Influence of Properties and Morphology of Elastomeric Phase on the Behavior of Ternary Reactive Blends of Polyamide 6/Rigid Polymer/Elastomer

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ABSTRACT: A ternary blend of the PA6 matrix with a finely dispersed rigid polymer and elastomer is a system with well-balanced mechanical properties. Its micromechanical behavior, especially that of the elastomer phase, apparently differs from corresponding binary mixtures. This study shows the influence of the elastomer type, modulus, and reactivity on the behavior of ternary blends in comparison with analogous binary PA6/elastomer combinations. The presence of rigid reactive poly(styrene-*co*-maleic anhydride) (SMA) enhanced the properties of all the systems studied. For nonreactive elastomers, the dominant effect was refinement of their size due to enhanced viscosity, whereas for functionalized low-modulus elastomers, the very good balance of properties was due to synergistic influences of both finely dispersed phases. Of interest is the enhanced toughness of ternary blends also for more rigid elastomers having a low toughening efficiency in binary blends. An appropriate addition of rigid SMA together with an elastomer enhances the energy absorption of the matrix, probably without cavitation of very small elastomer particles. Of importance also is the simultaneous strain-hardening effect of deformed rigid particles. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3647–3651, 2003

Key words: polyamides; toughness; elastomers

INTRODUCTION

Ternary reactive blends consisting of a polyamide 6 (PA6) matrix with finely dispersed elastomers like the maleated ethylene–propylene copolymer (EPR–MA) and rigid poly(styrene-*co*-maleic anhydride) (SMA) are systems with fairly balanced properties.[1] The toughness of this ternary blend is close to that of a system containing elastomer only, but the strength and modulus of the blend are higher. This seems to be a consequence of a synergistic interaction of both elastomeric and rigid dispersed particles. As a result, SMA shows also a toughening effect and, in fact, replaces the elastomer. Properties, in particular, toughness, of the ternary blend can be improved by limiting the SMA reactivity by a combination with PS.[2] On the other hand, a similar dilution of the elastomer had no effect on or even decreased the toughness even though the elastomer particle size, due to effective reactive compatibilization, was lower than 100 nm, that is, below the preferred range of particle sizes in a binary blend.[3,4] At the same time, the toughness of the ter-

nary blend, containing nonreactive EPR and SEBS, was relatively high (80–90% of the fully reactive system) in spite of significantly rougher elastomer particles. Rather surprising is the fact that further addition of the elastomer (for total content of both components above 15%) does not enhance the toughness.

From the literature data, it follows that the toughness of elastomer-toughened PA6 is determined by the interparticle distance,[5,6] size,[3,4] and type[7–9] (mechanical characteristics) of the dispersed particles. It is well accepted that the cavitation of rubber particles[10,11] can relieve multiaxial stress near the defect and is a prerequisite for the enhanced ductile deformation for which matrix shear yielding is the principal energy-absorbing mechanism. The energy absorption caused by cavitation is only a small part of the total fracture energy, but of importance is strain hardening[12] by stretching rubber during further deformation of the system. According to Gaymans,[13] the important parameters in rubber toughening are the stress state of the material and the cavitational behavior of the rubber together with the stability of a cavitated structure and the deformational behavior of the matrix. The ability to cavitate depends (except for elastomer properties) also on its particle size.[14,15] For a PA6/EPR combination, the lower limit of the phase size (0.1 μm) is determined by difficult cavitation[3,11] of smaller rubber particles. The upper limit of ~1 μm then corre-

