

Ternary Reactive Blends of Nylon-6 Matrix with Dispersed Rigid Brittle Polymer and Elastomer

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ABSTRACT: Except by elastomers, the toughness of nylon-6 (N-6) can be improved by the addition of rigid poly(styrene-*co*-maleic anhydride) (SMA). In this case, strength and stiffness are also enhanced. Combination of SMA with maleated ethylene-propylene rubber or styrene-ethene/butene-styrene with a total content below 15% gives a ternary blend having a toughness level close to elastomer toughening, whereas the strength and stiffness reached at least the Nylon-6 values. An explanation is a synergistic combination of both elastomer and rigid polymer toughening mechanisms. An opposite effect on mechanical behavior was found with high contents of both additives. Except for worsened strength and stiffness, in some cases, a higher elastomer content even did not enhance the toughness. This effect can be explained by too fine phase structure found, causing the matrix ligament dimension to be below its minimum critical value. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1404–1411, 1999

Key words: ternary blend; toughening; reactive compatibilization; nylon-6

INTRODUCTION

Impact resistance of ductile polymers can be also improved by blending with a stiffer, usually brittle polymer component like poly(styrene-*co*-acrylonitrile) (PSAN) in the case of polycarbonate¹ (PC) or poly(styrene-*co*-maleic anhydride) (SMA) for nylon-6 (N-6).^{2,3} Though the enhancement of toughness in these systems is lower than in systems toughened by elastomers, the advantage of rigid-rigid toughening is a simultaneous increase in strength and stiffness (whereas reduction of these parameters is a disadvantage of the addition of elastomers).

From the articles dealing with ductile matrix/rigid brittle inclusion blends having well-balanced mechanical properties,^{4–11} it is clear that such a system must have a sufficiently fine phase structure and high interfacial adhesion (i.e., must be compatible or effectively compatibilized). It was shown that in this case, the loading also causes plastic deformation of dispersed rigid particles with a ductile matrix. As a result, the rigid particle absorbs mechanical energy instead of brittle fracture occurring in the bulk.

This effect is explained by the assumption that the global uniaxial tensile stress results in a local triaxial stress state around the inclusion, its magnitude being determined by disparities in elastic constants between the two phases. If the inclusion has a sufficiently higher modulus and a lower Poisson's ratio than the matrix, the compressive stress evolved exceeds the brittle-to-ductile transition pressure¹² and the brittle particle becomes ductile.

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In our previous works dealing with N-6/SMA,^{3,13} the properties of SMA were modified by the reaction with a fatty amine or with aminated liquid rubber to study the range of dispersed-phase properties, where this toughening occurs. Though an increase in toughness was found, the modified SMA (and in the second case also the liquid rubber partly contained in the N-6 matrix) caused a decrease in the blend modulus by influencing negatively the N-6 crystallinity and thus its stiffness.

In the present work, high molecular weight maleated elastomers, such as ethylene-propylene rubber (EPR-MA), dispersed in the N-6 matrix together with SMA is used to study a system with simultaneous rigid polymer and elastomer toughening. Because the best results for the binary N-6/SMA blend have been found at 10% SMA, a low total content of dispersed phase was also chosen for ternary systems.

EXPERIMENTAL

Materials

Materials used were as follows:

1. N-6 (Ultramid B3) BASF (Germany), $M_n = 18,000$.
2. SMA (Dylark 332) ARCO (USA), maleic anhydride content 14%, $M_n = 180,000$.
3. Ethylene-propylene elastomer functionalized with 0.6% maleic anhydride, (EPR-MA) (Exxelor VA 1801) EXXON (USA).
4. EPR (Buna AP 331) HÜLLS (Germany).
5. Styrene-ethene/butene-styrene functionalized with 2% of maleic anhydride, 29% styrene, (SEBS-MA) (Kraton FG 1901 X), SHELL (USA).
6. Styrene-ethene/butene-styrene, 29% styrene, (SEBS) (Kraton G1652).

Blend Preparation

Before mixing, N-6 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 preparation of dog-bone specimens (gauge length, 40 mm) in a labo-

ratory micro-injection molding machine (DSM). The barrel temperature was 265°C, that of mold 80°C.

