Mechanical Properties of Weakly Segregated Block Copolymers. 3. Influence of Strain Rate and Temperature on Tensile Properties of Poly(styrene-*b*-butyl methacrylate) Diblock Copolymers with Different Morphologies

R. Weidisch,*,† M. Stamm,† G. H. Michler,‡ H. Fischer,§ and R. Jérôme⊥

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany;
Martin-Luther-Universität Halle-Wittenberg, Institut für Werkstoffwissenschaft,
D-06099 Halle, Germany; TNO Institute of Applied Physics, P.O. Box 595, Eindhoven,
The Netherlands; and Center for Education and Research on Macromolecules,
University of Liège, SartTilman B6, B-4000 Liège, Belgium

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ABSTRACT: Poly(styrene-*b*-butyl methacrylate) diblock copolymers, PS-*b*-PBMA, with different morphologies are investigated with respect to the influence of strain rate and temperature on tensile properties. In the first part the mechanical properties of bicontinuous and perforated lamellar structure are compared with other morphologies. Diblock copolymers with bicontinuous structures (39% PS) show a much higher tensile strength as well as a higher strain at break than diblock copolymers with lamellar structures (50% PS). In the second part the dependence of tensile properties on strain rate and temperature are discussed for different morphologies. A diblock copolymer with a polystyrene content of 76% PS reveals hexagonally packed PBMA−cylinder, and the tensile strength, strain at break, and Young's modulus exceed the values of pure polystyrene at all measured strain rates. The interesting properties of PS-*b*-PBMA diblock copolymers are discussed with respect to the phase behavior, interface formation, and chain conformation.

Introduction

The investigations of polymer blends during several decades have shown that mechanical properties can be improved in the case of strong interfacial adhesion between the components and by adding small amounts of elastomers. Rubber toughening has proved so effective that the technology has been extended to almost all commercial glassy thermoplastics.[1,2] Immiscible polymer blends show in later stages of phase separation macrophase separated structures, which often lead to a deterioation of mechanical properties due the immiscibility of the components. In block copolymers, on the other hand, microphase separated morphologies at a size scale of typically 10−100 nm can be observed.[3] In several investigations the existence of different ordered structures including BCC spheres, hexagonally packed cylinder (HEX), ordered bicontinuous double diamond (OBDD), cubic bicontinuous ("gyroid"), lamellar, and perforated lamellar structures (HPL) has been reported.[4−7] It was shown that block copolymers, for example poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers (SBS), can show improved mechanical properties as compared to SB diblock copolymers. SBS triblock copolymers are one example for thermoplastic elastomers (TPE) which are well-known for unique thermomechanical properties associated with a phase morphology of PS domains dispersed in a continuous rubbery PB matrix. In such TPE's the mechanical performance of vulcanized rubbers is combined with the straightforward processing of thermoplastics due to the physical network of the flexible chains.[8] However, special attention has been paid to poly(alkyl methacrylate)s as candidates for the outer blocks.[9] In contrast to SBS triblock copolymers, SB diblock copolymers show only a small tensile strength due to the absence of the bridged midblock conformation which is believed to be important for SBS triblock copolymers.

Russell et al.[34,35] have found a microphase separation of poly(styrene-*b*−*n*-butyl methacrylate), PS-*b*-PBMA, diblock copolymer melts on heating. SAXS experiments seem to indicate the existence of both an upper critical order transition (UCOT) and a lower critical order transition (LCOT).[34]

In our previous papers[10,11] we have shown that the tensile strength for poly(styrene-*b*-butyl methacrylate) diblock copolymers (PS-*b*-PBMA) in the composition range between 70% and 80% PS exceeds markedly the value of pure PS. Especially, for a block copolymer with 74% PS it was observed that not only the tensile strength but also the strain at break is higher than that of pure PS. It is surprising that already diblock copolymers can show such good mechanical properties which can be attributed to the influence of the microphase separated morphologies in block copolymers on deformation mechanisms.[13]

Whereas in our previous studies the influence of morphologies, phase behavior, and molecular weight on mechanical properties was discussed,[11,12] in the present study the influence of different morphologies including the bicontinuous structure, strain rate, and temperature on tensile properties of PS-*b*-PBMA diblock copolymers will be presented.

Experimental Section

Polymerization−General Procedure. All polymerizations were carried out in carefully flamed glass reactors in THF

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† Max-Planck-Institut für Polymerforschung.
‡ Martin-Luther-Universität Halle-Wittenberg.
§ TNO Institute of Applied Physics.
⊥ University of Liège.
* Corresponding author.

