Influence of Shear Stress Treatment on Stress-Strain Properties of Methyl Methacrylate-Crosslinked Butyl Acrylate Core-Shell Polymers

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ABSTRACT: The incorporation of multilayer toughness modifiers to glassy polymers proceeds frequently by kneading the polymers in a molten state. This process influences the primary structure of the modifier and the properties of the blend in dependence on a shear stress intensity. In this article, we compare the properties of polymer materials prepared from a multilayer poly(methyl methacrylate) core, butyl acrylate copolymer interlayer, and methyl methacrylate copolymer shell particles {P[MMA-(BAC-co)-(MMA-co)]} by press-molding from powder and from polymer obtained by stirring a melt of this powder in the chamber of a Brabender mixer (200°C, 60 rpm, 10 min). The powder is obtained from a latex by coagulation after polymer synthesis in emulsion. Tensile testing shows different responses of the particle polymers when crosslinked in the middle layer by diallylphthalate (DAP) or by triallylcyanurate (TAC). Although many of the properties of the samples with DAP are improved by kneading, the presence of TAC in polymer particles led mostly to less desirable properties. The maximum percent strain in the polymer with 4.2 wt % of DAP upon shearing increases from 27% to 50%. In the samples with 4.5% TAC the maximum percent strain falls from 39% to 7%. Comparison of Young's modulus E for identical samples shows an analogous effect: a shift from 429 MPa to 638 MPa and from 624 MPa to 548 MPa. The design of the polymer particles used in this work leads to the conclusion that stress during kneading induces a partial desintegration of the crosslinked cage around the particle core. Thus, the varied behaviors of polymers used in this study are connected with the BAC-co network structure and its transformations during the shear stress treatment of the initial polymer material. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 493–501, 1999

Key words: poly(methyl methacrylate); poly(butyl acrylate); core-shell particles; microgels; processing; tensile properties

INTRODUCTION

Incorporation of dispersed rubbery particles into a brittle glassy polymer matrix has frequently been used to improve the toughness of polymer material.[1] Methyl methacrylate (MMA) polymers (PMMA) are modified in preferentially by higher polyacrylates [e.g., poly(butyl acrylate)] (PBAC), which possess: (1) a glass transition temperature (T_g) low enough[2] to be in a viscoelastic state at service temperatures, and (2) a refractive index

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close to that of PMMA so a transparent toughened multiphase polymer can be produced.

Much attention has been devoted to elucidate the effects of the rubber phase on the enhancement of toughness of a brittle matrix, and numerous data have elucidated the principal factors for exploitation of the rubber phase in PMMA modification.[3–5]

Compatibility between components is desirable to prevent debonding of the modifier particles from the matrix.[1] However, to preserve PBAC heterogeneities of the required size in a compatible PMMA matrix, the elastomeric additive should be crosslinked to prevent a single-phase system. Otherwise, the toughness of the material is attained to the detriment of yield stress, a decrease of Young's modulus, and a decrease of T_g.

Because the effect of modification depends on several variables[6–15] [such as the (1) choice of polymers, (2) topology of macromolecular chains, (3) arrangement of layers in multilayer polymer particles, and (4) size of elastomeric heterogeneities], the rubber component in the form of well-defined bead particles is often synthesized separately in advance.

In addition, the method of inclusion of a modifier into the matrix also influences the properties of a multiphase polymer material. The shear stress during stirring the polymer melts raises the spherical heterogeneities of rubber or transforms the structure of particles of a toughness modifier.

In this article, we compare the properties of the polymer material prepared from multilayer core-shell particles by two different procedures. In the first procedure, the core-shell particles in a powder form were press-molded; in the second one, the powder was melt-kneaded before being press-molded. The multilayer spheres P[MMA-(BAC-co)-(MMA-co)] consist of a PMMA core, a BA copolymer middle layer, and a MMA copolymer shell.

EXPERIMENTAL

The polymers of core-shell architecture were synthesized by a several-step seeded emulsion polymerization as described recently.[16] In these materials, the particles have a hard PMMA core covered with a crosslinked rubbery shell of PBAC copolymer (BAC-co) and an outer shell of PMMA copolymer (MMA-co). Besides BAC, the feed for the rubbery interlayer contains a copolymerization crosslinking agent diallylphthalate (DAP) or triallylcyanurate (TAC), and an additional comonomer [MMA (9 wt %)]. The upper MMA-co layer consists of copolymer MMA with 16 wt % of BAC.