TABLE I
Composition and Modulus (G) of Applied Elastomers

Elastomer	Type	G (MPa)
EPR–MA (Exxelor 1801)	Maleated (0.6%) ethylene–propylene elastomer (Exxon Mobil, Köln, Germany)	5.6
EPR (Buna AP 331)	Ethylene–propylene elastomer (Degussa-Hüls AG, Frankfurt, Germany)	5
EPR–AA (Polybond 1016A)	EPR grafted with acrylic acid (8%) (BP Chemicals, Middlesex, UK)	6.6
SEBS-MA (Kraton FX1901X)	Maleated (2%) styrene/ethene-butene/styrene copolymer (Ottignies-Louvain-La-Neuve, Belgium)	7.5
SEBS (Kraton G 1652)	Styrene/ethene–butene–styrene copolymer (Ottignies-Louvain-La-Neuve, Belgium)	7
PE–AA	Ethylene–acrylic acid (8%) copolymer (BASF, Ludwigshafen, Germany)	49
PE–GMA	Ethylene–glycidyl methacrylate (6%) copolymer (Atofina, Carling, France)	61
L4700 (Lotader L 4700)	Maleated ethylene/ethylacrylate copolymer (Atofina, Carling, France)	3
L3318 (Lotader L 3318)	Maleated ethylene/ethyl acrylate copolymer (Atofina, Carling, France)	60
CPE (Daisolac G 235)	Chlorinated PE (35% Cl) (Mitsubishi Corp., Tokyo, Japan)	6
PIB (Oppanol B 50)	Polyisobutylene, M_w 3.8×10^5 (BASF, Ludwigshafen, Germany)	
SBR (Carom 1500)	Styrene-butadiene random copolymer (Carom, Onesti, Romania)	6

sponds with the interparticle distance and instability of the larger cavities formed.[12,13]

Due to the unusual behavior of a dispersed elastomer in the presence of rigid polymeric particles, as shown above, this study was focused on the influence of the elastomer type and functionality on the ternary blend behavior, especially in comparison with corresponding binary blends. The aim was the understanding of the deformational and energy-absorbing behavior of these systems.

EXPERIMENTAL

Materials

The polyamide 6 (PA6) (Ultramid B3) used was from BASF, Ludwigshafen, Germany; M_n = 18,000. The poly(styrene-co-maleic anhydride) (SMA; Dylark 332) used was from Arco (Nova Chemicals, Calgary, Canada), with a maleic anhydride content of 14% and M_n = 180,000. The basic parameters of the 12 elastomers used are shown in Table I.

Blend preparation

Prior to mixing, PA6 was dried at 85°C for 12 h in a vacuum oven. The blends were prepared by mixing the components in the W 50 EH chamber of a Brabender Plasti-Corder at 250°C and 50 rpm for 10 min. The material removed from the chamber was immediately compression-molded at 250°C to form 1-mm-thick plates. Strips cut from these plates were used for the preparation of dog-bone specimens (gauge length, 40 mm) in a laboratory microinjection-molding machine (DSM). The barrel temperature was 265°C, and that of the mold, 80°C.

Testing

Tensile tests were carried out at 22°C using an Instron 6025 apparatus at a crosshead speed of 20 mm/min.

The stress at break, σ_b, and the Young's modulus, E, were evaluated. The tensile impact strength, a_t, was measured using a Zwick hammer with an energy of 4 J and one-side notched specimens.

Morphological observations

Phase structure was observed using scanning electron microscopy (SEM) and cryo-fractured samples. For better visualization of the SMA phase, the samples were etched in ethyl methyl ketone for 1 h. The elastomer phases were etched with n-heptane for the same time or with boiling xylene for 2 min. The size of the dispersed particles was evaluated from their micrographs using a MINI MOP image analyzer (Kontron Co., Germany).

RESULTS AND DISCUSSION

Size of dispersed elastomer in binary and ternary blend

Table II shows a comparison of the average particle size of dispersed elastomer particles for binary and corresponding ternary blends with various elastomers. For uncompatibilized systems, there exists a significant difference between binary and ternary blends; the significantly lower particle size for the ternary blend is undoubtedly caused by higher shear forces during mixing in the presence of reactive SMA, in addition to the lower elastomer content. This effect is best visible for the PA6/PIB combination; the roughest structure of the binary blend is accompanied by a most significant reduction in the elastomer size for the ternary blend (Table II). The differences in particle size for various elastomers are caused by different viscosity ratios and compatibility with PA6. The size of the rigid SMA-phase particles was practically the same for all the above blends, amounting to about 100 nm.