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Table 1. Characterization Data of Samples: Molecular Weight (M_n), Volume Fraction (Φ_{PS}), and Polydispersity (M_w/M_n), χN Values at 120 °C (Determined from Eq 2) for PS-*b*-PBMA Diblock Copolymers Used in This Study

sample	M_n [kg/mol][a] (M_w/M_n)	Φ_{PS}[b] block	morphology (TEM)	χN
PBMA	285.0 (1.03)	0		
SBM 15	406.8 (1.05)	0.15	PS spheres	38.3
SBM 25	277.0 (1.05)	0.23	PS cylinder	27.0
SBM 30	278.0 (1.06)	0.30	PS cylinder	27.5
SBM 35	270.0 (1.08)	0.35	PS cylinder	27.2
SBM 39	254.0 (1.05)	0.39	bicontinuous	25.9
SBM 40	212.1(1.05)	0.40	perforated lamellae	21.7
SBM 50	278.0 (1.07)	0.51	lamellae	29.5
SBM 70	286.0 (1.05)	0.70	lamellae	32.1
SBM 72	426.0 (1.04)	0.72	lamellae/PBMA cylinder	48.1
SBM 74	463.0 (1.03)	0.74	lamellae/PBMA cylinder	52.6
SBM 76	459.0 (1.09)	0.76	PBMA cylinder	52.4
SBM 83	383.1 (1.04)	0.83	PBMA spheres	44.6
PS	315.0 (1.02)	1		

[a] Total molecular weight and polydispersity determined by size exclusion chromatography (SEC); values are based on the PS standards. [b] Volume fraction of PS determined by ^1H NMR.

as the solvent at − 78 °C under an argon atmosphere using syringe techniques. After several cycles of degassing from calcium hydride, the styrene was introduced into the reactors by condensation under reduced pressure. THF was condensed from oligomeric polystyrene anions. Then the desired amount of initiator was added at once, and after 15 min the living polystyrene anions were end-capped with diphenylethylene. Butyl methacrylate as the second monomer was added dropwise very slowly by syringe. The polymerization was terminated by adding methanol after another 30 min. Then the polymer obtained was precipitated in a 7/3 methanol/water mixture at −30 °C, washed, and dried in a vacuum for several days.

The molecular weights, dispersities, volume fractions, and morphologies of all used PS-*b*-PBMA diblock copolymers were determined by size-exclusion chromatography (SEC), ^1H NMR, and transmission electron microscopy (TEM), respectively. Furthermore, in Table 1 are given the values of χN for each sample.

Sample Preparation. 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.

Measurements. SEC measurements were carried out using a Knauer-GPC with a RI/Visco-detector and a polystyrene standard linear column.

Ultrathin sections (50 nm) were cut at room temperature using glass knives in a Ultramicrotome (Reichert). The polystrene blocks of some diblock copolymers (see Figures 2 and 3) were stained with RuO_4 vapor. TEM investigations were performed with a BS500 microscope operated at 90 kV.

Tensile tests were performed using a universal testing machine (Zwick 1425) at different strain rates and temperatures. For each temperature and strain rate at least 10 samples were measured in order to avoid preparation effects. The tensile bars had a thickness of 0.5 mm and a total length of 50 mm. The toughness of the diblock copolymers was estimated as absorbed energy from the stress−strain curves.

Mechanical Properties of Diblock Copolymers with Different Morphologies

To investigate the influence of microphase separated morphologies of PS-*b*-PBMA diblock copolymers on the mechanical properties, diblock copolymers with different compositions were used (Table 1).

Our previous investigations[14] have shown that PS-*b*-PBMA diblock copolymers with high molecular weights (M_n > 200 kg/mol) show spherical, hexagonal, and lamellar structures depending on the PS block length. For diblock copolymers with 72% and 74% PS a coexistence of regions with lamellae and hexagonally packed cylinders (LAM/HEX) was observed.[11] The TEM picture in Figure 1 gives an example and indicates a coexistence of ordered areas of lamellae (LAM) and hexagonally packed cylinders (HEX), where parts of the sample are cut parallel and perpendicular through the PBMA cylinders and other parts are cut through the lamellae. This structure cannot be expected from Leibler's theory,[33] which is based on equal Kuhn segment length and volume of the respective homopolymers. However, in the case of PS-*b*-PBMA diblock copolymers the segment length and monomer volume of PS and PBMA are different. Furthermore, in the weak segregation limit (WSL) and intermediate segregation regime (ISR) the differences of the free energies for different structures are very small, which makes it difficult to achieve the equilibrium morphology for samples with high molecular weights. Very long annealing times (about 1 week at a temperature of 150 °C) also resulted in the structure as shown in Figure 1.