Testing

Tensile tests were performed at 22°C using an Instron 6025 apparatus at a crosshead speed of 20 mm/min. The stress-at-break, σ_b , and Young's modulus, E , were evaluated. Tensile impact strength and the J -integral were selected as toughness characteristics. Tensile impact strength, a_b , was measured using a Zwick hammer with an energy of 4J and one-side notched specimens.

An instrumented Charpy impact tester with 100 J work capacity was used for the J -integral evaluation. Experimental parameters were: notch depth $a = 2$ mm ($a/W = 0.2$); support span $s = 40$ mm ($s/W = 4$) (W , width of test specimen); pendulum hammer speed $v_H = 1.5$ ms⁻¹. During impact tests, the load (F), deflection (f), diagrams were recorded. The total deformation energy up to the maximum impact load (A_G) was divided into elastic (A_{el}) and plastic (A_{pl}) parts. The values of the J integral were determined from the following eq. (1), proposed by Sumpter and Turner¹⁴:

$$J_{Id}^{STEA} = \eta_{el} \frac{A_{el}}{B(W-a)} + \eta_{pl} \frac{A_{pl}}{B(W-a)} \cdot \frac{W - a_{eff}}{W - a} \quad (1)$$

where

$$\eta_{el} = 0.5 + 5.5(a/W) - 5(a/W)^2 \quad (2)$$

$$\eta_{pl} = 2 - \frac{(1 - a/W) \cdot (0.892 - 4.476a/W)}{1.125 + 0.892(a/W) - 2.238(a/W)^2} \quad (3)$$

and a_{eff} is the crack length at the onset of unstable crack propagation.

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 EPR and SEBS phases were etched with n-heptane for the same time. The average matrix ligament thickness (τ) was calculated according to Wu's relation¹⁵:

Table I Mechanical Properties of Binary Blends and Their Components

Composition (% wt)	σ_b (MPa)	E (MPa)	a_t (22°C) (kJ · m ⁻²)	a_t (-20°C) (kJ · m ⁻²)
N-6/SMA 90/10	75	2465	36	32
N-6/EPR-MA				
96.7/3.3	71	2335	44	46
95/5	65	2255	52	48
90/10	59	2100	73	61
80/20	46	1760	90	65
90/5/5 ^a	55	2120	65	47
N-6/SEBS-MA				
95/5	64	2295	46	45
90/10	60	2145	71	55
90/5/5 ^b	63	2180	74	42
N-6	72	2380	30	26
SMA	29	3405	—	—

^a Combination EPR-MA/EPR.^b Combination SEBS-MA/SEBS.

$$\tau = d[(\pi/6\phi)^{1/3} - 1] \quad (4)$$

where d is the average diameter of dispersed particles and ϕ their volume fraction.

RESULTS AND DISCUSSION

Binary Blends

Mechanical properties of 90/10 blends of N-6 with SMA and both EPR-MA and SEBS-MA are shown

in Table I. The toughness (a_t) of the N-6/SMA blend is about 20% higher than the N6 matrix value and also tensile strength (σ_b) and modulus (E) increased.³ For similar N6/EPR-MA and N-6/SEBS-MA blends, the more than two-fold increase in a_t is accompanied by a significant decrease in other parameters.

Ternary N-6/SMA/EPR-MA Blend

From the concentration dependences of mechanical properties (Table II), it is obvious that the best

Table II Mechanical Properties of Ternary Blends N-6/SMA/Reactive Elastomer

Composition (% wt)	σ_b (MPa)	E (MPa)	a_t (22°C) (kJ · m ⁻²)	a_t (-20°C) (kJ · m ⁻²)
N-6/SMA/EPR-MA				
90/3.3/6.7	71	2360	72	51
90/5/5	74	2415	71	49
90/6.7/3.3	75	2440	53	48
85/10/5	72	2450	71	55
80/10/10	61	2140	73	53
75/10/15	55	1860	70	48
70/15/15	53	1880	63	39
60/20/20	47	1780	65	36
N-6/SMA/SEBS-MA				
90/6.7/3.3	74	2445	54	53
90/5/5	76	2430	76	56
85/10/5	72	2455	69	55
80/10/10	61	2180	41	25
75/10/15	54	2000	55	31
70/15/15	53	1825	45	33

mechanical properties are found at up to 15% of the additive content. In this respect, the ternary system resembles the binary N-6/SMA.^{3,13}

