersed size compared with other samples when PA6, EPDM-*g*-MA, and epoxy were blended simultaneously. It is worth noting that the epoxy plays a part in compatibilization and efficiently decreases the dimension of EPDM-*g*-MA. Interestingly, in comparison with N1, N3 shows a larger elastomer phase size together with more distinct boundaries within the matrix. In this blending sequence, a detailed consideration on the changes of the matrix's viscosity and the interfacial adhesion between the matrix and EPDM-*g*-MA were essential for illustration. Also, the morphology
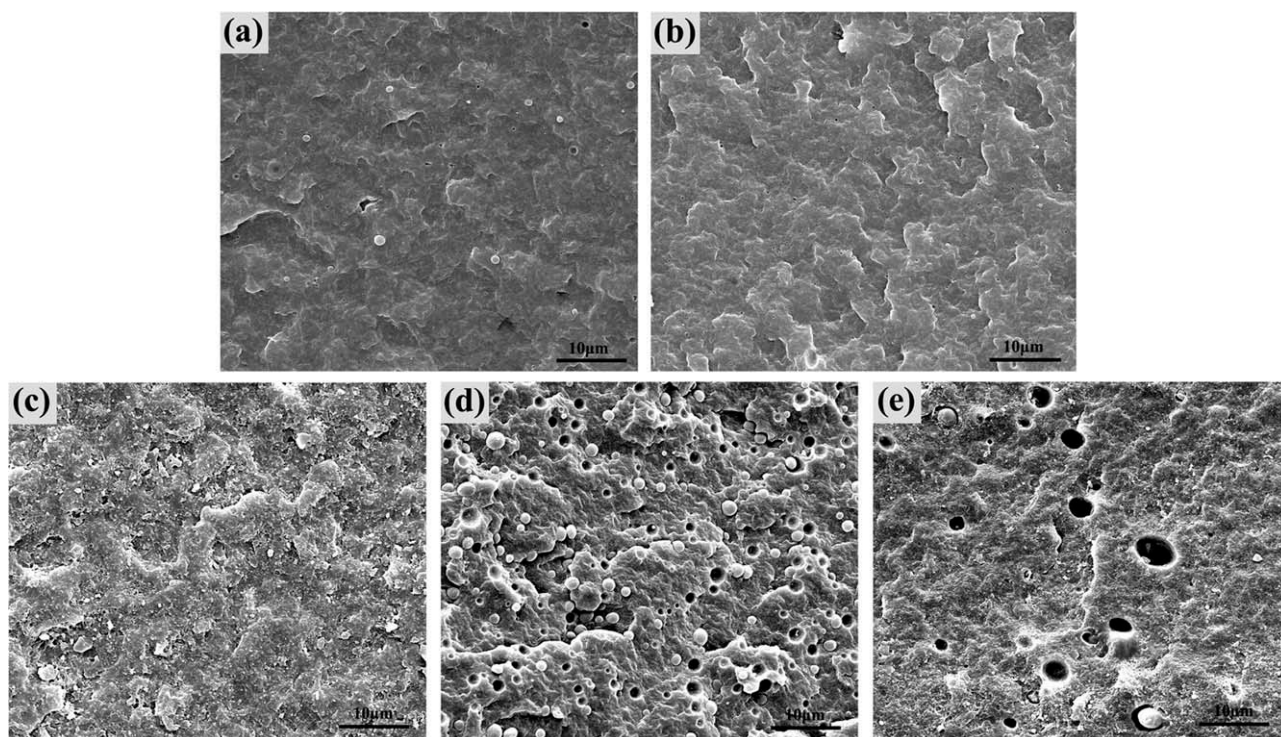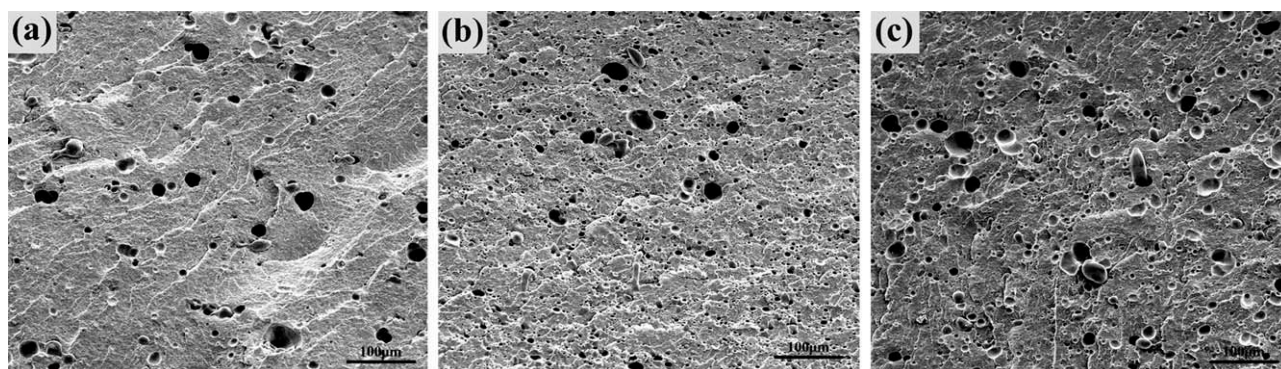
Figure 3 SEM micrographs of PA6/EPDM-*g*-MA, PA6/EPDM-*g*-MA/epoxy blends: (a) PA6/EPDM-*g*-MA; (b) N1; (c) N2; (d) N3; and (e) N4.

