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PREPARATION AND PROPERTIES OF SUBMICROMETER PARTICLE METHYL METHACRYLATE-BUTYL ACRYLATE POLYMERS WITH MULTILAYER MORPHOLOGY

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ABSTRACT

Multilayer submicrometer particles having a core and a shell consisting of poly(methyl methacrylate) and an interlayer of a crosslinked copolymer of poly(butyl acrylate) were prepared by seeded emulsion polymerization. The interlayer encapsulates the core and hinders the encapsulated polymer from being dissolved. On dispersion stirring of the melt of a multilayer polymer, the encapsulation is disrupted and the amount of insoluble polymer corresponds to the mass of the middle layer of poly(butyl acrylate). The impact resistance of films prepared from slightly crosslinked polymer samples increases markedly. Provided that the density of the interlayer network is high, the stirring causes the impact resistance of the polymer to be gradually reduced so that for highly crosslinked polymer material it becomes lower than for untreated polymer.

INTRODUCTION

A widely used method of overcoming the brittleness of many atactic polymers in the glassy state is modification by elastomers. A rubber component, as a block or graft copolymer, is put into a glassy matrix where it forms heterogeneous elastomer particles of the required elasticity and dimensions [1]. Since the effect of modification depends on the size of the heterogeneities, elastomeric polymer particles are

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often synthesized separately in advance. Modifiers of toughness used for thermoplastic polymers, such as PMMA or SAN copolymers, consist of submicrometer particles containing elastomer with another polymer in one or more layers. The elastomeric component is usually crosslinked. The topological arrangement of macromolecular chains is fixed by covalent bonds which preserve the local mobility of segments. Through binding of the polymer chains, networks of various structures with different dynamic properties can be formed.

In addition to the choice of monomers, conditions for the synthesis of a microparticle and the method of sample homogenization also influence the properties of polymer materials as well as the properties of mixtures of a polymer with a microgel. A method for controlling the distribution of elastomeric heterogeneities of submicrometer dimensions in a polymer matrix is by the mixing of microgels prepared in advance. Since the heterogeneous discontinuity must have elastomeric properties, its miscibility with a modified matrix is usually insufficient. The effectiveness of modification is thus reduced. This drawback is removed by covering the particle core with a layer of compatibilizing polymer.

Toughness modifiers for poly(methyl methacrylate) (PMMA) polymers often use polymers of acrylic acid esters with an alcohol chain of C_2–C_8 as the elastomeric component. These polymers have glass transition temperatures (T_g) which are low enough [2] and good compatibility with PMMA. In order to build up heterogeneities of the required size (tenths of microns) in a modified matrix, the elastomeric additive must be crosslinked. The crosslinking preserves the shape of the particle during the preparation of mixtures and prevents compatible polymers from dissolving an elastomer in a matrix.

Much attention has been devoted to investigations of the mechanism for the effect of rubber particles on the impact resistance of a brittle matrix [3–11]. Quantitative data on the properties of the particles alone in relation to their synthesis and composition are, however, scarce. The modifier used is most often characterized by the particle size and by qualitative data referring only to the shape and the number of layers with the polymer type and the commercial description [7, 9]. The properties of microgel polymer particles of the copolymer of styrene with divinylbenzene have been described in detail [10]. However, there are only a few quantitative data about the synthesis of core-shell polymer particles and relationships with their effects in polymer blends.

For this reason we synthesized three-stage submicrometer particles with a core and shell from PMMA and an interlayer from poly(butyl acrylate) (PBAC). This material alone or in blends with PMMA should serve as a tough, impact-resistant thermoplastic material. We investigated the effect of the core size, degree of crosslinking of the interlayer, and the thickness of the elastomeric layer on the impact resistance of the polymers prepared.

EXPERIMENTAL

Polymer Synthesis

Multilayer submicrometer polymer particles with well-defined structure are most often prepared by several-step seeded emulsion polymerization [12]. Distilled water (0.325 dm^3) as a disperse medium is added to a 1 dm^3 reactor with a stirrer and an N_2 inlet. Gases dissolved in water are removed by heating it to boiling. With continuous introduction of N_2, the water is cooled to 323 K for the first step of the synthesis.

