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Synergism for the Improvement of Tensile Strength in Block Copolymers of Polystyrene and Poly(*n*-butyl methacrylate)

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Whereas polymer blends show a macrophase separation, block copolymers form a microdomain morphology on a typical size scale of 10−100 nm depending on molecular weight and composition. Poly(styrene-*b*-isoprene) diblock copolymers for example show in the strong segregation limit spheres, hexagonally packed cylinders (HEX), ordered bicontinuous double diamond (OBDD), and lamellar (LAM) structures depending on the PS-block length.[1−4] Recently, two nonclassical morphologies, hexagonally perforated layers (HPL) and the bicontinious cubic phase (also denoted as "Gyroid-"phase), were found in the weak segregation limit.[5−7] Commonly used copolymers like poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers are important for technical applications, revealing the behavior of an elastomer. Such a kind of thermoplastic elastomers (TPE) consist of a glassy hard block and a rubbery soft block.[8]

Recently, Russell and co-workers[9,10] have found a microphase separation in poly(styrene-*b*-*n*-butyl methacrylate) diblock copolymer melts on heating. These diblock copolymers exhibit both an upper critical order transition (UCOT) and a lower critical order transition (LCOT). In our prevoius papers,[11,12] we have reported the morphologies of these diblock copolymer systems depending on polystyrene content and block molecular weight. In the present study, an originally unexpected synergism effect concerning the improvement of the tensile properties in block copolymers consisting of polystyrene and poly(*n*-butyl methacrylate) will be presented.

The PS-*b*-PBMA diblock copolymers and the poly(*n*-butyl methacrylate-*b*-styrene-*b*-*n*-butyl methacrylate) triblock copolymers (PBMA-*b*-PS-*b*-PBMA) used in this study are listed in Table 1. All samples were dissolved in toluene, and the solvent was allowed to evaporate slowly over 5−7 days at room temperature. Then the films were dried to constant weight in a vacuum oven at 120 °C for 3 days. Tensile tests were performed using a universal testing machine (Zwick 1425) at a strain rate of 1.6×10^{-4} s^{-1}. Tensile bars were employed with a thickness of 0.5 mm and total length of 50 mm.

In contrast to other polymeric systems we find for sample SBM76 a tensile strength (Figure 1) which is about 40% higher than that of pure PS. This synergism for the tensile strength was found in a small composition range between 70% and 80% PS content of the diblock copolymers.

Table 1. Molecular Weight (M_n), Volume Fraction (Φ_{PS}), and Polydispersity (M_w/M_n) for the Block Copolymers Used in This Study

sample	total molecular weight 10-3 × M_n[a]	PS vol fraction Φ_{PS}[b]	polydispersity M_w/M_n
	Diblock Copolymers		
SBM 9	412.0	0.09	1.03
SBM 15	406.8	0.15	1.05
SBM 29	246.0	0.29	1.04
SBM 40	212.1	0.40	1.05
SBM 55	534.0	0.55	1.06
SBM 67	450.0	0.67	1.05
SBM 72	425.0	0.72	1.06
SBM 74	463.0	0.74	1.08
SBM 76	459.0	0.76	1.07
SBM 83	383.1	0.83	1.04
	Triblock Copolymers		
BMASD 9	334.1	0.09	1.10
BMASD 37	275.8	0.37	1.10
BMASD 52	201.1	0.52	1.10
BMASD 72	305.3	0.72	1.05
BMASD 90	299.2	0.90	1.08

[a] Size exclusion chromatography (SEC); values are based on the PS standards. [b] ^{1}H-NMR.

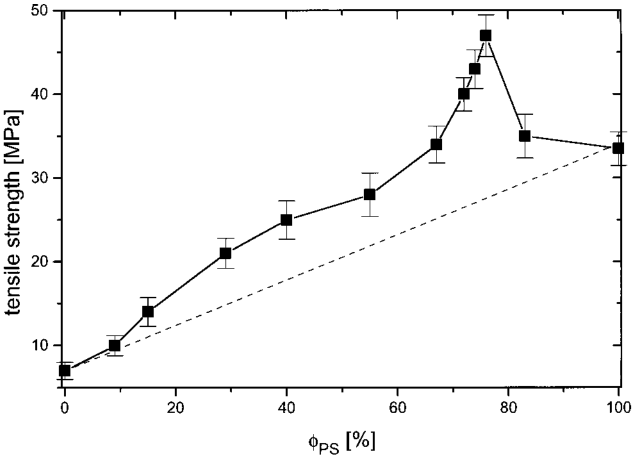

Figure 1. Dependence of tensile strength on the volume fraction Φ_{PS} for diblock copolymers PS-*b*-PnBMA measured at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}$ s^{-1}.

Whereas most polymer blends show either a linear or a decreasing dependence of tensile strength on the hard component content, the tensile strength of PS-*b*-PBMA diblock copolymers for all compositions is higher than that of the linear dependence (dashed line in Figure 1). This means that also for diblock copolymers with a high PBMA content, a strong increase of tensile strength is observed. The increase of the PS-content to 67% leads to a value which is almost the same as that of pure PS. With a further increase of polystyrene content up to 83% PS the block copolymers become brittle and behave almost like polystyrene.