of both N2 and N4 appeared coarse because of the different dispersion state of epoxy in their blends. For N2, it seems that the addition of epoxy caused a crosslinking reaction with rubber phase. Thus, a distinct dispersed phase particle could not be observed after etch with the solvent. It is presented that the rubber particles in N4 appeared to be a distinctly inhomogeneous and larger dimension. Beyond doubt, it could be regarded as an unstable phase morphology, in agreement with others work.[19]

Now, to reasonably explain the previous phenomenon, two PA6/EPDM/epoxy (90/10/0.5) blends were prepared with the same blending sequences of N1 and N3, respectively. The resulted blends were denoted as n1 and n3, respectively. For comparision,

PA6/EPDM blend was prepared as well. Figure 4 shows the morphologies of PA6/EPDM and PA6/EPDM/epoxy blends. The average size of rubber phase in the binary blend is up to 9.2 μm [Fig. 4(a)], whereas the sizes of EPDM phase were deceased obviously after incorporation of the epoxy as shown in Figure 4(b), which is origined from the compatibilization effect of epoxy resin. From Figure 4(b,c), it can be seen that the average dispersed phase size of n1 (7.3 μm) is smaller than that of n3 (8.2 μm). According to Wu's theory,[22] the dispersed phase size is related to the viscosity of the matrix. Therefore, the slight difference in rubber particles of blends is probably attributed to a variation of the matrix's viscosity. Concerning this issue, the effect of

Figure 4 SEM micrographs of PA6/EPDM and PA6/EPDM/epoxy blends: (a) PA6/EPDM; (b) n1; and (c) n3.
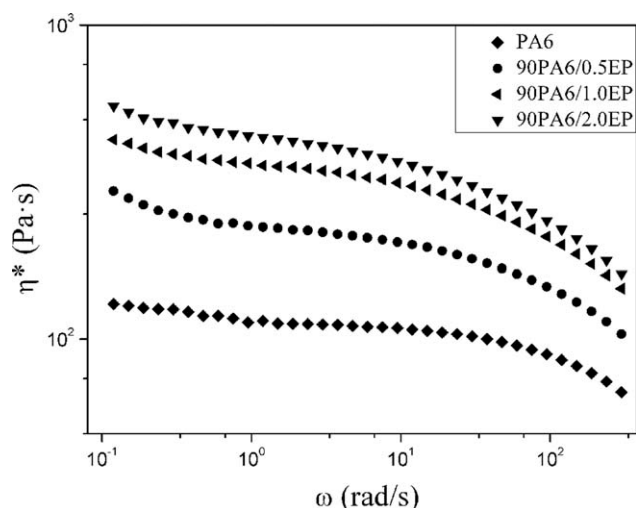
Figure 5 The complex viscosity of the PA6, PA6/epoxy blends with different content.

the addition of epoxy on viscosity is discussed in the following section.

Dynamic rheological behaviors

A decrease in matrix viscosity can alter the balance of drop breakup versus coalescence of elastomer particles, resulting in larger particle size.[22,23] For N3 and n3, the epoxy was premixed with PA6, and it selectively located in PA6 phase. Therefore, the matrix should be regard as PA6/epoxy blend, but for N1 and n1, the matrix could be regard as neat PA6. As shown in Figure 5, the complex viscosity (η^*) of PA6/epoxy was higher than that of neat PA6 in the whole frequency range and increased with the epoxy content. On the basis of the experimental results, a deduced conclusion could be drawn, that is, the size of rubber particles dispersed in the matrix should be minimized due to the increased matrix's viscosity. This consequence could be calculated by the equation[22]:

$$C_a = \eta_m \gamma R / \delta \qquad (3)$$

where C_a is equilibrium constant between the breakup and coalescence of dispersed particles, η_m the matrix's viscosity, γ shear rate, R the size of dispersed phase particle, and δ the interfacial tension. According to this description, it is clear that if η_m has an obvious increase, R should be reduced. However, there appeared an opposite result, not in agreement with the reports in the literatures.[14,24] The sizes of rubber phase in N3 and n3 were also larger than those in N1 and n1, respectively. Therefore, another factor, the interfacial tension of two phases, should be taken into account for explaining the phenomenon. To a large extent, the influence of inter-

facial tension in this blending system counterbalanced that of another factor, the matrix's viscosity. Although the average size of rubber particles in n3 (7.3 μm) had not much difference compared with that in n1 (8.2 μm), these was a sharp contrast between N1 and N3. It is sure that EPDM-g-MA had a more polarity than EPDM so that a notable variation of interfacial tension would occur in PA6/EPDM-g-MA/epoxy blending system. Premixing PA6 with the epoxy, as a result, caused a variation of the interfacial tension between PA6 and EPDM-g-MA. As is known to all, the end-groups amino bond of polyamide could react with MA group, and this reaction was commonly named as imidizations [see Fig. 2(a)]. Also, the epoxide groups of epoxy resin may react with either amino end groups or carboxyl groups of PA6 forming a copolymer *in situ* at the interface, as seen in Figure 2(b).

Figure 6 shows the complex viscosity of different blends where obvious differences exist. For all the ternary blends, each sample had a higher value of complex viscosity (η^*) in comparision with PA6/EPDM-g-MA blend, which was due to the addition of epoxy resin. It is noted that the viscosity of N4 was the highest and N2 had the lowest value. The viscosity could be regarded as an indirect reflection of the interaction of molecular chains. According to the different categories of reactions, the relationship with the viscosity of blends can be evaluated approximately. Now that incorporation of epoxy resin largely affected the viscosity of blending system, the degree of chemical reaction between PA6 and epoxy may determine the tendency of the measured viscosity. It is believed that N4 and N3, which ensured epoxy to locate in PA6 selectively, were easy to reach a high viscosity for more chances of
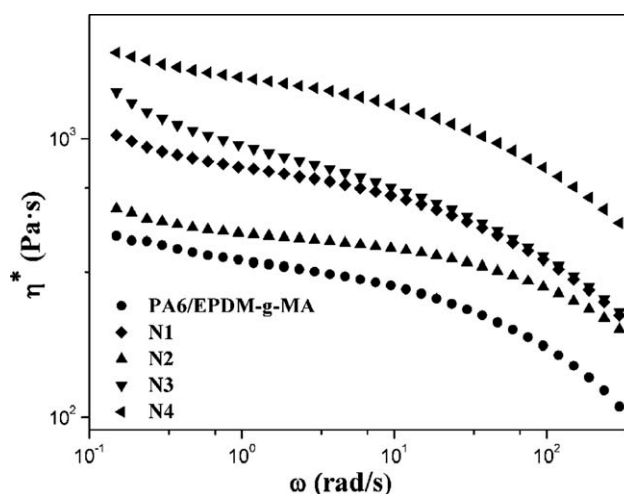
Figure 6 The complex viscosity of the PA6/EPDM-g-MA blend and PA6/EPDM-g-MA/EP blends prepared with different blending sequences.

TABLE I
Mechanical Properties of the Samples

Sample code	Tensile strength (MPa)	Elongation at break (%)	Notched izod impact strength (kJ/m^2)
PA6	66.48	126.78	5.13
PA6/EPDM	53.83	66.65	4.65
PA6/EPDM-*g*-MA	56.05	66.83	21.24
N1	56.89	66.48	22.88
N2	62.36	31.99	14.81
N3	55.12	52.62	16.57
N4	63.62	15.29	9.14

chemical reaction. For N4, the presented maximum viscosity was due to a higher concentration ratio of PA6 to epoxy. In the same way, the viscosity of N2 was lower than that of N1, which is because most of epoxy reacted with EPDM-g-MA before blending PA6 in N2 so that the chances of reactions between PA6 and epoxy must be greatly reduced. It is concluded that the reactions between PA6 and epoxy might create the different viscosity of ternary blends induced by blending sequence.

Mechanical properties

The mechanical properties of the specimens including notched impact strength, elongation at break, and tensile strength are shown in Table I. The tensile strength and notched impact strength of PA6 effectively decreased after addition of EPDM, which was due to the incompatibility between the matrix and rubber phase. As can be seen, blends prepared by different blending sequences show distinct differences in mechanical properties, particularly in impact strength. For N2 and N4, they had a higher tensile strength compared with that of N1 and N3, but their notched impact strength dramatically decreased, even similar to that of PA6 for N4. N1 exhibited the highest impact strength, and the impact strength of N3 was relatively higher than those of N2 and N4. The important point to be noted here is that the addition of epoxy in N1 seemed to present a slight improvement of the tensile strength and impact strength, which was because a lower additive amount of epoxy resin could not produce a strong response to mechanical properties.