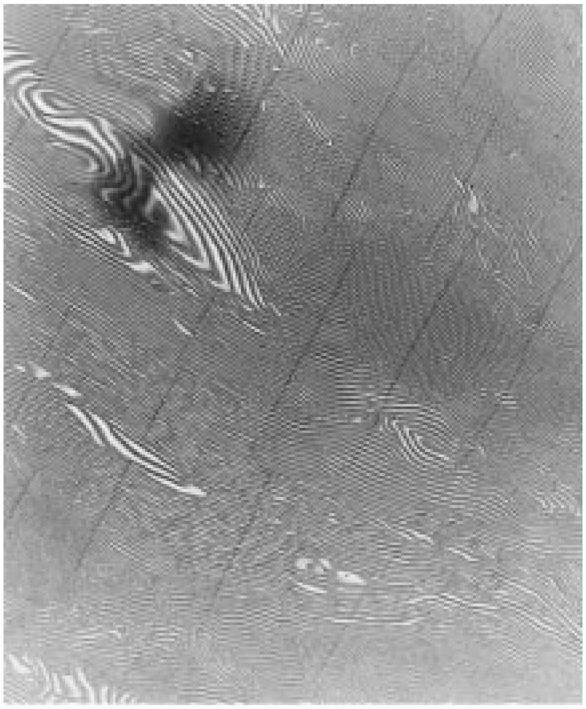

Figure 1. TEM micrograph of SBM72 ($\Phi_{PS} = 0.72$, $M_n = 426$ kg/mol) with ordered areas of lamellar structures and hexagonally packed PBMA cylinders (stained with RuO_4).

A further increase of PS content up to 76% leads to a morphological change into hexagonally packed PBMA cylinders shown in Figure 2. Sufficient contrast for the TEM investigation was achieved by staining the polystyrene blocks with ruthenium tetroxide (RuO_4) at 23 °C for 10−15 min. It was shown for other block copolymers that the interface thickness can be estimated from TEM images using staining with RuO_4, if a short staining time of about 5 min[36] is used instead of 30−45 min as described elsewhere.[37,38] In Figure 2 between the PS matrix and the light PBMA cylinder the interface can be recognized as a dark line. Possible reasons for the preferential staining of the interface between the phases may be seen in a better accessibility of PS chains surrounded by PnBMA and an enhancement of the reactivity of those chains for RuO_4 due to strain in the interfacial region.[36] From an analysis of

Figure 2. TEM micrograph of SBM76 ($\Phi_{PS} = 0.76$, $M_n = 459$ kg/mol) with hexagonally packed PBMA cylinders (stained with RuO_4). The dark annular ring between the gray PS matrix and the light PBMA cylinders correspond to the interface.

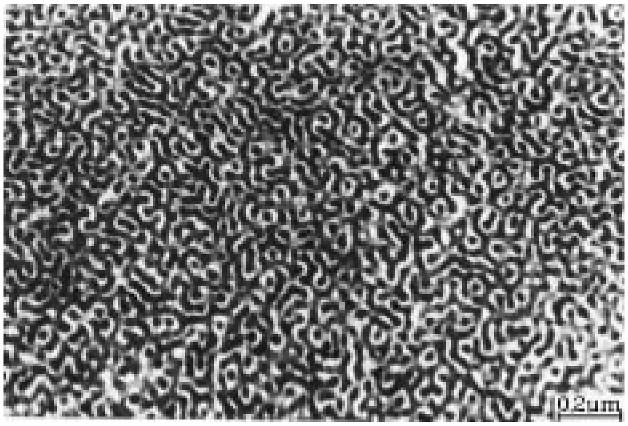

Figure 3. TEM micrograph of SBM39 ($\Phi_{PS} = 0.39$, $M_n = 254$ kg/mol) with bicontinuous structure (stained with RuO_4).