Components of the polymerization feed (Tables 1, 2, and 3) were added in the following order. First, secondary sodium alkane sulfonate emulsifier (E-30, Leuna-Werke, FRG). After complete dissolution with constant stirring at 200 rpm, all the methyl methacrylate (MMA) was added. Then a water-soluble initiator ($K_2S_2O_8$) was added. A catalyst for peroxide decomposition ($Na_2S_2O_4$) was added last. A small amount of lipophilic initiator of benzoyl peroxide soluble in MMA ensures the start of polymerization. The rate of polymerization is high, and complete monomer conversion is reached in 10 minutes after the initiator is added. The overall time of synthesis of the particle core in the first step of polymerization was 60 minutes. The synthesis of the elastomer layer proceeded immediately upon addition of all the butyl acrylate (BAC) with diallyl phtalate (DAP) as the crosslinking monomer. The feed for the interlayer also contained 10 vol% MMA, and the polymerization proceeded with a gradual rise in temperature. Complete monomer conversion and a temperature of 353 K were achieved in 30 minutes. In this step the initiator was added to the feed in the first synthesis only. The third step of the synthesis was the formation of a shell composed of a copolymer of MMA and 20

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TABLE 1. The Synthesis of the Particle Three-Stage Polymer PMMA-PBAC-PMMA of Submicrometer Size Using Emulsion Polymerization. Water Phase (325 g) with 9 g Emulsifier E-30. The Components of the Reaction Mixture and the Properties of the Particle Polymers with Different Core Sizes Are Presented

	Synthesis			
	1	2	3	4
MMA, mL[a]	75	100	150	250
I: Core (wt%)	41	47.8	57.9	69.6
II: Middle layer (wt%)[b]	32	28.3	22.8	16.5
III: Shell (wt%)[c]	27	23.9	19.3	13.9
Particle diameter (nm) after:				
I	76	90	113	207
II	89	103	117	245
III	97	127	144	395
Insoluble gel (wt%)	15	54	61	88
Gel after stirring (wt%)	36	36	28	15
Impact resistance ($kJ \cdot m^{-2}$)	4.1	5.8	6.6	5.7
Impact resistance after stirring ($kJ \cdot m^{-2}$)	33	17	17	17

[a] Benzoyl peroxide = 0.05, $K_2S_2O_8$ = 0.2, $Na_2S_2O_4$ = 0.1 (wt%).

[b] BAC = 50, DAP = 1.25, MMA = 5 (mL). $K_2S_2O_8$ = 0.1, $Na_2S_2O_4$ = 0.1 (wt%).

[c] MMA = 50 mL, $K_2S_2O_8$ = 0.1 wt%.

TABLE 2. The Synthesis of the Particle Three-Stage Polymer PMMA-PBAC-PMMA of Submicrometer Size Using Emulsion Polymerization. Water Phase (325 g) with 9 g Emulsifier E-30. The Components of the Reaction Mixture and the Properties of the Particle Polymers with Different Crosslinking Densities of the PBAC Interlayer

	Synthesis				
	5	6	7	8	9
I: Core (wt%)[a]	55.8	55.6	55.4	55	54.6
II: Middle layer (wt%)[b]	21.7	21.9	22.3	22.8	23.4
DAP (wt%)	1	2.3	4.2	6.9	9.9
III: Shell (wt%)[c]	22.5	22.5	22.4	22.2	22.0
Particle diameter (nm)	122	125	104	119	108
Insoluble gel (wt%)	54	55	53	61	64
Gel after stirring (wt%)	20	27	31	41	42
Equilibrium swelling (toluene, 295 K)	80	69	46	20	19
Equilibrium swelling after stirring	52	43	46	23	28

[a] MMA = 150 mL, benzoyl peroxide = 0.05, $K_2S_2O_8$ = 0.2, $Na_2S_2O_4$ = 0.1 (wt%).
[b] BAC = 50, MMA = 5 (mL).
[c] MMA = 50 mL, $K_2S_2O_8$ = 0.1 wt%.

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vol% BAC. The polymerization was carried out at 333 K with an additional amount of $K_2S_2O_8$ without catalyst. Full monomer conversion was reached in 60 minutes.

Monomer conversion was determined gravimetrically several times during synthesis. The tables show monomer conversions at the end of each step of the synthesis.

In the first series of polymerizations we examined the latex particle size after completion of each individual step to verify whether the original particles grow gradually. In the following syntheses, only the particle size of the resulting latex was assessed. A BI-90 Particle Sizer (Brookhaven Instruments Corp.) was used.

The polymers were separated from the dispersion by freezing them out at the temperature of solid CO_2. After melting, the coagulated polymer particles were decanted with methanol and dried in air at about 323 K.