A pronounced difference in notched impact strength of blends indicates the influences of blending sequences. The differences in toughness of N1–N4 could be attributed to the distinct morphology. For N1, the best balanced mechanical properties were achieved for its fine and well-dispersed morphology. For N2, a crosslinking reaction appeared to occur between epoxy and EPDM-g-MA when preblending epoxy with EPDM-g-MA firstly. It is detri-

mental to have epoxy located in the elastomer, which was because the epoxy stiffened the EPDM-*g*-MA phase and reduced the latter's ability to cavitate resulting in a decreased toughening efficiency.[22] In both N3 and N4, PA6 matrix could chemically react with epoxy before a preblend of PA6/epoxy was obtained. It seemed reasonable to elucidate that this chemical reaction aroused a notable change in the interfacial tension. Thus, it is clear that the domains in N3 and N4 are considerably larger than others' (see Fig. 3). N3 (16.57 kJ/m^2) had a higher notched impact strength than N4 (9.14 kJ/m^2). This may be due to the fact that the average size of dispersed phase in N3 is not only distinctly smaller than that in N4 but also the size distribution of the rubber in N3 is more uniform. Evidence is presented which suggests that there existed a higher interfacial tension in N4 when blending EPDM-g-MA with a pre-blend of PA6/epoxy. Additionally, elongation at break could be regarded as a significant evaluation of toughness of materials and its variation tendency was in accordance with impact strength. Considering the combination with the values of notched impact strength and elongation at break, we can draw a conclusion that the toughness of different blends follows the order N1 > N3 > N2 > N4.

On the basis of the above discussion, it is clear that the mechanical properties of PA6/EPDM-*g*-MA/epoxy intensely depended on the designed blending sequence. Therefore, by altering the blending sequence could realize an anticipative goal to control the mechanical properties. The ideal mixing sequence to satisfy the balanced mechanical properties is one-step procedure that is simultaneously blending PA6 and EPDM-*g*-MA with epoxy.

Thermal properties

The thermal stability and melt and crystallization behaviors of blends were investigated by TG and DSC, respectively. Table II shows TG and DSC results of PA6/EPDM-*g*-MA/EP ternary blends. For T_o (the initial degradation temperature) and T_t (the

TABLE II
TG and DSC Results of the PA6/EPDM-*g*-MA/EP Ternary Blend Samples

Sample code	TG			DSC	
	T_o (°C)	T_t (°C)	$T_{degr.}$ (°C)	X_c (%)	T_{cp} (°C)
PA6	411.6	460.7	447.1	33.4	190.47
PA6/EPDM-*g*-MA	413.7	457.6	438.1	33.1	188.98
N1	407.3	452.9	432.2	31.6	188.81
N2	407.5	452.6	435.5	35.2	189.65
N3	401.3	458.0	437.1	31.4	189.78
N4	409.7	464.3	445.0	33.0	188.38

terminal degradation temperature) of all samples, there indicates an invisible difference. It is found that N4 has a higher $T_{degr.}$ (the maximum degradation temperature) compared with N1, N2, and N3. According to DSC results, the blending sequence could not affect the crystallization peak temperature (T_{cp}) obviously, but crystallinity (X_c) of N2 and N4 were higher than those of N1 and N3. To some extent, an increasing crystallinity could contribute to strength and stiffness of polymer-based material, in agreement with the result of mechanical testing. In summary, the effect of different blending sequence on thermal property is slight, which might be ascribed to the fact that the matrix PA6 as a rich component would play a dominant role in thermal performance.

CONCLUSIONS

The microstructure in ternary blends was significantly influenced by the blending sequence, which affected their mechanical properties, particularly the notched impact strength. The variation of reactive sequence among each component leaded to notable changes of interfacial tension, inducing the differences of toughness. It was shown that a distinct large dimension of rubber phase was observed when blending PA6 and epoxy first followed by mixing a preblend of PA6/epoxy with EPDM-g-MA. The relationship between the morphology and mechanical properties was illustrated. It is presented that the optimum blending sequence to achieve the best balanced mechanical properties is blending PA6, EPDM-g-MA, and epoxy simultaneously in which the undesired detrimental reactions would be effectively suppressed. Although the balanced mechanical properties of ternary blends have been obtained through the preferred blending sequence, further

studies are being developed to improve the toughness while reducing the loss in strength and stiffness.

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