Layered polymer particles were isolated from latex by a freezing-thawing procedure at dry-ice temperature. The white polymer powder was washed with water and methanol and subsequently dried in air at 50°C.

Table I presents the composition of polymer samples used in this study.

The mean diameters of polymer particles in the final latexes were determined by a BI-90 Particle Sizer (Brookhaven Instruments Corp.). The measured sizes of samples A–E and F–I were 105–125 nm. Secondary sodium alkane sulfonate emulsifier E-30 (Leuna-Werke, Germany) was used in synthesis. Diameters of samples K–Q were 67–70 nm, and sodium dodecyl sulfate emulsifier was used in the emulsion polymerization.

Double bell-shaped specimens were used in the stress-strain measurements (ASTM: D-638M-84, type M-III). They were press-molded either directly from the particle bead polymer powder or from the polymer obtained by treating the powder by shear stress. A Plasti-Corder Brabender mixer operating at 200°C and 60 rpm was used. The stirring to constant torque, which did not exceed 10 min, provides a measure of the degree of particle transformation. Totally digital Instron 4301 instrument at room temperature and a crosshead speed of 1 mm min^{-1} was used.

RESULTS AND DISCUSSION

Emulsion polymerization offers the opportunity to synthesize polymer particles of predefined composition, size, and macromolecular topology. Macromolecules in particles are often crosslinked to ensure that they retain their morphology during subsequent blending and processing. In multilayer polymer particles, each layer can be crosslinked; but, for compatible PMMA-PBAC polymer systems, the transformation of an elastomer component into a network is the most important step to maintain the two-phase system.

The prepared particle polymers were designed as three-stage beads with a hard core (PMMA)

Table I Composition of Polymer Samples Used in this Study

Sample	Crosslinking Agent in BAC-co (wt %)	Particle Components (wt %) Core PMMA	Middle Layer BAC-co	Shell MMA-co
A°	0	56.0	21.5	22.5
A	1	55.8	21.7	22.5
B	2.3	55.6	21.9	22.4
C	DAP 4.2	55.4	22.3	22.3
D	6.9	55.0	22.8	22.2
E	9.9	54.6	23.4	22.0
K	0.5	55.9	21.6	22.5
L	1.0	55.8	21.7	22.5
M	2.3	55.6	21.9	22.4
N	TAC 4.5	55.4	22.3	22.3
O	6.0	55.1	22.7	22.2
P	7.3	54.9	22.9	22.2
Q	10.9	54.5	23.5	22.0
PMMA	0	100.0	—	—
F	4.2	62.3	12.6	24.2
G	DAP 4.2	55.4	22.3	22.3
H	4.2	45.3	36.5	18.2
I	4.2	39.9	43.9	16.2

Polymer particles crosslinked in the BAC-co middle layer by various concentrations of DAP and TAC and particles with a various volume of BAC-co.

and a rubbery crosslinked interlayer (BAC-co) covered with a shell polymer of high T_g (MMA-co). The two methods for preparation of test bars allowed us to consider the effects of shear stress during processing on the properties of the polymer material.

In a previous study,[16] we examined non-notched test bars of polymer samples A–I for impact strength, which depends on the DAP concentration (used as a crosslinking agent in BAC-co component of the bead polymer). The results are briefly summarized herein to provide continuity.

The energy needed for destruction of the test bars by a Charpy pendulum increases 2.5 times at 5 wt % DAP, compared with unmodified PMMA. A further increase of DAP concentration had only a slight effect on the impact strength.

Polymers shear-treated in the melt show an entirely different behavior. The highest resistance of the test bars to break in was observed for the polymer sample with the BAC-co component crosslinked already by 1 wt % of DAP. Subsequently, a systematic decrease of the impact strength from 30 kJ m^{-2} to 6 kJ m^{-2} occurred as the amount of DAP was increased to 10 wt %. The lower value is very close to the impact of unmodified PMMA and represents only half of the impact strength for only press-molded polymer. These results point out the strong effect of shear stress on a crosslinked interlayer in multilayer core shell polymer particles P[MMA-(BAC-co)-(MMA-co)].