On the other hand, properties of the 90/5/5 N-6/SMA/EPR-MA blend are fairly better balanced in comparison with appropriate binaries. As a result, the a_t of the ternary blend is close to the binary 90/10 N-6/EPR-MA combination (Table I) and, at the same time, σ_b and E values are slightly higher than those of N-6 (and thus more close to N-6/SMA blends). From the results in Table II it is further obvious that the 85/10/5 blend has similar properties, whereas the system with a lower amount but the same SMA/EPR-MA ratio (90/6.7/3.3) has higher σ_b and reduced a_t (still significantly higher than that of N-6/SMA). If the EPR-MA proportion was further increased (90/3.3/6.7 blend), the minor gain in a_t at the expense of σ_b and E was found.

Morphological observations of the 90/5/5 blend (Fig. 1) show that the sizes of both separately dispersed SMA and EPR were close to 100 nm. For SMA, it was somewhat lower, the size of the largest particles of EPR-MA slightly exceeding this value. A similar phase structure was found also for all the above mentioned binary and ternary blends. In the binary N-6/EPR-MA blend, except for most dispersed particles having about 100-nm size, a small part reached a size close to 200 nm.

Quite opposite results have been found with ternary blends containing higher amounts of both additives. For instance, systems with 10% SMA and 5, 10, and 15% EPR-MA showed virtually unchanged a_t and significantly lowered σ_b and E with increasing EPR content (Table II). Finally, with 70/15/15 and 60/20/20 blends, even lower toughness (together with other parameters) was found. The phase structure was still very fine as is shown in Figure 2 (e.g., the size of SMA inclusions in the 70/15/15 blend was ≈ 100 nm, that of EPR-MA ≈ 150 nm; in 60/20/20 blend the SMA particles were still lower than 150 nm and those of EPR-MA below 300 nm).

The fact that the increasing content of EPR does not lead to an increase in a_t indicates that a higher (more than 15%) total content of inclusions probably reduces the effectiveness of both toughening mechanisms. The known worsening of N-6/SMA properties with increasing SMA contents^{3,13} may also participate in the lowering of a_t in the ternary system. Additionally, a lower stiffness of the surrounding matrix (by the presence of elastomer) can suppress plastic deformation of SMA.

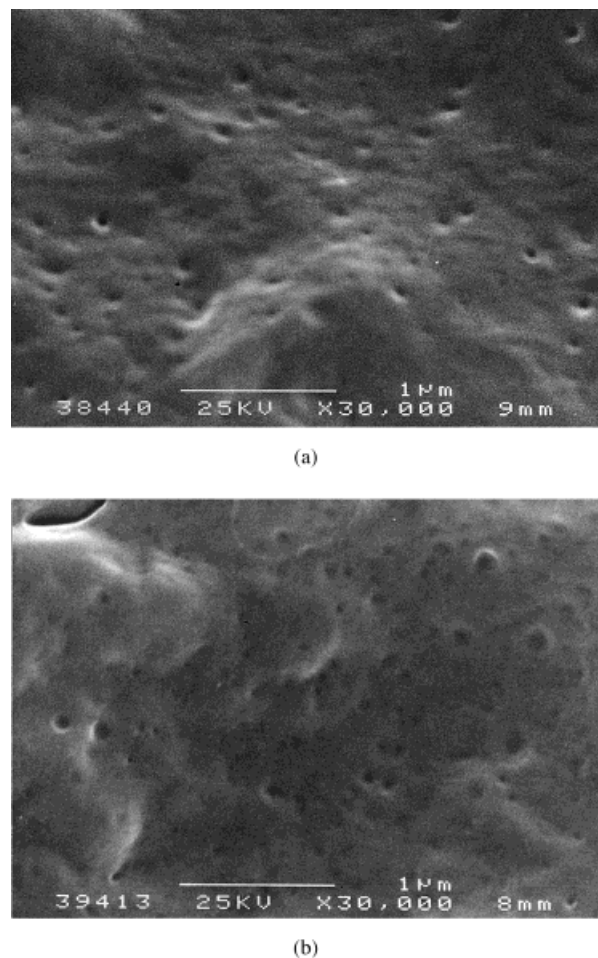
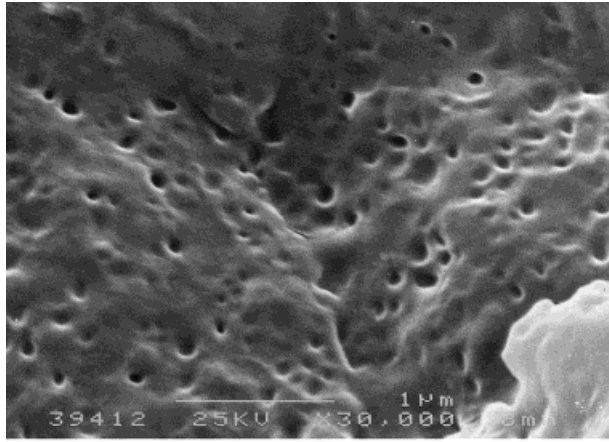