In Figure 2 the stress−strain behavior of a diblock copolymer with 74% PS is compared to pure polystyrene. It is obvious that the PS-*b*-PBMA diblock copolymer with 74% PS has not only a higher strength but also a larger strain at break than pure polystyrene.

Furthermore the Young's modulus as indicated by the slope of the stress−strain curves at small strain shows almost the same value as for pure PS in both cases. This

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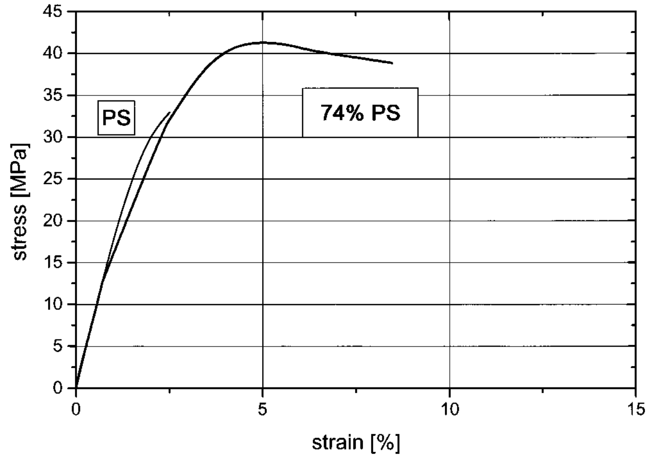

Figure 2. Stress–strain curves for pure polystyrene (M_w = 315 kg/mol) and SBM74 (Φ_{PS} = 0.74, M_n = 463 kg/mol).

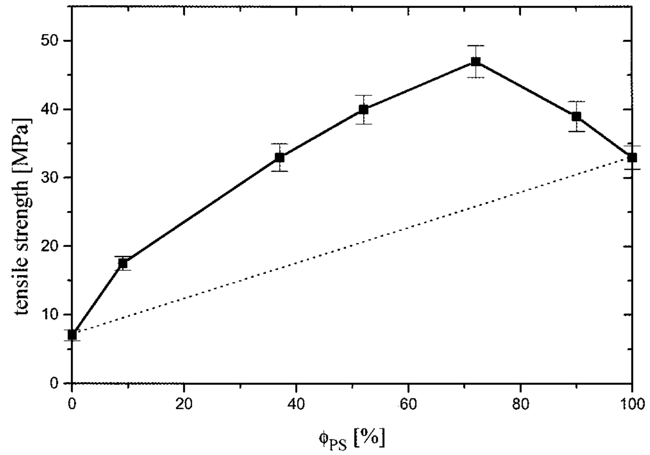

Figure 3. Dependence of the tensile strength on the volume fraction Φ_{PS} for triblock copolymers PnBMA-*b*-PS-*b*-PnBMA measured at a strain rate of $\dot{\epsilon}$ = 1.6 × 10^{-4} s^{-1}.

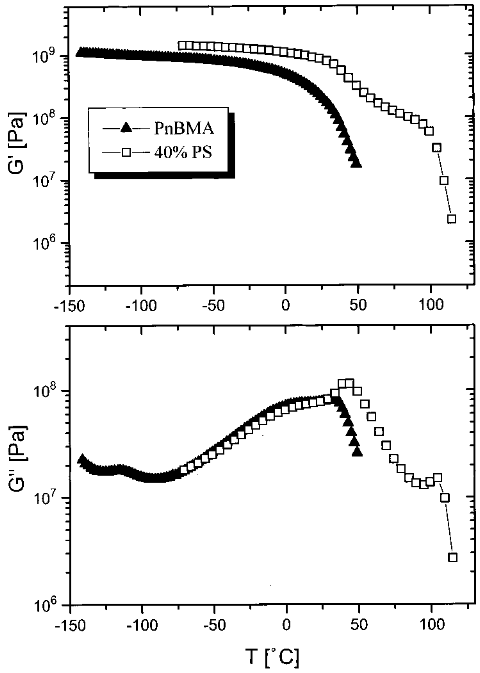

Figure 4. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for SBM40 (Φ_{PS} = 0.40, M_n = 212 kg/mol) and pure PBMA (M_w = 363 kg/mol) measured at a frequency of 1 Hz.

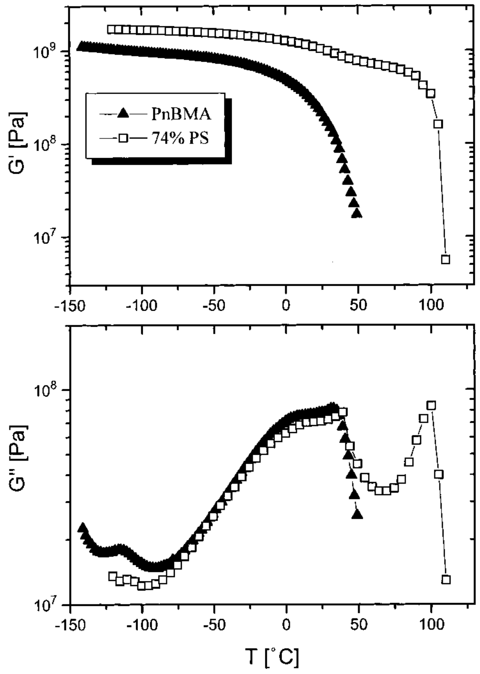

Figure 5. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for SBM74 (Φ_{PS} = 0.74, M_n = 463 kg/mol) and pure PBMA measured at a frequency of 1 Hz.