Monomers were redistilled before use under the reduced pressure of N_2. The inhibitor of polymerization was removed as usual. Other solvents and reagents were of analytical grade.

The insoluble portion and the degree of the swelling of polymer were followed after dissolving in toluene at 298 K after 5 days. Parts of a 1-mm thick film prepared on a press at 493 K were used.

The samples for five parallel measurements of impact resistance (Charpy) had dimensions of 40 × 5 × 4 mm (Czechoslovak standard-CSN). They were prepared as for thinner films from powders by press-molding in a Fontijne press at 493 K.

The second parts of the samples used for toughness evaluation were processed before pressing by stirring the melt at 60 rpm and 473 K in the chamber of a Plasti-Corder Brabender until a constant torque was established (6–8 minutes).

TABLE 3. The Synthesis of the Particle Three-Stage Polymer PMMA-PBAC-PMMA of Submicrometer Size Using Emulsion Polymerization. Water Phase (325 g) with 9 g Emulsifier E-30. The Components of the Reaction Mixture and the Properties of the Spherical Particle Polymers with Different Thicknesses of the PBAC Interlayer

	Synthesis			
	10	11	12	13
I: Core (wt%)[a]	62.3	55.4	45.3	39.9
II: Middle layer (wt%)[b]	12.6	22.3	36.5	43.9
III: Shell (wt%)[c]	24.2	22.3	18.2	16.2
Particle diameter (nm)	109	104	116	144
Insoluble gel (wt%)	52	53	67	67
Gel after stirring (wt%)	28	31	44	41
Impact resistance ($kJ \cdot m^{-2}$)	9	14	40	43
Impact resistance after stirring ($kJ \cdot m^{-2}$)	9	14	40	56
Melt viscosity (arbitrary units) (473 K):	25.5	22.5	21.7	10
Maximum Equilibrium	23.5	19	17.5	7

[a] MMA = 150 mL, benzoyl peroxide = 0.05, $K_2S_2O_8$ = 0.2; $Na_2S_2O_4$ = 0.1 (wt%).

[b] BAC = 87.3, MMA = 5.5, DAP = 4.2 (wt%)

[c] MMA = 50, BAC = 10 (mL), $K_2S_2O_8$ = 0.1 wt%.

RESULTS AND DISCUSSION

The increase of the toughness of the polymer materials is achieved by improving their ability to dissipate the energy of external tension through the formation of a plastic zone in front of the crack tip. Brittle polymer matrices are modified by elastomers which form mostly spherical heterogeneities in the composite. The effective cross-section of such an elastomer toughness modifier can be increased by increasing the diameter of its particles when the concentration of the elastomer component in a composite is simultaneously raised. Multilayer spherical toughness modifiers with an elastomeric interlayer make it possible to locate the elastomer in a larger volume by increasing the core diameter with an unchanged amount of elastomer in the composite.

Table 1 shows polymerizations directed to the preparation of particles with various core sizes from PMMA. We varied the amount of MMA in the first step of the synthesis. The same amount of elastomeric copolymer BAC with 10 vol% MMA and 2.5 vol% DAP was polymerized around primary particles in all syntheses. The synthesis of the modifier was completed by a surface layer of the MMA-*co*-BAC copolymer. The particle sizes determined show the increase of both the PMMA core by increasing the amount of MMA in the first step of emulsion polymerization and

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the particle diameter by adding monomers in the second and the third steps of the synthesis. The result is in agreement with our aim of preparing multilayer particles and not a blend of particles of various size.

On the assumption that spherical polymer particles are formed via emulsion polymerization and their number does not vary in the synthesis, the calculated increase in their volume correlates reliably with the polymer particle diameter determined. In a dispersion with the highest polymer concentration, coagulation of the original particles also occurs, as indicated by their size. Their enlargement exceeds the amount of polymer formed in the synthesis of the surface layer by several times.

The impact resistance of test specimens prepared by press molding from a particle polymer increases only slightly with increasing particle cross-section (Table 1). The values of fracture energies are close to those of unmodified suspension PMMA. Bars produced from a particle polymer which was processed before press molding by disperse stirring in a chamber of the Brabender plastograph at 473 K showed a higher fracture energy. Based on sol-gel analysis, the effect of stirring is also explained by a change in the structure of the crosslinked elastomer layer in addition to improvement in the contacts of polymer particles.