Figure 1 Phase structure of N-6/SMA/EPR-MA 90/5/5 blend: (a) etched SMA; (b) etched EPR-MA.

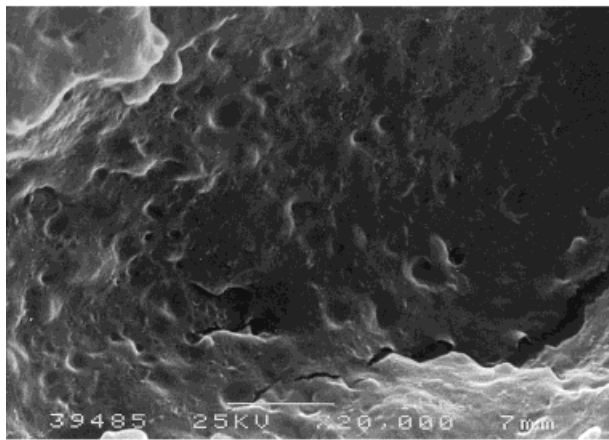
This system might then behave like an N-6/elastomer blend containing a rigid inorganic filler (reported to have relatively low toughness with higher contents of both additives¹⁶). On the other hand, the very fine phase structure of ternary reactive blends even at the 60/20/20 composition (Fig. 2) represents a very low value ($\approx 0.01 \mu\text{m}$) of matrix ligament¹⁵ dimension (τ). Taking into account that the critical minimum ligament thickness (τ_{cr}) of N-6 is reported¹⁷ to be at least $0.05 \mu\text{m}$, rather this subcritical τ value seems to be a possible reason for the mentioned lowering of a_t with increasing additive concentration.

N-6/SMA/SEBS-MA Blend

This blend showed similar or slightly improved mechanical behavior in comparison with related ternary blends containing EPR-MA up to 15% of the total additive content (Table II). Morphologi-



(a)



(b)

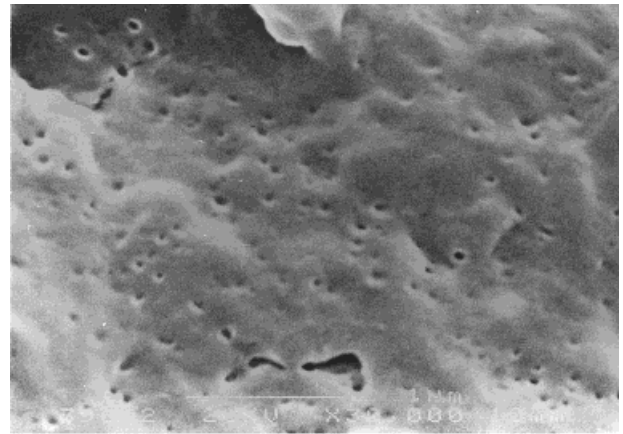
Figure 2 Phase structure of N-6/SMA/EPR-MA 60/20/20 blend: (a) etched SMA; (b) etched EPR-MA.

cal observations of the 90/5/5 blend have shown a rather rougher dispersion of SEBS-MA particles (size up to ≈ 200 nm) in comparison with the analogous EPR-MA containing system (Fig. 1). On the other hand, impairment of properties with increasing additive content was more significant for SEBS-MA blends (Table II) despite comparable dimensions of dispersed phases (Figs. 3 and 4). The faster decrease in toughness for a higher content of dispersed phase in the SEBS-MA than in the EPR-MA-containing blend can be partly explained by different properties of both elastomers.¹⁸ Because differences between both blends were found at higher contents of finely dispersed components with a very low matrix ligament thickness (close to its critical minimum value¹⁷), the lower a_t of the SEBS-MA-containing system may just indicate its higher minimum τ_{cr}