STRESS-STRAIN DEPENDENCIES

The influence of a crosslink density of the elastomeric interlayer BAC-co on the mechanical behavior of tested samples is exemplified in Figures 1–3. The sets of the stress-strain curves compare samples crosslinked by various amounts of DAP and TAC. Figure 1 presents data from samples molded from primary multilayer particle polymers. Figure 2 shows the curves for samples prepared from polymers treated by shear in a molten state before molding. The curves in Figure 3 were obtained by testing the primary and treated polymers where the BAC-co layer was crosslinked by TAC.

The common characteristics of the stress-strain dependencies are: a pronounced yield point, the yield strain being 10–14%; stress soft-

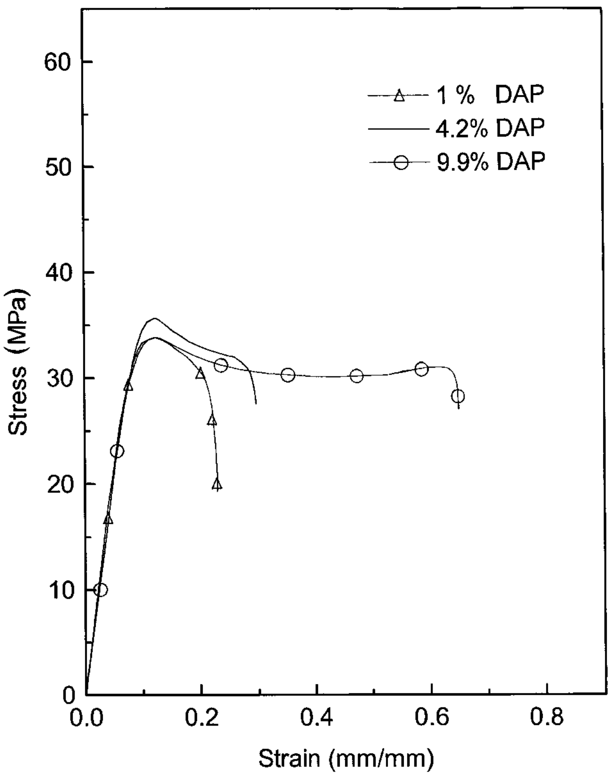

Figure 1 Stress-strain curves for polymer materials based on the three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of crosslinking the interlayer by DAP. Samples A, C, and E (primary polymer).

ening in most samples continues to the break point without a flat region and stress hardening; and the ultimate stress always is lower in comparison to the yield stress. From the shape of the curves, one can presume that the motion and orientation of molecular segments during testing sample are low for the polymers with TAC and for the primary polymers with low concentrations of DAP. Nevertheless, the curves recorded both for the BAC-co layer more densely crosslinked by DAP and for the polymers shear treated pass through a flat region after the yield point and a stress softening. Stress hardening was indicated in curves only for the samples with the highest concentrations of DAP. The crosslinking and kneading of the polymer melt in the Brabender chamber allow a higher extent of segmental motion than in previous samples prepared from nontreated particle polymers and those slightly crosslinked with DAP. The opposite effect was observed in the case of samples crosslinked with TAC. The results show that less elastic materials are obtained after shear stress treating of these particle polymers.

However, there are major differences among the samples regarding the relationships between elongation, crosslinking agent concentration, and shear treatment of the primary polymer.

EFFECT OF BAC NETWORK ON ELONGATION

An important requirement in the design of tough-layered PMMA-PBAC polymer particles is that the elastomeric BAC-co component be crosslinked to have the internal rubbery phase insoluble in PMMA. It is expected that the crosslinking preserves also the particle size and morphology during processing and blending. On the other hand, the crosslinks decrease chain flexibility and free-volume around segments of the polymer chains