the width of those dark lines we obtain an interface thickness of about 10 ± 2 nm, which is relatively large as compared to other block copolymer systems reported in the literature.[39,40] It was shown previously for a PS-*b*-PBMA diblock copolymer with lamellar structure that the interface width observed by TEM yields comparable values as compared to the interface width obtained by neutron reflectometry.[23] Spherical structures were observed at a PS content of 83%.[14] This indicates that the composition range of the hexagonal structure on the PS-rich side of the phase diagram is smaller than for PS-*b*-PI diblock copolymers. In the composition range 30−40% hexagonally packed PS cylinders (HEX) are observed, perforated lamellar structure (HPL) is present at a PS content of 40%,[11] and bicontinuous structures (Figures 3 and 4) were found at a PS content of 39% PS. The morphology shown in Figure 3 is complex, although reminiscent of a gyroid structure. This structure appears to be bicontinuous, but the details can be only obtained from scattering methods. In Figure 4 one example of the morphology consisting of perforated lamellae of PS is shown. It is obvious that parts of the sample are cut perpendicular through the perforated lamellae and other parts are cut through the lamella plane. In both directions the holes in the stained PS layers are visible. HPL or bicontinuous structures were not observed for high PS contents, which indicates the existence of an asymmetrical phase diagram for PS-*b*-PBMA diblock copolymers.

Figure 4. TEM micrograph of SBM40 ($\Phi_{PS} = 0.40$, $M_n = 212$ kg/mol) with perforated lamellae of PS (stained with RuO_4).

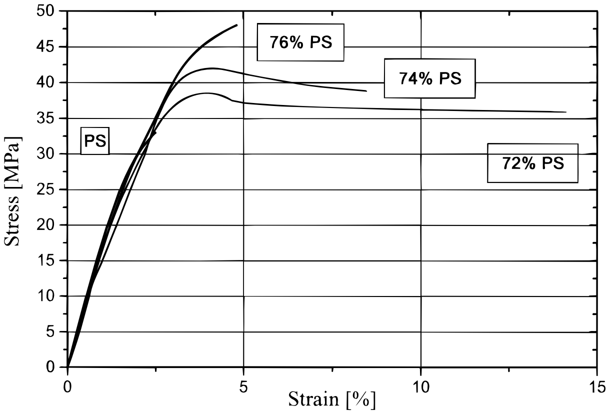

Figure 5. Stress−strain curves for diblock copolymers in the composition range between 72% and 76% PS and pure PS (M_w = 315 kg/mol) at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}$ s^{-1}.

We find for a diblock copolymer with 76% PS a tensile strength which is about 40% higher than that of pure PS.[10] In the composition range between 72% and 76% PS not only a higher tensile strength but also a larger strain at break as compared to pure PS was observed (Figure 5). Sample SBM70 with 70% PS reveals a lamellar structure, and the tensile strength is almost the same as that of pure PS. The strain at break is much larger than that of block copolymers in the composition range 72−76% PS and of pure PS (Figure 6). For sample SBM72 with 72% PS the mechanical properties are strongly altered compared to those of sample SBM70 with 70% PS (Figure 6). This can be attributed to the change from lamellar structures (SBM70) to LAM/HEX structures (SBM72) where a matrix of polystyrene is present. At the transition LAM/HEX → HEX at a PS content of 76% the strain at break decreases, and the block copolymers become brittle. This transition is also connected with a further increase of tensile strength, which shows a maximum for hexagonal packed PBMA

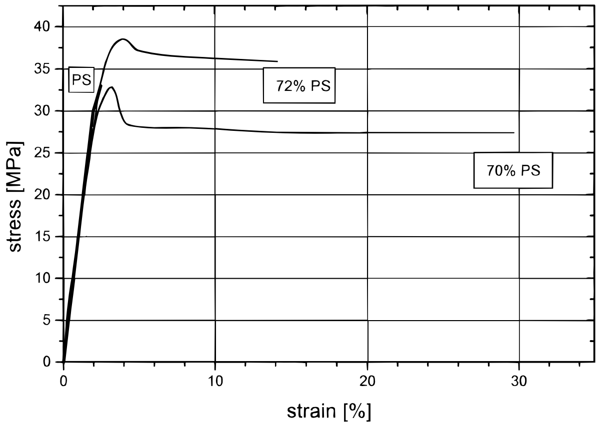

Figure 6. Stress−strain curves for SBM70 ($\Phi_{PS} = 0.70$, $M_n = 286$ kg/mol), SBM72 ($\Phi_{PS} = 0.72$, $M_n = 426$ kg/mol), and pure PS ($M_w = 315$ kg/mol) at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}$ s^{-1}.

