

Influence of the Component Reactivity on the Properties of Ternary Reactive Blends Nylon 6/Rigid Brittle Polymer/Elastomer

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Received 21 September 1999; accepted 14 February 2000

ABSTRACT: The ternary reactive blend of Nylon 6 matrix with dispersed poly(styrene-*co*-maleic anhydride) and maleated SEBS or EPR represents a toughened system with enhanced strength and, at least, the retained stiffness of the matrix. In the present work, the influence of changed reactivity of dispersed phases, including the application of one or both nonreactive components, on the phase structure and related mechanical behavior is studied. Lowering of the reactivity of the elastomer caused a decrease of blend properties, whereas suitable dilution of SMA by PS brought better properties in comparison with a fully reactive system. With the nonreactive N6/PS/SEBS blend, the formation of blended bicontinuous inclusions causes worsening of toughness. This documents the importance of separate dispersion of both phases for good mechanical behavior in the system studied, which is shown to be assured by application of at least one reactive component. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1597–1603, 2000

Key words: ternary reactive blend; dispersed rigid polymer and elastomer; varying reactivity; Nylon 6

INTRODUCTION

In the case of some binary blends consisting of a finely dispersed rigid polymer in a ductile matrix [Nylon-6/poly(styrene-*co*-maleic anhydride) (SMA),^{1,2} polycarbonate/poly(styrene-*co*-acrylonitrile)³], increases in strength and stiffness also can be accompanied by a minor gain in toughness. This behavior is explained by the ability of well-bonded fine particles of the rigid brittle polymer (compatible or effectively compatibilized^{4–7}) to deform plastically together with the matrix if the system is loaded (“cold drawing concept”).⁴

For Nylon 6 (N6) with separately dispersed SMA and reactive elastomer (maleated EPR or SEBS) with total content of both components below 15%, we have recently found all properties enhanced over the matrix value, but with significantly higher toughness corresponding to a system containing elastomer only.^{8,9} A plausible explanation is a synergistic combination of both elastomer and rigid polymer toughening mechanisms. A detrimental effect on mechanical behavior was found for high contents (>20%) of both additives. Except for decreased strength and stiffness, a higher elastomer content did not enhance even the toughness in some cases. This effect can be explained by a too fine phase structure causing the matrix ligament dimension to be below its minimum critical value.

Similarly, Harada et al.⁷ observed enhanced strength, stiffness, and toughness with retained

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Contract grant sponsor: Grant Agency of the Academy of Sciences of the Czech Republic; contract grant number: A4050706.

Journal of Applied Polymer Science, Vol. 78, 1597–1603 (2000)
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low-temperature toughness for the N6/elastomer-(EPR-MA) 80/20 system upon addition of a suitable amount of a separately dispersed imidized acrylic polymer. With a similar blend containing the SEBS-MA/SEBS combination, the only difference was the worse low-temperature impact strength.

The objective of the present work is to study the influence of lowered reactivity of components, including application of one (semireactive blend) or both nonreactive dispersed phases, on the phase structure of a ternary blend N6/SMA/reactive elastomer and the related mechanical behavior.

EXPERIMENTAL

Materials

Materials used were: Nylon-6 (N6L) (Ultradid B3) BASF, $M_n = 18,000$; (N6H) (Ultradid B4), $M_n = 33,000$; Poly(styrene-*co*-maleic anhydride) (SMA) (Dylark 332) Arco, maleic anhydride content, 14%, $M_n = 180,000$; ethylene-propylene elastomer functionalized with 0.6% of maleic anhydride, (EPR-MA) (Exxelor VA 1801) Exxon; ethylene-propylene elastomer (EPR) (Buna AP 331) Hüls; styrene-ethene/butene-styrene functionalized with 2% of maleic anhydride, 29% styrene, (SEBS-MA) (Kraton FG 1901 X), Shell; and styrene-ethene/butene-styrene, 29% styrene, (SEBS) (Kraton G1652).

Blend Preparation

Prior to mixing, N6 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 laboratory micro-injection molding machine (DSM). The barrel temperature was 265°C, that of 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 (experimental error $\leq \pm 4\%$), and Young's modulus, E (experimental error $\leq \pm 3\%$), were evaluated.

Tensile impact strength, a_t (experimental error $\sim \pm 10\%$), was measured using a Zwick hammer with an energy of 4 J and one-side notched specimens.

For all mechanical tests, at least 8 "dry" (stored in a desiccator) specimens were used.