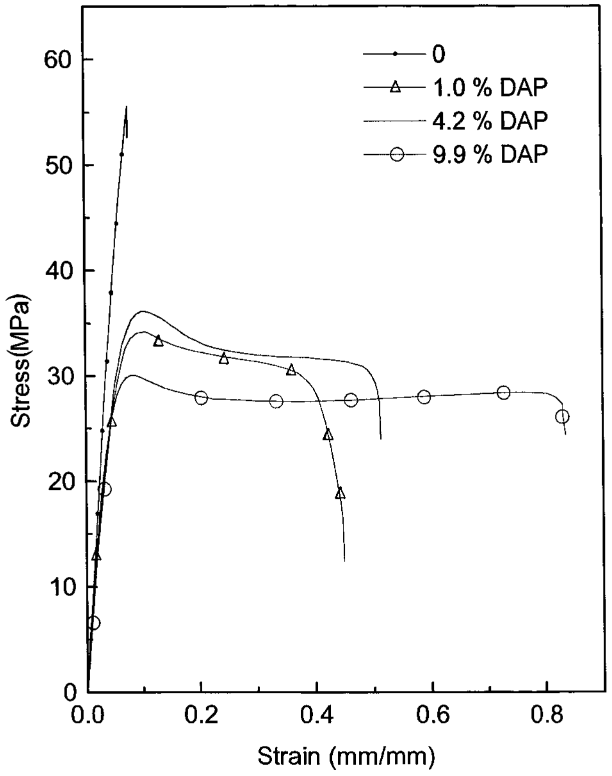

Figure 2 Stress-strain curves for polymer materials based on the melt kneaded three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of crosslinking the interlayer by DAP. Samples A, C, and E (● = seed PMMA polymer particles).

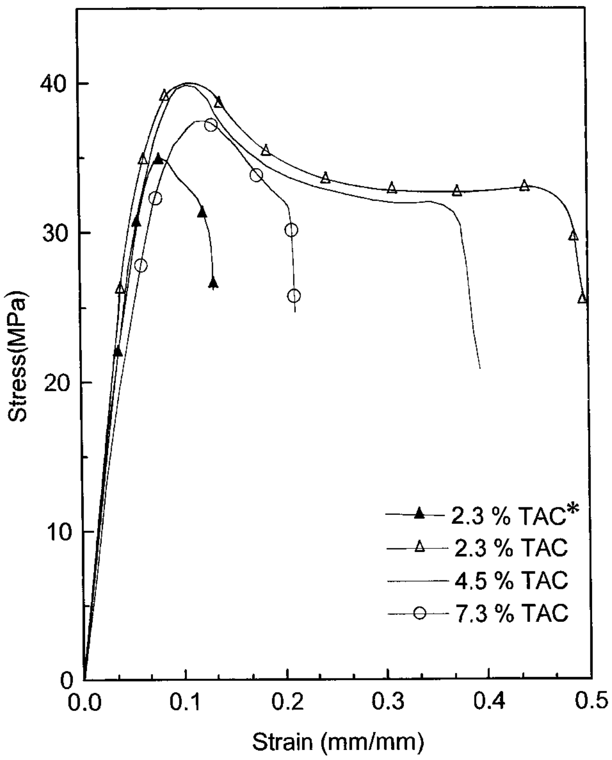

Figure 3 Stress-strain curves for polymer materials based on the three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of crosslinking the interlayer by TAC. Samples M, N, and P (primary polymer; TAC* = melt-kneaded polymer).

with an almost unpredictable effect on the toughness.

Tensile testing of samples A–E and K–Q reveals that crosslinking induced greater fracture strains up to 70–80% (BAC-co layer with 1 wt % TAC in the primary polymer or with 9.9 wt % DAP in the shear-treated polymer), compared with 6.6% ultimate strain for the core PMMA (Tables II and III). Although DAP crosslinks favor sample elongation in the whole concentration range, TAC develops the more complicated strain dependence on the concentration of the crosslinking agent in the analogous particle polymers. The reduction of the ultimate strain from the maximum at 1 wt % TAC (74%) to the minimum strain at 7.3 wt % TAC (18%) by raising a crosslink density points up the very rigid BAC-co network for this crosslinking agent. TAC, in comparison with DAP, introduces three chain junctions to the network. We assume that this structure effectively hinders segmental rotation and recoiling of the polymer chains; hence, under stress, the deformation of samples is low.

The poor performance of these polymers after their shear treatment can be explained by the same effect as above. Moreover, the stiff network with TAC junctions is more sensitive to scission by shear stress. The rigid fragments of the TAC crosslinked BAC-co network are considered herein as an ineffective admixture for improving the ductility of synthesized particle polymers with TAC.