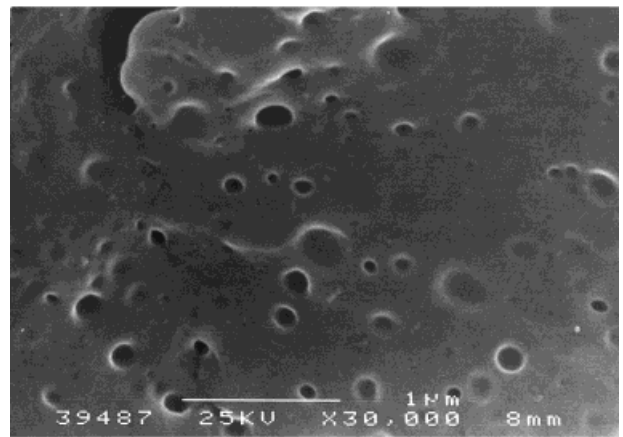
value in comparison with the EPR-MA blend. Quite tentatively, another (unknown) influence seems to be the concentration dependence of the assumed interaction between fine elastomer and rigid SMA particles.

J-Integral Results

In the case of a binary N-6/SMA blend, its J_{Id} value (reflecting the resistance against unstable crack growth) is very little changed in comparison with that of N-6 (Table III). The highest J_{Id} value was found for the binary N-6/EPR blend, relatively high J_{Id} was also found for the ternary N-6/SMA/EPR 90/5/5 blend. These results correspond with the a_t values in Tables I and II. Surprisingly, the analogous N-6/SMA/SEBS blend, having the highest a_b , showed a significantly



(a)



(b)

Figure 3 Morphology of 80/10/10 blend with reactive and nonreactive elastomer: (a) N6/SMA/EPR, etched EPR; (b) N-6/SMA/EPR-MA, etched EPR-MA.