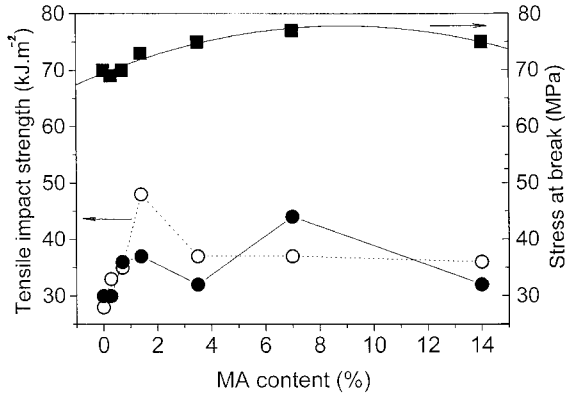
Morphological Observations

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 size of dispersed particles was evaluated from their micrographs using a MINI MOP image analyzer (Kontron Co., Germany).

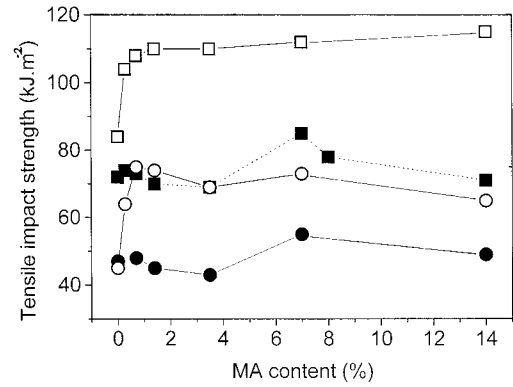
Table I Properties and Particle Size of Ternary 90/5/5 Blends with a Combination of Reactive and Nonreactive Component

Composition	σ_b (MPa)	a_t (22°C) (kJ · m ⁻²)	a_t (-20°C) (kJ · m ⁻²)	E (MPa)	d (μm) Rigid p.	d (μm) Elastom.	Torque (N · m)
N6L/SMA/EPR-MA	74	71	49	2415	0.06	0.08	11
N6L/PS/EPR-MA	59	72	42	2480	2	0.15	4.5
N6L/SMA/EPR	72	68	46	2425	0.11	0.25	
N6L/SMA/EPR ^a	72	70	48	2425	0.1	0.2	
N6L/PS/EPR	60	52	45	2490	2.2	3.9	4
N6H/SMA/EPR-MA	85	115	65	2400	0.07	0.065	16
N6H/PS/EPR-MA	67	84	43	2440	0.7	0.1	12
N6H/PS/EPR	66	67	34	2450	0.7	2	11

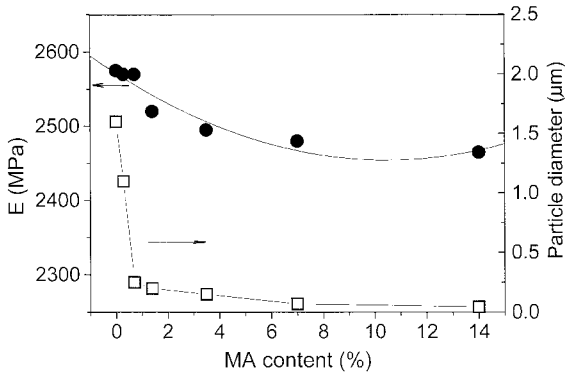
^a EPR/EPR-MA 50/50 combination.



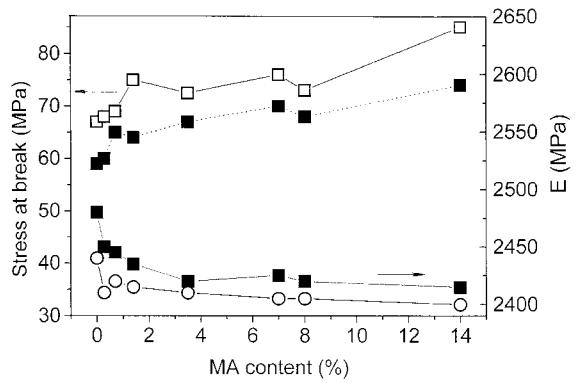
(a)



(a)



(b)



(b)