DEFORMATION PROPERTIES OF PRIMARY AND SHEAR-TREATED POLYMERS

The basic mechanical properties of the primary polymers only press-molded to samples prepared from the polymers treated in advance by shear stress show significant differences in deformation

Table II Tensile Properties and Effect of the Shear Treatment of Polymer Materials Based on the Three-Layer P[MMA-(BAC-co)-(MMA-co)] Particles at Various DAP Concentrations in the Interlayer

		Young's Modulus (MPa)		Maximum % Strain (%)		Stress at Break (MPa)	
Sample	DAP (wt %)	Primary	Treated	Primary	Treated	Primary	Treated
A°	0	553	552	29	33	28.0	15.1
A	1	452	644	22	43	0.20	15.6
B	2.3	420	587	21	27	0.18	14.3
C	4.2	429	638	27	50	0.13	11.8
D	6.9	425	577	56	58	0.17	14.8
E	9.9	444	584	62	80	0.19	17.0

Each value represents an average of five measurements.

Table III Tensile Properties and Influence of Kneading the Melt of Polymer Materials Based on the Three-Layer P[MMA-(BAC-co)-(MMA-co)] Particles at Various TAC Concentrations in the Interlayer

		Young's Modulus (MPa)		Maximum % Strain (%)		Stress at Break (MPa)	
Sample	TAC (wt %)	Primary	Treated	Primary	Treated	Primary	Treated
A°	0	553	552	29	33	28.0	15.1
K	0.5	626	584	45	14	22.0	28.2
L	1.0	602	603	74	10	23.4	25.9
M	2.3	642	642	53	13	23.6	25.9
N	4.5	624	548	39	7	23.5	18.9
O	6.0	662	537	24	8	27.7	19.4
P	7.3	606	540	18	8	31.1	18.7
Q	10.9	695	542	22	9	28.4	20.5

Each value represents an average of 10 measurements.

behavior. In addition, the type of crosslinking monomer is also important in determining the final properties of the particle polymer material. The values of Young's modulus *E* obtained from tensile testing are shown in Tables II, III, and IV. Data are plotted against the concentration of crosslinking comonomer, DAP or TAC, and against the fraction of the rubber component, BAC-co, in Figures 4–6.

The tested particle polymers with DAP that underwent a shear stress treatment of their melt possess evidently higher Young's modulus than nontreated polymers. Lightly higher values of strain and stress at break over nonsheared materials were observed. However, at the yield point, values of similar parameters are higher for the primary polymer (Figs. 1 and 2). The increasing crosslink density of the BAC-co layer decreases Young's modulus to a minimum at 2.3 wt % of DAP, followed by a moderate rise.

The increasing fraction of BAC-co in polymer particles leads to a systematic and substantial reduction of Young's modulus. The samples prepared from the treated polymer reveal higher values of Young's modulus. Their tensile strength is also reduced, but the elongation has a maximum at 36.5 wt % of the BAC-co in polymer particles (Table IV). This maximum, which was also observed in a rubber-modified polystyrene[1] is assumed to result from a broadening of the rubber particle size distribution. The larger particles reduce relatively the number of sites for initiation crazes, and the increasing number of small particles acts as a crack source. In our case, the rubber phase is located on the hard PMMA core as a shell

Table IV Tensile Properties and Influence of Kneading the Melt of Polymer Materials Based on the Three-Layer P[MMA-(BAC-co)-(MMA-co)] Particles at Various Fractions of the BAC-co Interlayer Crosslinked by 4.2 wt % of DAP

		Young's Modulus (MPa)		Maximum % Strain (%)		Stress at Break (MPa)	
Sample	BAC-co (wt %)	Primary	Treated	Primary	Treated	Primary	Treated
PMMA[a]	0	848	—	6.6	—	55	—
F	12.6	500	780	31	39	0.27	23.0
G	22.3	429	638	27	50	0.13	11.8
H	36.5	275	386	89	68	0.13	16.3
I	43.9	133	272	48	38	2.80	5.9

Each value represents an average of five measurements.

[a] Seed PMMA polymer particles.