TABLE II
Size of Elastomer Particles in Binary 90/10 PA6/Elastomer and Ternary 90/5/5 Ternary PA6/Elastomer/SMA Blends

(a) Nonreactive elastomers

Size	Elastomer type									
	SBR		EPR		SEBS		8–9EIB		CPE	
	Binary	Ternary	Binary	Ternary	Binary	Ternary	Binary	Ternary	Binary	Ternary
In μm	1.5	0.9	4.2	0.25	4.7	0.2	35	<2	2.6	0.15

(b) Reactive elastomers

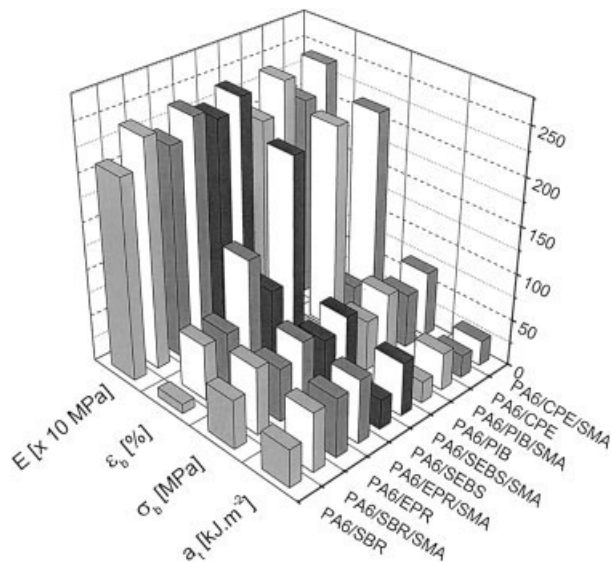| Size	Elastomer type									
	EPR–MA		EPR–AA		SEBS/MA L 4700		PE–AA L3318		PE–GMA	
	Binary	Ternary	Binary	Ternary	Binary	Ternary	Binary	Ternary	Binary	Ternary
In μm	0.12	0.06	0.25	<0.6	0.08	0.08	0.12	<0.1	0.5	0.3

Figure 1 Comparison of mechanical properties of binary 90/10 and corresponding ternary 90/5/5 blends with nonreactive elastomer.

In the case of reactively compatibilized blends, except for lower dispersed-phase dimensions for binaries, the reduction in size for the ternary blend also was less significant (especially for systems with effective compatibilization like PA6/SMA/EPR–MA or SEBS–MA). The minor diminishing of elastomer inclusions is due mainly to its lower concentration. The size of SMA particles was approximately 60 nm for blends with maleated and GMA-containing elastomers and about 80 nm for those with PE–AA.

Mechanical properties

Nonreactive elastomers

From Figure 1, it follows that all the observed parameters (i.e., stress at break, elongation, tensile impact strength, and stiffness) are significantly enhanced for ternary blends in comparison with binaries. This is primarily a consequence of the above-mentioned refinement of the phase structure. Although the strength increase seems to be caused by a relatively low elastomer content, its value is close to the matrix strength (in spite of the presence of elastomer), which indicates also the existence of a synergistic effect[1] of the ternary system. This is further confirmed by higher toughness and especially by a significantly enhanced elongation at break. The second influence seems to be dominant for systems with a small difference in the elastomer size between binary and ternary blend behavior (e.g., those with SBR; see Table II and Fig. 1).

Reactively compatibilized blends

In this case (Fig. 2), the difference between the properties of binary and ternary blends is less significant.

For EPR–MA, PE–GMA, and L3318, the elongation of the binary blend even exceeds that for the ternary one. The enhancement of the tensile strength and modulus is analogous to that for the nonreactive elastomer-containing systems. For elongation, due to the fine and uniform phase structure of reactive binary blends (in comparison with nonreactive blends; see Table II), the presence of a rigid phase and a lower elastomer content mostly cause its reduction in the ternary system. The toughness was unchanged by partial replacement of the low-modulus elastomer with rigid SMA. On the other hand, with elastomers having a higher modulus and, thus, a reduced toughening ability in the binary system (due to higher resistance to cavitation), enhancement of toughness in combination with the rigid polymer particles was found. Due to the sufficiently fine phase structure in binary blend, that is, practically no change in the particle size (especially for PEGMA), a favorable mutual influence of rigid and elastomeric inclusions seems to be the dominant effect. The explanation could be the enhanced ability of elastomer particles to cavitate due to the simultaneous existence of a stress field developed by rigid particles and having just the opposite character[16] (to that of the elastomer particles), that is, compressive. On the other hand, cavitation of these very small (and, in the case of PE–GMA, also relatively rigid) particles is not very probable (so far, experimental verification or excluding the cavitation of particles of the size around 100 nm in our blends has been without success). This is supported by the work of Liu et al.,[17] which reported good toughening of both epoxies and thermoplastic polymers using premade ultrafine (<100 nm) vulcanized rubber particles, where cavitation can most probably also be excluded. Good toughening without
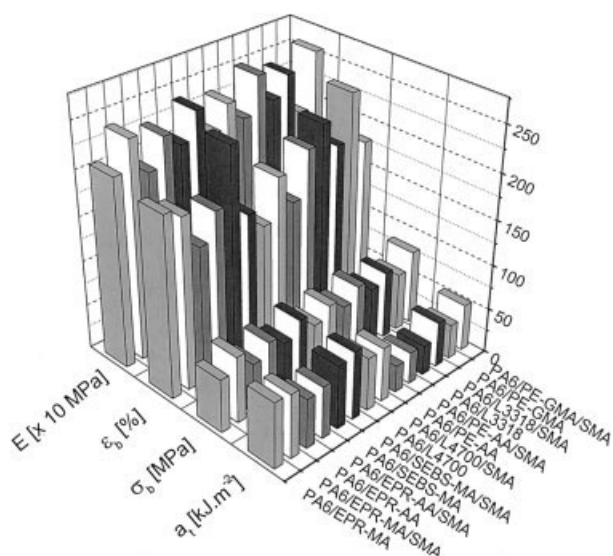
TABLE III
Dependence of Properties of Blends with More Rigid Ethylene-based Elastomers on Composition