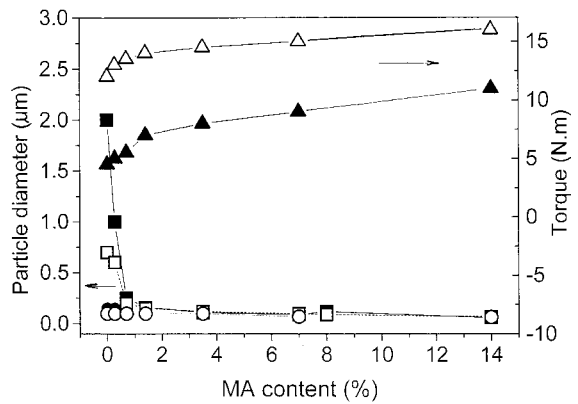
Figure 1 (a) Properties of the N6L/(PS/SMA) 90/10 blend in dependence on the MA content in the dispersed phase. ○ 22°C, ● -20°C. (b) Stiffness and particle size in dependence on the functionality for the N6L/(PS/SMA) 90/10 blend.

RESULTS AND DISCUSSION

N6/(PS/SMA)/(EPR/EPR-MA) Blend with N6L Matrix

The comparison of semireactive blends with a fully reactive (N6L/SMA/EPR-MA) one (Table I) shows a not very significant difference in properties. For SMA replaced by PS, only slight decreases in σ_b and low-temperature toughness were found in spite of a significantly rougher particle size (2 μm) in comparison with SMA (0.06 μm). Toughness is most probably determined by the presence of very fine (below 0.1 μm) particles of EPR-MA. For EPR-MA replaced by EPR, only a slight decrease in toughness was found.

When EPR/EPR-MA 50/50 combination was used, the properties were comparable to the fully reactive blend (particle size was $\sim 0.15 \mu\text{m}$),



(c)

Figure 2 (a) Toughness of the N6/EPR-MA/(PS/SMA) blend in dependence on the rigid phase functionality. ■ N6L matrix 22°C, ● -20°C; □ N6H matrix 22°C, ○ -20°C. (b) Properties of the N6/EPR-MA/(PS/SMA) 90/5/5 blend in dependence on the rigid phase functionality. ■ ● N6L matrix, □ ○ N6H. (c) Dispersed particles dimensions and torque at 250°C of the N6/EPR-MA/(PS/SMA) 90/5/5 blend in dependence on the rigid phase functionality. ▲ N6L; △ N6H; N6L ■ rigid phase, ● elastomer; N6H □ rigid phase, ○ elastomer.

Table II Properties and Particle Size of Ternary 90/5/5 Blends with a Combination of Reactive and Nonreactive Styrene/Ethene-Butene/Styrene Copolymers

Composition	σ_b (MPa)	α_t (22°C) (kJ · m ⁻²)	a_t (-20°C) (kJ · m ⁻²)	E (MPa)	d (μm) Rigid p.	d (μm) Elastom.	Torque (N · m)
N6L/SMA/SEBS-MA	76	76	56	2430	0.055	0,08	13
N6L/PS/SEBS-MA	66	68	42	2470	1.3	0.1	5
N6L/SMA/SEBS	67	57	33	2440	0.1	0.2	8
N6L/SMA/SEBS ^a	63	64	35	2435	0.08	0.1	
N6L/PS/SEBS ^a	61	45	30	2460	1.3	0.12	4
N6L/PS/SEBS	63	38	31	2480	1.75	4	3.5
N6H/SMA/SEBS-MA	79	76	66	2415	0.05	0.05	16
N6H/PS/SEBS	65	55	20	2465	0.85	0,9	10

^a SEBS/SEBS-MA 50/50 combination.

whereas for the analogous N6/(EPR/EPR-MA) binary blend, best properties are reported.¹¹

With the nonreactive N-6/PS/EPR blend, despite a significantly rougher particle size (2.2 μm for PS, 3.9 μm for EPR) and also an unfavorable matrix ligament thickness¹² (over 2 μm), the level of mechanical properties was still relatively good, especially when compared with N6/PS (Fig. 1). This confirms the advantage of ternary blends (with separately dispersed phases) also in this case.

Figure 2 shows the influence of the varying degree of SMA dilution by PS on ternary blend properties and structure. The initial enhancement of properties with increasing reactivity is not very significant despite a marked reduction of the PS phase size (dominating effect of finely dispersed EPR-MA mentioned above). Due to a lowering of stiffness² and increase of viscosity with increasing reactivity, the 95/5 PS/SMA combination (0.7% MA) is at an optimum, also taking into account blend processing. The best balanced mechanical behavior was found for the 50/50 combination (7% MA); the slightly lowered toughness of the fully reactive blend is in agreement with findings for analogous reactive binary N6/elastomer¹¹ and N6L/(SMA/PS) (Fig. 1) blends (except for too low particle size; also, the probably unfavorably thick interface can be considered). On the other hand, σ_b only slowly increases with increasing reactivity of the rigid phase (similarly to the binary blend in Fig 1.), indicating the dependence of strength on the interfacial bonding and particle size. From the above results it is obvious that mechanical properties are relatively independent of the size of rigid particles in a relatively broad range (with practically constant size of elastomer).