We found that the gel content in the samples prepared by press molding increase with an increasing PMMA particle core (Table 1). If we consider that the amount of BAC for the middle layer was always the same and only this feed contained the crosslinking comonomer DAP, the presence of insoluble polymer in an amount several times greater than the mass of the middle layer can be accounted for by the formation of a crosslinked cage around the particle core. The partial penetration of PBAC–DAP into the core surface layer cannot be excluded, but we do not consider additional crosslinking of the PMMA core by reaction with a multifunctional monomer. On the contrary, the gel content in films from the polymer melt stirred in advance approaches the mass of the crosslinked PBAC interlayer (Table 1). This means that, during stirring under shear stress, the cage of the crosslinked PBAC was disrupted and the particle core was dissolved and extracted with toluene. The results confirm that crosslinked PBAC forms a shell around the PMMA core. Moreover, additional sol-gel analyses of the blended polymer foils consisting of PMMA and crosslinked P(BAC-*co*-DAP) particulate polymers proved the unhindered extraction of PMMA. The gel content in the foils corresponds to the amount of P(BAC-*co*-DAP) component in these blends (Table 4). The polymer mixture for molding the foils was obtained by mixing PMMA and P(BAC-*co*-DAP) emulsions prepared in separate syntheses and subsequent isolation by the freeze–thaw procedure.

In tough thermoplastic compositions it is necessary to prevent dissolution of the elastomeric component in a matrix of the brittle polymer. With compatible polymers this requirement is satisfied by crosslinking of the elastomer. For the polymer particles described here, it means crosslinking of the middle layer from PBAC prepared in the second step of the synthesis. Table 2 contains data on the preparation and properties of these polymers. The polymer network density in the interlayer was changed by raising the concentration of DAP from 1 to 10% in BAC. This effect is confirmed by the swelling in toluene films pressed from these polymers. The gel content exceeds the mass of the interlayer by 2.4 to 2.7 times as a function of the degree of crosslinking. After the shear stress on the polymer melt during stirring, the amount of gel was reduced so that, in the least crosslinked

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TABLE 4. The Impact Resistance (Charpy) of Nonnotched Test Bars Prepared from PMMA and P(BAC-*co*-DAP) Spherical Submicrometer Particle Polymer Mixture

Sample	P(BAC-*co*-DAP) in mixture, wt%	Impact resistance, $kJ \cdot m^{-2}$	Gel, wt%	Degree of swelling[a]
a	22.3, DAP share 2.3	7	27	
b	36.5	6	35	22 ± 5
c	43.9	4	46	
d	22.3, DAP share 4.2	10	23	
e	36.5	7	37	15 ± 2
f	43.9	7	44	
g	22.3, DAP share 9.9	6	24	
h	36.5	7	35	13 ± 2
ch	43.9	2	43	

[a] Extraction and equilibrium swelling in toluene, 296K; ratio of swollen to dry gel.

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sample, it corresponds to the mass of the PBAC layer. As the density of the polymer network gradually increases, extraction from the interior of the particle becomes more difficult, even after disperse stirring of the melt. The gel content, which exceeds the mass of the rubber layer, varies from 0 to 80% in samples with the highest density of the PBAC network. This makes these types of microparticle polymers different from polymers with the same degree of crosslinking of the rubber layer and with particle cores of various sizes.

We again observed entirely different relations of impact resistance with samples prepared by press molding directly from the microparticle polymer and from polymers whose melts were stirred in a chamber of the plastograph (Fig. 1). The fracture energy of the first type of samples as a function of DAP concentration (or of the polymer network density) has a maximum at 6% of the crosslinking agent in the BAC feed. The second type of samples shows a systematic decrease of the impact resistance with increasing degree of crosslinking. After stirring, the fracture energy of the polymer with 1% DAP is threefold higher and the fracture energy of the polymer with 10% DAP is only half of the fracture energies of the polymer samples press-molded only.

From the point of view of the impact resistance of the polymer prepared, the result shows that the crosslinking density of the PBAC layer has an optimum value for unperturbed particles. Gels modified by shear stress would be more resistant to impact strength if a network of the rubber layer of the original particle were only slightly crosslinked. On the contrary, a PBAC layer strongly crosslinked after disperse stirring functions in a polymer as heterogeneities with insufficient adhesion to the matrix, thus unfavorably affecting the material's impact resistance. This conclusion agrees well with the very low impact resistance observed for blended polymer foils based on a mixture of discrete PMMA and P(BAC-*co*-DAP) particles (Fig. 1, Table 4).