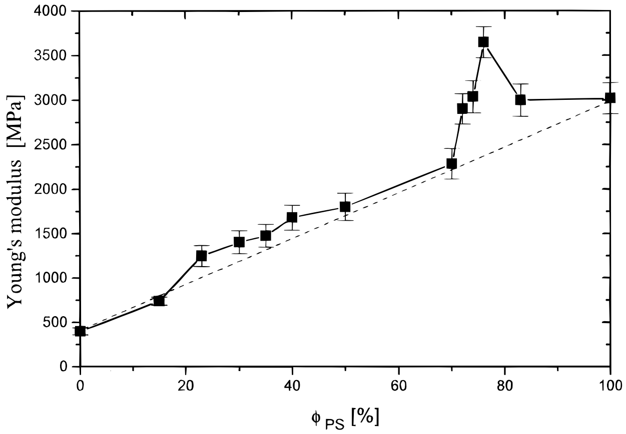

Figure 7. Depencence of Young's modulus on volume fraction of PS.

cylinders at 76% PS (sample SBM76, Figure 5). Furthermore, the Young's modulus at this composition as indicated by the slope of the stress−strain curves at small strain shows a higher value than for pure PS. In Figure 7 the Young's modulus shows a maximum for LAM/HEX and HEX structures in the composition range 72−76% PS. These samples possess a PS matrix in contrast to the lamellar structures, which seems to enhance the stiffness and tensile strength. For block copolymers with 83% PS the Young's modulus decreases and shows almost the same value as that of pure PS. This means that for hexagonally packed cylinders at 76% PS the important properties such as tensile strength, stiffness (Young's modulus), and strain at break are significantly improved as compared to that of pure PS. For block copolymers with spherical structures at a PS content of 83% PS not only the Young's modulus but also the tensile strength decreases, and the properties are almost like polystyrene.[11]

Many authors have reported the existence of perforated lamellar and bicontinuous structures in block copolymer systems.[6,7] It is interesting to investigate the correlation between those morphologies and mechanical properties because especially for bicontinuous structures improved mechanical properties may be expect due to their high storage modulus.[26] In Figure 8 the mechanical properties of block copolymers in the composition range 30−50% PS are shown. Diblock copolymers with 39% PS reveal a bicontinuous structure and show not only a higher strain at break but also a much higher stiffness and tensile strength than a diblock copolymer with lamellar structure (50% PS). While the tensile strength and Young's modulus for sample SBM35 (35% PS) with hexagonally packed PS cylinders are markedly smaller than that of block copolymers with bicontinuous structures, their strain at break is much higher (Figure 8). One may conclude that for PS-*b*-PBMA diblock copolymers with hexagonally packed PS cylinders (SBM 35) the presence of a PBMA matrix leads to a more homogeneous deformation. This is connected with a decrease of tensile strength due to the lower cavitation stress of PBMA compared to that of pure PS. Perforated lamellar structures (40% PS) show intermediate mechanical properties. The perforated lamellar structure shows a higher strain at break but a lower stiffness and tensile strength.

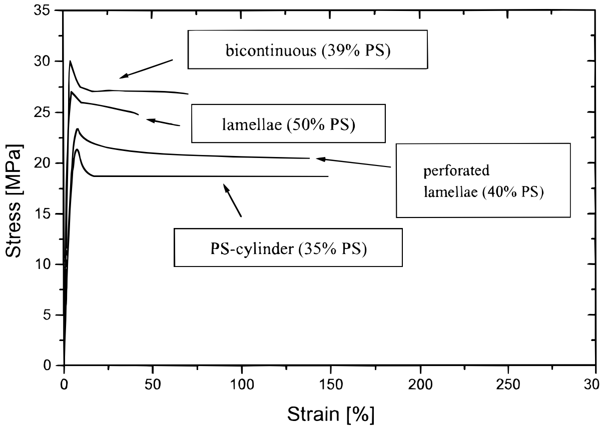

Figure 8. Stress−strain curves for diblock copolymers with different morphologies and pure PS ($M_w = 315$ kg/mol) at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}$ s^{-1}.

For PS-*b*-PBMA diblock copolymers with bicontinuous structures (sample SBM39, 39% PS), the important tensile properties such as tensile strength, Young's modulus, and strain at break are improved as compared to those of a diblock copolymer with about 10% higher PS content (sample SBM 50, lamellar structure). Our investigations have shown that the perforated lamellar structure and hexagonally packed PS cylinder are more effective for an enhancement of toughness than lamellar structures. In contrast, the bicontinuous structure is very effective for an enhancement of tensile strength and stiffness.