N6/(PS/SMA)/(EPR/EPR-MA) Blend with N6H Matrix

When N6 with a higher molecular weight was applied, several differences were found (despite similar phase structures at a higher degrees of component reactivity). Most important is a significantly higher strength and toughness (Table I, Fig. 2, in agreement with results for a binary N6/elastomer blend,¹³ but not found for a binary N6/SMA¹⁴ (the properties of both N6 are comparable). Though the PS particle size (0.7 μm) was finer than that for an N6L/PS/EPR-MA blend, the difference from the fully reactive blend is even more significant. A similar situation was also found for a N6H/PS/EPR blend (Table I). Though the 95/5 PS/SMA ratio (0.7% MA) is also an optimum, except for strength, also slight increase of toughness follows up to 100% SMA (with low-temperature toughness having maximum at 50/50 ratio). These results show that properties of the blend with the higher molecular-weight N6 are more dependent on the component functionality. Due to its probably lower content of terminal amino groups, the amount of grafted copolymer can be lower, and the comparable fine-phase structure can be achieved due to higher viscosity; note the finer particle size for nonreactive components in Table I (with a probably favorable effect of the less thick interface).

N6/(PS/SMA)/(SEBS/SEBS-MA) Blend with N6L Matrix

The differences between fully reactive and semi reactive (i.e., PS- or SEBS- blends) ternary blends in Table II are somewhat more significant than those of analogous EPR-MA(EPR)-containing

blends (Table I) despite a finer phase structure in the first case. The decrease of properties is more remarkable for the blend with SEBS-MA replaced by SEBS. Additionally, the properties of the blend with a 50/50 SEBS-MA/SEBS combination were also lower than for the fully reactive blend. This can be explained by possible different behaviors of both elastomers¹⁰ when dispersed in this ternary blend (in comparison with binary blends). With various PS/SMA combinations [Fig. 3(a)–(c)], the dependences of properties and particle size on MA content are comparable with those of the corresponding EPR-MA blends [Fig. 2(a)–(c)].

On the other hand, substantially lower toughness was found for the nonreactive N6/PS/SEBS blend despite dispersed phase dimensions similar to the analogous EPR blend. SEM observations show a quite different type of phase structure. Except for a part of single PS (or PS with SEBS subinclusions) inclusions, relatively large blended (IPN-like) bicontinuous structure was observed [Fig. 4(a)]. The lowered toughness is a consequence of apparently low toughening ability of relatively stiff and large (and polydisperse) blended particles together with the absence of single elastomer particles. This result confirms the advantage of separately dispersed components (see a significantly higher toughness of an analogous N6L/PS/EPR blend or of the related semireactive blends in Table II).

Also, the N6/PS/(SEBS/SEBS-MA) blend (Table II) still has a relatively low toughness despite significantly finer ($0.15\ \mu\text{m}$), elastomer particles. In this case, SEM observation shows that at least a part of the SEBS particles are in contact with the PS phase [Fig. 4(b)].

N6/(PS/SMA)/(SEBS/SEBS-MA) Blend with N6H Matrix

For the nonreactive blend, blended particles also were found [Fig. 4(c)]. Due to a higher matrix viscosity, the size is significantly lower ($0.5\ \mu\text{m}$). The toughness (especially at low temperature) is relatively low, which confirms the above-mentioned disadvantage of such a structure.