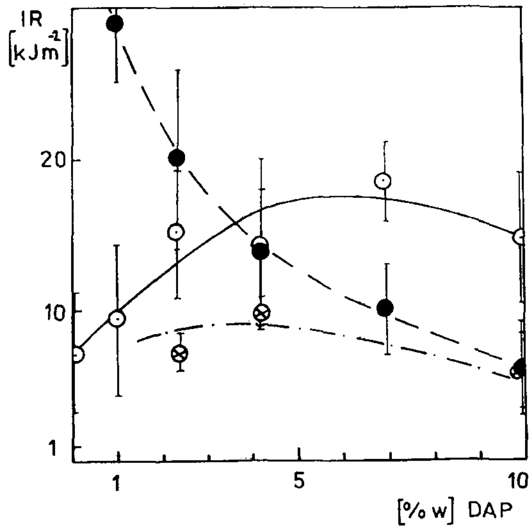

FIG. 1. The dependence of the impact resistance (with standard deviations indicated) of the particle three-stage polymer PMMA-PBAC-PMMA on the amount of the crosslinking agent in the elastomer PBAC layer. Five parallel measurements for each sample. Test bars were prepared by press molding from the original polymer (○) and after shear stress (●); the symbol ⊗ indicates the blended polymer based on the mixture of discrete particles of PMMA and P(BAC-*co*-DAP).

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Finally, in the synthesis of microparticles of PMMA-PBAC-PMMA, our aim was to evaluate how the layer thickness of the elastomer polymer affects the impact resistance of the polymer. The crosslinking agent had the same concentration, so PBAC would have the same density as polymer network. A sample of polymer with the highest PBAC content but with only 0.83% DAP was also included in this series of particle polymers. The synthesis was carried out in an emulsion system which contained cetyl alcohol as coemulsifier. The polymer particles in the emulsion had a diameter of 144 nm before coagulation which is, compared with the other three polymers, an increase of 30%.

In sol-gel analysis of the press-molded films of these polymers, the toluene-insoluble portion was again higher than the portion of the elastomer component. After disperse stirring, the insoluble gel decreases as described for the previous series of particle polymers.

Figure 2 shows the dependence of the impact strength of the polymers on the content of PBAC in the middle layer of the particles. The result clearly indicates the dominant importance of the elastomer layer in a particle on the impact resistance of the pressed films. On the other hand, the shear stress effect during disperse stirring did not exert any influence on the fracture energy of these polymers. With increasing PBAC content there was a decrease in the torque (which indicates the melt viscosity) during the processing of these polymers. We can assume that the shear stress did not reach the value needed for transformation of the cage of the crosslinked PBAC. This view contradicts the fact that during disperse stirring the soluble portion of PMMA increased.

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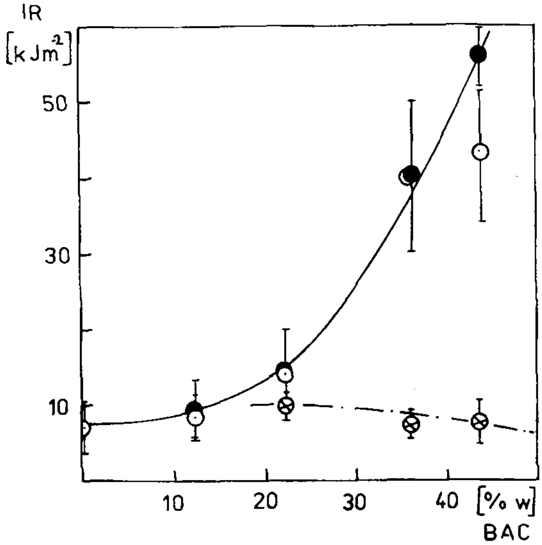

FIG. 2. The dependence of the impact resistance (with standard deviations indicated) of the particle three-stage polymer PMMA–PBAC–PMMA on the thickness of the elastomer interlayer of PBAC crosslinked with 4.2% DAP. Five parallel measurements for each sample. Test bars were prepared by press molding from the original polymer (○) and after shear stress (●); the symbol ⊗ indicates the blended polymer based on the mixture of discrete particles of PMMA and P(BAC-*co*-DAP).