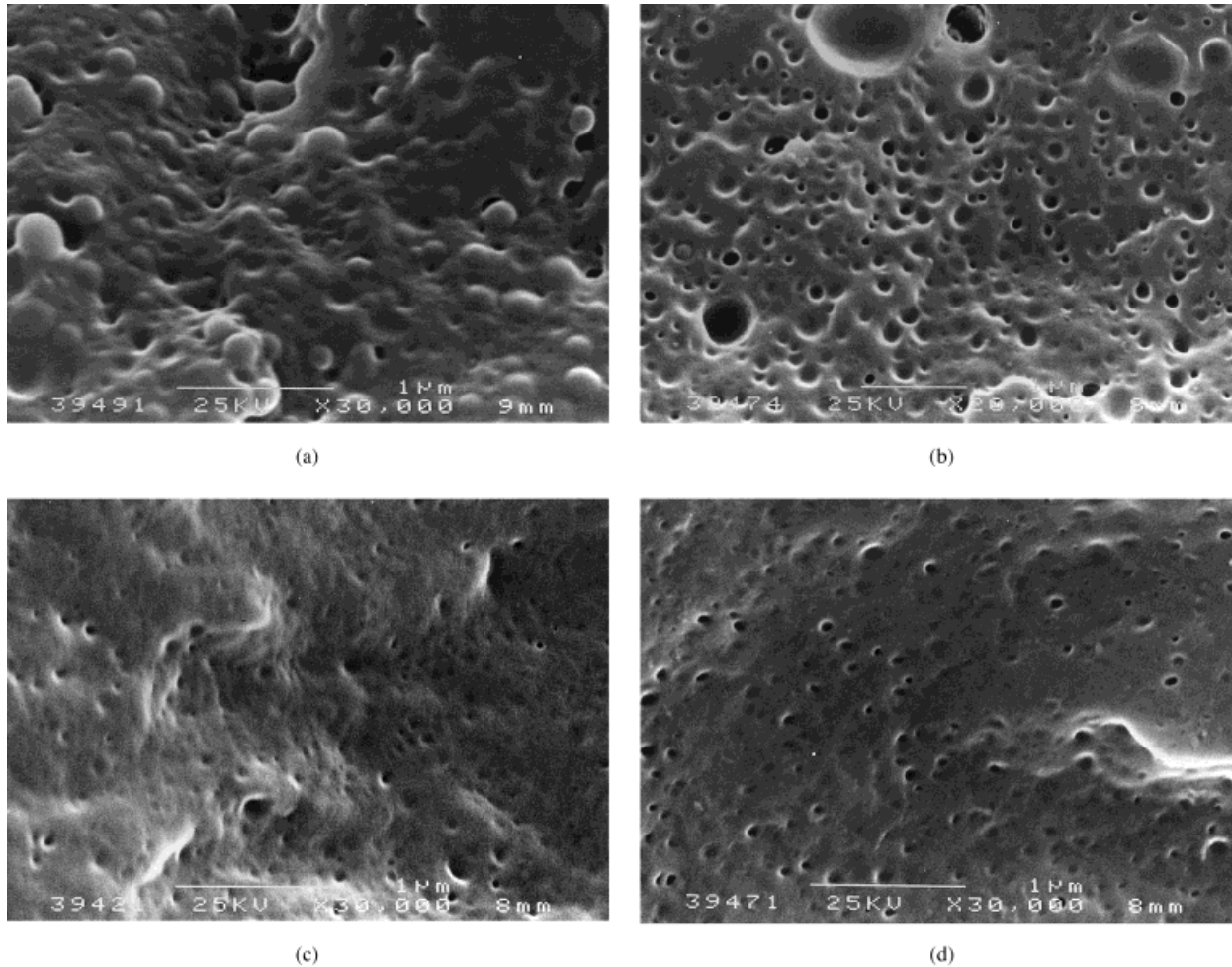


Figure 4 Morphology of 80/10/10 blend with reactive and nonreactive SEBS: (a) N-6/SMA/SEBS, etched SMA; (b) etched SEBS; (c) N-6/SMA/SEBS-MA, etched SMA; (d) etched SEBS-MA.

lower J_{Id} value. This fact indicating lowered resistance to unstable crack growth can be partly explained by the larger cross-section of test specimens for J_{Id} evaluation in comparison with a_t specimens. As a result, lowered resistance of this

blend to plane-strain loading conditions is considered probably also as a consequence of a too low ligament thickness (and higher minimum τ_{cr} value of SEBS-MA) discussed above.

Table III J -Integral Results of Selected Systems

Composition (% wt)	J_{Id} ($N \cdot mm^{-1}$)	a_t ($kJ \cdot m^{-2}$)
N-6	2.18 ± 0.34	30
N-6/SMA 90/10	2.21 ± 0.25	36
N-6/EPR-MA 90/10	9.58 ± 0.29	73
N-6/SMA/EPR-MA 90/5/5	7.63 ± 0.40	71
N-6/SMA/SEBS-MA 90/5/5	3.53 ± 0.29	76

Ternary Blends with Nonreactive Elastomers

The aim of the application of both unmodified EPR and SEBS was predominantly to evaluate the influence of the elastomer phase size on the blend behavior, namely with respect to the above mentioned subcritical¹⁷ dimension of τ at higher contents of finely dispersed reactive components.

As a first step, binary blends containing combinations of both a reactive and nonreactive elastomer were prepared. The results in Table IV show that roughening of the phase structure caused by the dilution of the reactive component

Table IV Mechanical Properties and Size of Dispersed Particles of Ternary Blends Containing Reactive and Nonreactive Elastomer

Composition (% wt)	σ_b (MPa)	E (MPa)	a_t (22°C) (kJ · m ⁻²)	a_t (-20°C) (kJ · m ⁻²)	Particle Size (μm)		τ (μm)
N-6/SMA/EPR					SMA	EPR	
90/5/5 ^a	74	2415	71	49	<0.1	>0.1	0.07
90/5/5	72	2420	67	44	0.1	0.1–1	0.09
90/5/2.5/2.5 ^b	72	2450	68	48	<0.15	0.1–1	0.10
80/10/10 ^a	61	2140	73	53	<0.1	<0.2	0.05
80/10/10	60	2200	49	41	<0.15	0.1–5	0.55
N-6/SMA/SEBS					SEBS		
90/5/5 ^a	76	2430	76	56	<0.1	0.1–0.2	0.09
90/5/5	67	2440	44	32	<0.15	0.1–0.2	0.1
90/5/2.5/2.5 ^b	63	2435	64	35	<0.15	<0.2	0.105
80/10/10 ^a	61	2180	41	25	<0.1	<0.15	0.045
80/10/10	61	2220	53	27	<0.2	0.1–0.5	0.1

^a Blend with maleated elastomer.