The dependence of mechanical properties on the varied reactivity of the rigid phase (varied PS/SMA ratio) is rather different from that for N6L-blends (Fig. 3). Strength and toughness reached maximum values at 90/10 PS/SMA ratio (1.4% MA), with a subsequent slight decrease (with the exception of low temperature toughness). Additionally, the enhancement of proper-

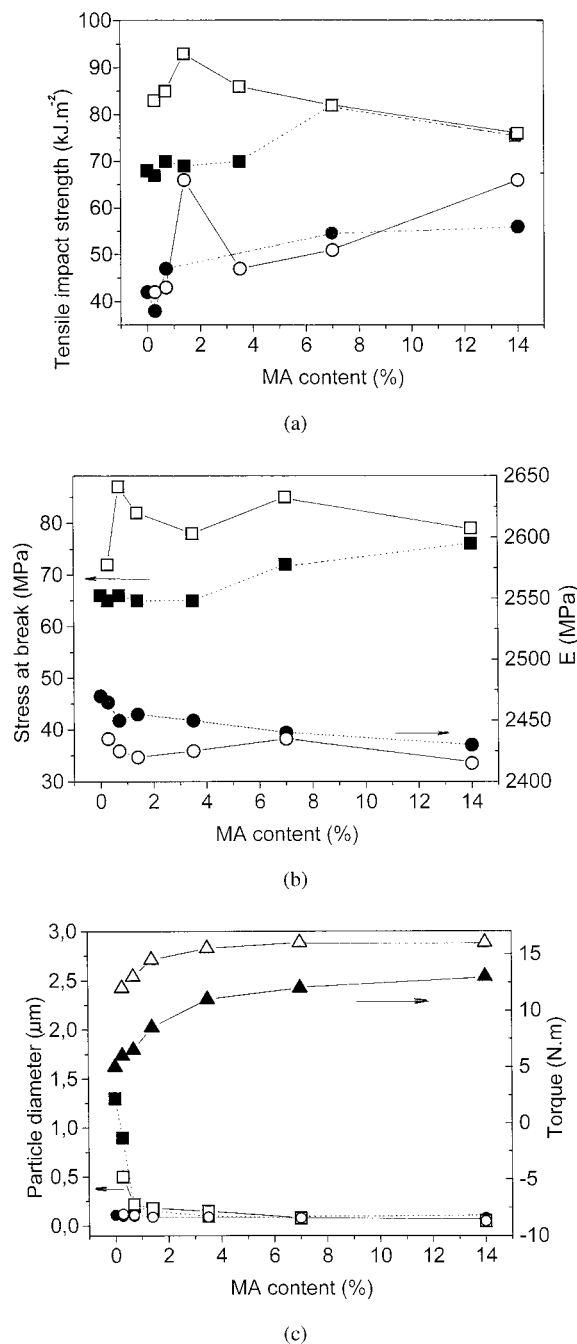
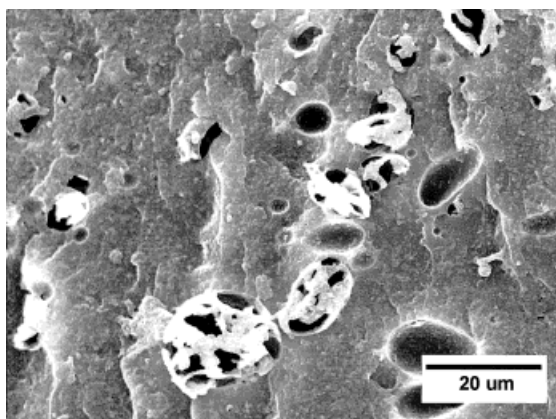
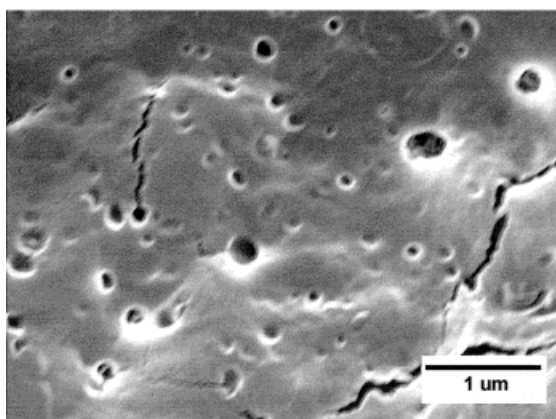