Blend composition	σ_b (MPa)	ε (%)	E (MPa)	a_t (+20°C) (kJ m^{-2})	a_t (−20°C) (kJ m^{-2})
PA6/L3318 95/5	64.5	220	2400	27	18
PA6/L3318 90/10	65	220	2220	33	28
PA6/L3318/SMA					
90/5/5	75	190	2430	50	32
87.5/5/7.5	77	170	2460	28	23
87.5/7.5/5	74.5	165	2340	57	37
85/7.5/7.5	73	190	2550	43	30
85/5/10	72	190	2380	26	26
85/10/5	74	190	2230	61	46
PA6/PEGMA 90/10	64	240	2010	38	
PA6/PEGMA/SMA					
90/5/5	82.5	150	2670	51	
87.5/5/7.5	78.5	170	2530	40	34
87.5/7.5/5	84.5	175	2650	52	33

elastomer cavitation was reported elsewhere[18]: Cheng et al.[19] reported even a higher toughening effect for an elastomer with enhanced cavitation resistance. Therefore, the toughening effect in the ternary system can be explained by enhanced initiation of plastic microdeformations in the matrix (due to the expected, probably synergistic, action of both types of particles as stress concentrators) combined with simultaneous strain hardening of the system by plastic deformation (cold drawing) of rigid SMA. This plastic deformation was observed in the PA6/SMA blend[20] and was undoubtedly responsible for the slightly enhanced energy-adsorbing capacity of this and analogous rigid–rigid systems with a finely dispersed well-bonded minority phase.[21,22]

From the composition dependence of the L3318 blend (Table III), it is obvious that the best toughness was achieved for all elastomer concentrations at a 5% SMA content. The same finding was obtained also for PEGMA. If the content of SMA increases further, a significant decrease in toughness was found (surprisingly, for PEGMA, also in strength). At the 5% SMA concentration, the concentration of stress fields (dissimilar to the elastomer) around these inclusions and also the extent of strain hardening are optimal. In the case of less rigid elastomers (EPR–MA, SEBS–MA), similar variations in composition lead to a less significant change in toughness.[1] Of interest is the fact that the best balanced behavior for L3318 was found with a "symmetrical" composition, whereas for PEGMA, it is at its higher content, that is, at the 87.5/7.5/5 composition (higher content of PEGMA caused also enhancement of strength).

Figure 2 Mechanical properties of binary 90/10 and ternary 90/5/5 blends with reactive elastomers.

CONCLUSIONS

Addition of reactive rigid SMA to blends of PA6 with uncompatibilized elastomers caused a significant re-

finement of the phase structure, leading to improvement of all mechanical properties, especially of strength. In the case of analogous systems with a reactively compatibilized elastomer, the influence of the synergistic effect of an elastomer–rigid polymer combination in the ternary blend is the greatest in mechanical behavior enhancement. This effect is most distinct for stiffer elastomer-containing blends, where sufficiently high toughness of the ternary system was achieved in spite of very low efficiency of these elastomers in the toughening of the binary blend.

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