leads to the conclusion that an increasing PBMA content can lead to an increasing toughness and strength combined with high stiffness (Young's modulus). This result is not to be expected for polymer blends or rubber modified polymers, which in most cases contrary to our findings show a decreasing strength and stiffness for an increasing rubber content.

For the triblock copolymers the tensile strength is also strongly increased with increasing polystyrene content (Figure 3). Here already triblock copolymers with a polystyrene content of 37% PS show a similar tensile strength as polystyrene. At ϕ_{PS} = 0.72 a maximum of tensile strength is found, which is also significantly higher than that of polystyrene.

These results indicate that for triblock copolymers the synergetic effect of tensile strength exists over a wider range than for diblock copolymers. It is surprising that the triblock copolymers with a polystyrene middle block can show such a high strength, because for example, the tensile strength of PS-*b*-PB diblock copolymers or PB-*b*-PS-*b*-PB triblock copolymers with 30% polybutadiene content is markedly smaller (typically about 20 MPa).

Presently we can only speculate on the possible reasons for these observations. First the synergetic effect causing the strength in these diblock and triblock copolymers may be due to a partial miscibility between PS and PBMA. Dynamic-mechanical analysis indicates a partial miscibility of the components, which can be expected to be only weakly incompatible.[17] In the case of strong segregated block copolymers, which form a sharp interface between the blocks, neat phases are expected. However for PS-*b*-PBMA diblock copolymers, only the glass transition temperature (T_g) of the PBMA block is shifted to higher temperatures, whereas the glass transition temperature of the PS block remains approximately at 100 °C. This is shown in Figures 4 and 5 for two unsymmetrical diblock copolymers. For both samples the glass transition temperature of the PBMA block is higher than that of pure PBMA. The glass transition temperature of PBMA is 31 °C at a frequency of 1 Hz. In contrast, the glass transition temperature of the PBMA block for sample SBM40 (212 kg/mol, 40% PS) is shifted to 43 °C, and for sample SBM74 (463 kg/mol, 74% PS) it is shifted to 39 °C. The glass transition temperature of the PS-block is approximately 100 °C for both samples. To explain this phenomenon we may to assume an asymmetrical phase diagram for PS-*b*-PBMA diblock copolymers. In this case an asymmetric phase composition is expected, and an essentially pure polystyrene matrix phase and a PS/PBMA mixed phase may exist. This asymmetry of phase composition could have a pronounced effect on mechanical properties.

As a second reason for the observed synergism the influence of the interface between phases should be considered. Classical examples of blends with improved mechanical properties are PS/PPO homopolymer blends, where the synergetic effect is explained qualitatively by a contraction of free volume in the blend[14] as a consequence of energetic interactions during mixing. In rubber-modified polymers a multiple crazing mechanism was found,[15] which is the reason for an improvement of toughness compared to the homopolymers. Finally, for polymer alloys, biphasic structures can lead to an improvement of toughness. In this case, the spinodal decomposition structure provides improved energy dissipation between the dispersed phase and the matrix polymer due to the interconnected network structure.[16] Generally, the particle size and interparticle distance are important criteria for toughness enhancement which for copolymers are controlled by composition, chain architecture, and thermal history. Therefore, in our case a complex correlation between microphase separation, morphology, and deformation processes would be expected.

In a first test experiment the width of the interface between PS and PBMA phases of a PS-*b*-PBMA diblock copolymer was measured by neutron reflection, confirming our assumption of a partial miscibility of PS-*b*-PBMA diblock copolymers and a broadening of the interface width of the copolymer as compared to other block copolymers.[13] The influence of the interface on mechanical properties is still under discussions and needs further investigations.

Further, a correlation between formed morphologies and deformation processes of this block copolymer system have to be considered, which, however, will be described elsewhere.[12] Our previous investigations[11] have been shown, that in the case of PS-*b*-PBMA diblock copolymers reported in this study, ordered morphologies with spherical, hexagonal, and lamellar structures exist depending on the PS-block length. More detailed investigations showed the existence of a perforated lamellar structure (HPL) and bicontinuous structures and a coexistence of lamellae and hexagonally packed cylinders. The complex morphology for diblock copolymers at a polystyrene content of 74% PS, which displays a coexistence of lamellar and hexagonal rodlike structures, can be discussed as one reason for the improved mechanical properties compared to that of pure PS.[11,12] This unexpected morphology, comparing with poly(styrene-*b*-isoprene) diblock copolymers, which show hexagonally packed cylinders at the same composition, may due to the asymmetry of the phase diagram of poly(styrene-*b*-butyl methacrylate) diblock copolymers.

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