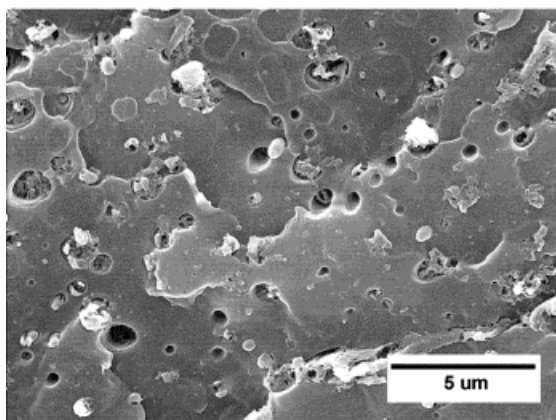
Figure 3 Toughness of the N6/SEBS-MA/(PS/SMA) 90/5/5 blend in dependence on the rigid phase functionality. ■ N6L matrix 22°C, ● -20°C; □ N6H matrix, 22°C, ○ -20°C. (b) Properties of the N6/SEBS-MA/(PS/SMA) 90/5/5 blend in dependence on the rigid phase functionality. ■ ● N6L matrix; □ ○ N6H. (c) Particle diameter and torque at 250°C of the N6/SEBS-MA/(PS/SMA) 90/5/5 blend in dependence on the functionality of the rigid phase. ▲ N6L, △ N6H; N6L ■ rigid phase, ● elastomer; N6H □ rigid phase, ○ elastomer.



(a)



(b)



(c)

Figure 4 Phase structure of ternary blends with etched elastomeric component. (a) N6L/PS/SEBS 90/5/5 blend; (b) N6L/PS/(SEBS/SEBS-MA 50/50) 90/5/5 blend; (c) N6H/PS/SEBS 90/5/5 blend.

ties with increasing N6 molecular weight is somewhat lower for SEBS-MA blends in comparison with EPR-MA blends (Fig. 2). The lower tough-

ness for SEBS-MA blends (Fig. 3) in comparison with EPR-MA (a less significant difference was also found for N6L) partly corresponds with the above-mentioned findings of Harada et al.¹⁰

CONCLUSIONS

Varying reactivity of the rigid component, the best mechanical behavior was found for the ternary blend with SMA diluted by PS. Virtual “independence” of the particle size in a certain range seems to be a consequence of the dominating influence of the finely dispersed reactive elastomer. This was not the case with the elastomer phase, where the best behavior was found with undiluted components; the explanation may be the relatively low MA content in comparison with SMA. Blends with the higher molecular-weight N6 have significantly enhanced properties with the same phase structure. This effect was less significant for SEBS blends together with lower toughness values in comparison with EPR blends. When compared with analogous binary N6/elastomer blends, a rather different influence of both rubbers on mechanical properties of the ternary system was found, indicating its more complex deformational behavior.

In the case of a nonreactive N6/PS/SEBS blend, the formation of blended bicontinuous particles significantly worsened the toughness; thus, the phase structure with separately dispersed particles is more advantageous in the blend studied.

This work was partly supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A 4050706).

REFERENCES

1. Lu, M.; Keskkula, H.; Paul, D. R. *Polymer* 1993, 34, 1874.
2. Kelnar, I.; Stephan, M.; Jakisch, L.; Fortelný, I. *J Appl Polym Sci* 1997, 66, 555.
3. Koo, K. K.; Inoue, T.; Miyasaka, K. *Polym Eng Sci* 1985, 25, 741.
4. Kurauchi, T.; Ohta, T. *J Mater Sci* 1984, 19, 1699.
5. Angola, J. C.; Fujita, Y.; Sakai, T.; Inoue, T. *J Polym Sci Part B Polym Phys* 1988, 26, 807.
6. Liu, T. M.; Xie, H.Q.; O'Callaghan, K. J.; Rudin, A.; Baker, W. E. *J Polym Sci, Part B Polym Phys* 1993, 31, 1347.

7. Nachlis, W. L.; Kambour, R. P.; MacKnight, W. J. *Polymer* 1994, 35, 3643.
8. Kelnar, I.; Stephan, M.; Jakisch, L.; Fortelný, I. *Polym Mater Sci Eng* 1998, 79, 206.
9. Kelnar, I.; Stephan, M.; Jakisch, L.; Fortelný, I. *J Appl Polym Sci*, to appear.
10. Harada, T.; Carone, E., Jr.; Kudva, R. A.; Keskkula, H.; Paul, D. R. *Polymer* 1999, 40, 3957.
11. Oshinski, A. J.; Keskkula, H.; Paul, D. R. *Polymer* 1996, 37, 4909.
12. Wu, S. *J Appl Polym Sci* 1988, 35, 549.
13. Yu, Z.-Z.; Ou, Y.-Ch.; Qui, Z.-N.; Hu, G.-H. *J Polym Sci Part B Polym Phys* 1998, 36, 1987.
14. Kelnar, I.; Stephan, M.; Jakisch, L.; Fortelný, I. *Polym Eng Sci* 1999, 39, 985.
15. Kayano, H.; Keskkula, Y.; Paul, D. R. *Polymer* 1998, 39, 2835.