The same impact strength of these particle polymers before and after disperse stirring of their melts can be explained in terms of the dependencies presented in Fig. 1. The samples containing various amounts of PBAC were crosslinked with 4.2% DAP. The polymer network formed at this composition of the elastomer layer probably has such a density that the positive effect on the impact resistance and the destruction effect eliminate each other in its transformation by shear stress. This is represented by the area around the cross section of the curves in Fig. 1.

Such an interpretation of the relation between the density and the structure of the polymer network and its transformation via shear stress and its impact resistance can be illustrated by the behavior of the sample with the highest PBAC content. The elastomer layer of the sample contains 0.83% of the crosslinking agent, and thus its network has a concentration of crosslinking bonds lower than in the other three types of polymers in this series. According to Fig. 1, the polymer belongs to the region of DAP concentrations where the structuralization effect of the shear stress prevails over the degradation effects. For this reason the value of the fracture energy of unstirred polymer reported in Fig. 2 does not lie on the curve and so can be considered as an effect of the low degree of crosslinking and not as a deviation from the dependence plotted there. After disperse stirring of the polymer, the impact resistance therefore increased, in contrast to the samples with 4.2% DAP. However, further experiments are needed in order to obtain more information about the influence of shear stress on multilayer microgel polymers and the impact resistance of the resulting polymer materials.

CONCLUSIONS

The results of this work demonstrated the influence of dispersion stirring on the impact resistance of polymer materials based on spherical three-stage submicrometer particles PMMA–PBAC–PMMA.

Polymers which undergo treatment by shear stress have higher impact resistances if a network of the rubber layer is only slightly crosslinked. With increasing of network density, PBAC microgels function as heterogeneities with insufficient interaction with the PMMA matrix. The amount of elastomer in polymer particles is of dominant importance in increasing the fracture energy. The high network densities of this layer have a negative rather than a positive influence on polymer sensitivity to impact fracture. Therefore the impact resistance of polymer blends based on multilayer submicrometer particles depends on the position of the elastomer layer and on the method of test-bar preparation.

Polymer films press molded from original particles in sol–gel analyses show an amount of gel which considerably exceeds the weight of the crosslinked PBAC content in the polymer particles. Under a shear stress the PBAC cage around the PMMA core is disrupted, and the PMMA core can be dissolved and extracted with solvents. This result supports the multilayer construction of polymer particles prepared in seeded emulsion polymerization.

There was no improvement in the impact resistance of test bars molded from polymer mixtures consisting of discrete particles of the PMMA component with crosslinked PBAC as the second component. The gel content corresponds to the amount of PBAC present in blended polymer sheets, contrary to sheets molded from multilayer polymer PMMA–PBAC–PMMA particles.

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REFERENCES

[1] A. J. Kinloch and R. J. Young, *Fracture Behaviour of Polymers*, Applied Science Publishers, London, 1983, pp. 421–467.

[2] H. Rauch-Puntigam and T. Volker, *Acryl- und Methacrylverbindungen*, Springer-Verlag, Berlin, 1976, p. 304.

[3] L. Könczöl, W. Döll, and G. H. Michler, *Colloid Polym. Sci.*, *270*, 972 (1992).

[4] O. S. Gebizlioglu, H. W. Beckham, A. S. Argon, R. E. Cohen, and H. R. Brown, *Macromolecules*, *23*, 3968 (1990).

[5] P. Laurienzo, M. Malincolnico, E. Martuscelli, G. Ragosta, and H. G. Volpe, *J. Appl. Polym. Sci.*, *44*, 1883 (1992).

[6] M. E. Boyce, A. S. Argon, and D. M. Parks, *Polymer*, *28*, 1680 (1987).

[7] A. S. Argon, R. E. Cohen, and O. S. Gebizlioglu, in *Mechanical Behaviour of Materials* (M. G. Yan et al., Eds.), Pergamon Press, Oxford, 1987, p. 1.

[8] N. Snah, *J. Mater. Sci.*, *23*, 3623 (1988).

[9] G. A. Papadopoulos and G. C. Papanicolaou, *Ibid.*, *25*, 4006 (1990).

[10] D. S. Parker, H.-J. Sue, J. Huang, and A. F. Yee, *Polymer*, *31*, 2267 (1990).

[11] M. Antonietti, W. Bremser, and M. Schmidt, *Macromolecules*, *23*, 3796 (1990).

[12] W.-D. Hergeth, H.-J. Bittrich, F. Eichhorn, S. Schlenker, K. Schmutzler, and U. J. Steinau, *Polymer*, *60*, 1913 (1989).

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