^b Combination of maleated and nonfunctionalized elastomer.

in the 90/5/5 N-6/EPR-MA/EPR blend (having relatively polydisperse structure with the particle sizes ranging from 0.1 to 1 μm) slightly lowered its toughness in comparison with the 90/10 N-6/E PR-MA blend (the EPR-MA size did not exceed 0.15 μm). At this low additive concentration, the existence of a finer phase structure of EPR-MA seems to be beneficial. On the other hand, the enhanced toughness for the analogously diluted N-6/SEBS-MA/SEBS blend (with dispersed particle size below 0.3 μm) indicates that the particle size in the N-6/SEBS-MA blend (not exceeding 0.15 μm) and τ most probably reached at least the minimum critical level. A comparison of properties of the binary blends with both the types of reactive elastomers, having virtually the same size of dispersed particles also, supports the above mentioned possible higher minimum τ_{cr} for dispersed SEBS in comparison with EPR.

In ternary 90/5/5 blends with EPR or the diluted EPR-MA (90/5/2.5/2.5), all properties were comparable with the analogous EPR-MA blend. A slight lowering of toughness for blends containing EPR corresponds to the results for binary blends and may be a consequence of a more polydisperse phase structure containing a small part of larger particles having a diameter up to 1 μm (Table IV). At the same time, the approximate value of τ ($\approx 0.1 \mu\text{m}$) was still well below its upper critical bound¹⁵ (0.3 μm) (and also exceeded minimum¹⁷ τ_{cr} value).

At the 80/10/10 composition, the lowering of toughness was more significant for the systems

containing EPR. This blend had a rougher and more polydisperse phase structure than the related blend containing EPR-MA (Fig. 3). In this case, just the existence of a relative small portion of larger EPR particles probably eliminated the still favorable value of τ (obtained using the average particle size). The above results confirm the importance of reactive blending in EPR-based ternary systems in the concentration range under study.

A comparison of analogous SEBS- and SEBS-MA-containing ternary blends confirms a peculiar behavior of these systems. On the one hand, the toughness of the 90/5/5 blend containing SEBS was markedly lower than a_t of the analogous SEBS-MA blend (with an a_t value of 90/5/2.5/2.5 lying approximately in the middle between them). This is in contradiction with the tendency found for the above mentioned a_t of SEBS and SEBS-MA binary blends (Table I) and also with virtually the same phase structure of both ternary blends (Table IV). In this respect, the only difference between SEBS- and SEBS-MA-containing blends seems to be the undoubtedly different interfacial bonding of elastomeric particles with the N-6 matrix. These findings most of all confirm complex deformational behavior of these blends and the necessity of a more thorough study in this respect.

On the other hand, the a_t value of the 80/10/10 SEBS blend was even higher than the a_t of the analogous SEBS-MA blend. In this case, the slightly rougher particle size shown in Figure 4 (0.1–0.5 μm) and thus higher τ value of the SEBS

blend is favorable because τ of the SEBS-MA blend (the absolutely lowest value in Table IV) is undoubtedly below its minimum critical dimension. (This fact is further supported by the expected higher minimum τ_{cr} value of SEBS in comparison with that of EPR shown above).

CONCLUSIONS

Simultaneous addition of finely dispersed SMA and a reactive elastomer to the N-6 matrix with the total contents of both additives below 15%, suitably combines the advantages of both rigid-rigid and elastomeric toughening. As a result, the α_t of ternary blend reaches the value of the elastomer-toughened N-6, whereas σ_b and E are unchanged or even higher than those of N-6. An explanation can be mutual synergistic influencing of both toughening mechanisms.

On the other hand, a further increase in the content of elastomer did not increase toughness, whereas strength and stiffness were lowered significantly. This effect seems to be partially a consequence of a too fine phase structure due to effective reactive compatibilization because in this case, the matrix ligament dimension is unfavorably low (below its minimum critical value). The different mechanical behavior of analogous EPR- and SEBS-containing blends having similar phase structure is rather tentatively explained by different interfaces and minimum critical ligament dimensions. For a better understanding of deformational behavior of these ternary blends,

further fractographic and morphological studies are in progress.

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