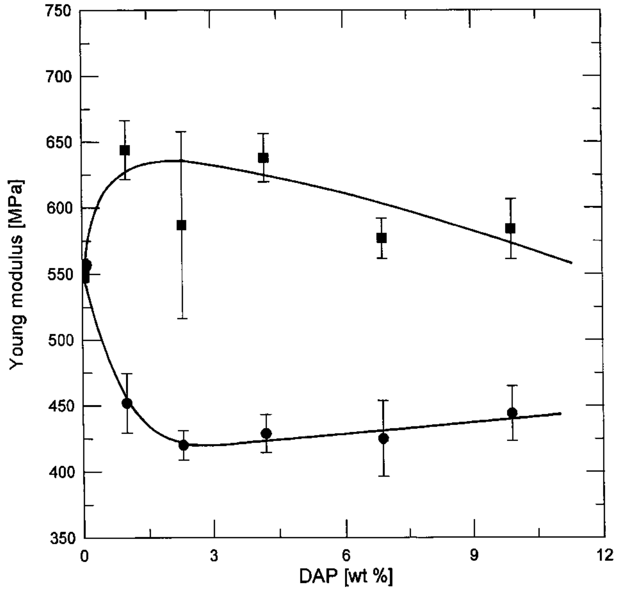

Figure 4 Young's modulus for polymer materials based on the three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of DAP concentration in the BAC-co middle layer: (●) primary polymer; (■) melt-kneaded polymer.

with variable thickness. The upper layer of particles is again the hard thin MMA-co shell. The average size of polymer particles is 110 ± 6 nm.

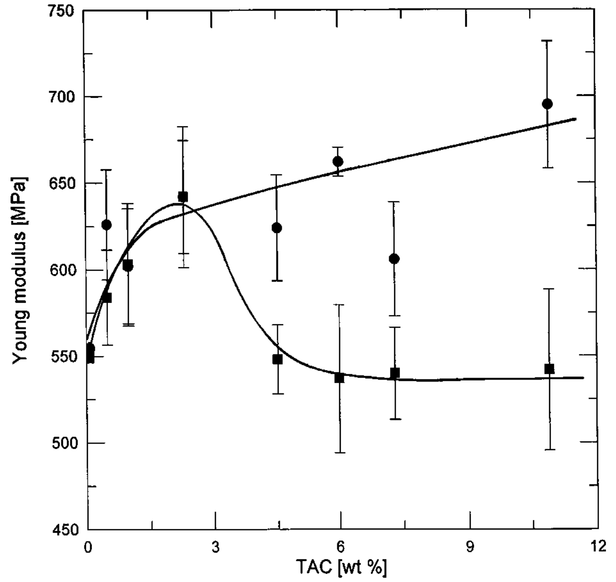

Figure 5 Young's modulus for polymer materials based on the three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of TAC concentration in the BAC-co middle layer: (●) primary polymer; (■) melt-kneaded polymer.

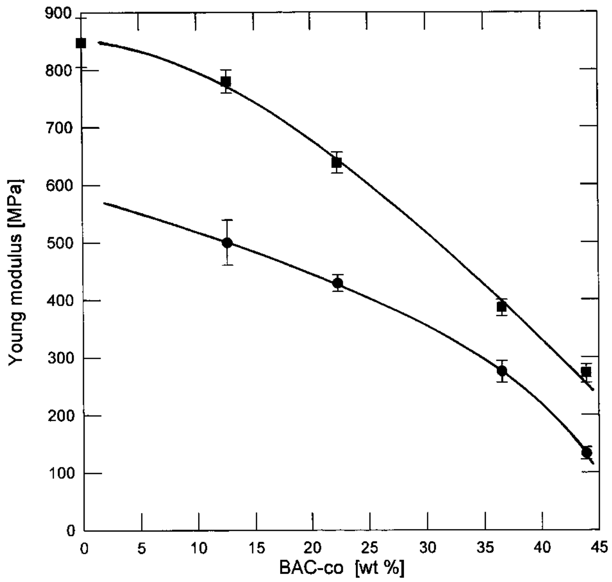

Figure 6 Young's modulus for polymer materials based on the three-layer P[MMA-(BAC-co)-(MMA-co)] particles. Influence of the fraction of the BAC-co rubbery middle layer crosslinked by 4.2 wt % of DAP: (●) primary polymer; (■) melt-kneaded polymer.

We explain the maximum in ultimate elongation for this type of polymer material by the particle growth process. The stage-by-stage synthesis and compatibility of the particle components lead to diffusive interfaces. It is expected that this part of polymer particles consists also of branched and grafted macromolecules that have a positive effect on sample elongation in tensile testing. However, the pure BAC-co network predominates in the polymer particles by increasing the thickness (volume fraction) of the crosslinked BAC-co layer. Hence, this structure allows for lower mobility of molecular segments and less elongation of polymer samples.

The interpenetration of the BAC-co layer to the adjoining layers supports the sol-gel analysis by swelling the polymer foils press-molded from these polymers. The swelling experiments confirmed also the increase in network density with greater DAP and TAC concentration (Table V). Note that the amount of insoluble polymer (gel) exceed the mass of the middle layer. This, in fact, is a consequence of the BAC-co crosslinked cage around the particle core. Under shear stress, while stirring the polymer in the Brabender chamber, the cage of BAC-co network is partly impaired and the amount of PMMA extracted from the particle core increases. Nevertheless, the

Table V Sol-Gel Analyses and Influence of Kneading the Melt of Polymer Materials Based on the Three-Layer P[MMA-(BAC-co)-(MMA-co)] Particles

Sample	A	B	C	E	K	L	N	P	F	G	H	I
	Crosslinking Agent[a] DAP				Crosslinking Agent[a] TAC				Middle Layer[b] BAC-co			
(wt %)	1	2.3	4.2	9.9	0.5	1	4.5	7.3	12.6	22.3	36.5	43.9
Gel (wt %)												
Primary	54	55	53	64	22	51	38	55	52	53	67	67
Treated	20	27	31	42	14	18	28	28	28	31	44	41
Swelling ratio												
Primary	80	69	46	19	97	52	45	27	—	—	—	—
Treated	52	43	46	28	55	32	23	20	—	—	—	—

Each value is an average of two determinations at equilibrium after swelling in toluene at 298K.

[a] The amount of BAC-co layer varies from 21.6 to 23.6 wt %.

[b] BAC-co layer crosslinked by 4.2 wt % DAP.

lower swelling ratios of networks from these samples reflect higher crosslink densities of BAC-co component in treated samples. This suggests the formation of new crosslinks simultaneously to the polymer chain scissions. The polymer-free mechanoradicals partly recombine and partly initiate subsequent incorporation of remaining double bonds of the crosslinker to the network. An increase of the BAC-co network density is more pronounced with the trifunctional TAC crosslinker than with to bifunctional DAP (Table V). The gel content in the foils consisting from PMMA and crosslinked PBAC discrete particles corresponds very well to the PBAC component.[16]

Based on the sol-gel analyses, the effect of shear stress treating on melted polymer particles is due primarily to changes in the structure of the crosslinked rubbery layer that contribute to better contact among polymer particles. These experiments also confirm that crosslinked BAC-co forms a cage around the PMMA core, and the microgel particles with a high portion of polymer branches favour toughness of material properties.

The BAC-co network crosslinked with TAC behaves in a different way. Its shear-treated melt shows lower values of Young's modulus, stress, and strain than polymer not treated in the Brabender chamber (Fig. 6, Table IV).

The dependencies of mechanical properties on the degree of crosslinking of BAC-co layer are complex. Unlike the BAC-co layer crosslinked with DAP, the network with TAC is more sensitive to destruction by shear. Three allyl groups of TAC monomer upon copolymerization with BAC form a rigid network that degrades under shear to incompatible and less elastic fragments unsuitable for an effective improvement in toughness.

CONCLUSIONS

The highly variable behavior of polymers containing a crosslinked elastomer component in the form of microgel particles can be explained as a result of the network structure and its transformations during shear stress treatment of the polymer melt. The particle microgel modifiers prepared in advance differed from those that originated in material while blending the components in a polymer melt. Moreover, a wide variety of microgel structures results from the great variability of the mechanisms of the elastomer network synthesis. This is clearly demonstrated by the completely different consequences to the blended PMMA particle polymer materials when the BAC-co layer is crosslinked with DAP or TAC. The loose, slightly crosslinked networks of BAC-co with DAP are more effective impact modifiers after shear stress treatment. The more rigid junctions of TAC at shear, however, induce transformations of the BAC-co network that deteriorate mechanical properties of the starting polymer material.

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