Influence of Strain Rate and Temperature on Tensile Properties. Whereas in our previous papers[11,12] the mechanical properties were discussed for small strain rates, in the following investigations the mechanical properties will be discussed also as a function of strain rate and temperature. The mechanical properties at higher strain rates are quite important for practical applications.

In Figure 9, the yield stresses of both homopolymers and three diblock copolymers are given as a function of strain rate. In all cases a linear dependence was found. The yield stress of PBMA shows a steeper increase with increasing strain rate than PS due to the proximity of the glass transition temperature of PBMA ($T_g = 31$ °C at $\omega = 1$ Hz) to the measurement temperature. At low strain rates PBMA is ductile and becomes brittle at very high strain rates, showing the behavior of a glassy polymer. For diblock copolymers with a PBMA matrix the yield stress shows almost the same dependence on strain rate as that of PBMA. At higher PS contents, the

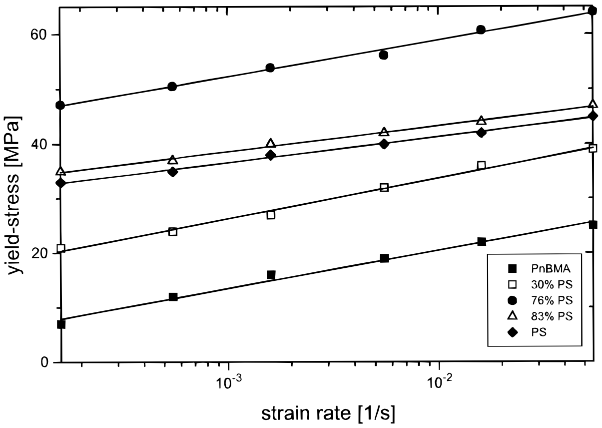

Figure 9. Dependence of yield stress on strain rate for different diblock copolymers and pure PS and PBMA.

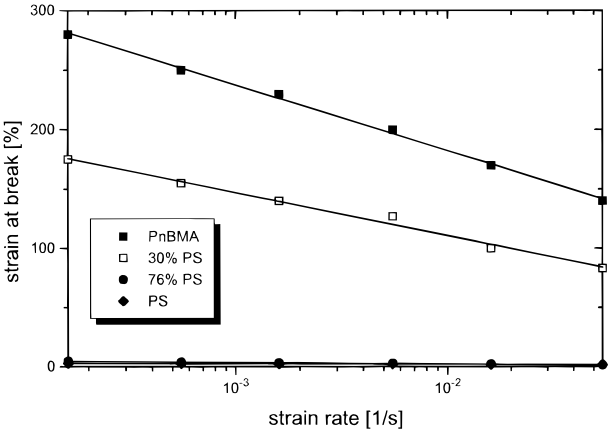

Figure 10. Dependence of strain at break on strain rate for PS-*b*-PBMA diblock copolymers with different compositions and for pure PS and PBMA.

yield stress reveals another dependence. Only for diblock copolymers with 83% PS is the dependence of yield stress on strain rate almost the same as for PS.

The result that the yield stress increased with increasing strain rate for all materials is consistent with the Eyring theory of thermally activated rate processes.[29] Assuming sufficiently high stress, the corresponding Arrhenius equation for the yield stress, σ_y, is given as

$$\frac{\sigma_y}{T} = \frac{\Delta H}{vT} + \frac{R}{v} \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0} \tag{1}$$

where ΔH is the activation energy per mole, v the activation volume per mole, R the molar gas constant, T the temperature, $\dot{\epsilon}$ the strain rate, and $\dot{\epsilon}_0$ a constant.

A linear dependence of the activation volume with PS content, as found for several polymer blends,[30] was not observed. The reason for this difference could be that the block copolymers form different microphase separated structures in contrast to the amorphous homopolymers PS and PBMA. As expected, the strain at break decreases with increasing strain rates (Figure 10). It strongly decreases even stronger as compared to the case of rubber toughened polymers due to the proximity of the glass transition temperature of PBMA to room temperature, at which the measurements were performed. For diblock copolymers in the composition range 70−80% still a different dependency of yield stress on strain rate exists (Figure 9) than observed for the homopolymers (PS and PBMA) and diblock copolymers at a PS content of 83% (sample SBM83). This confirms our previous observations at small strain rates that spherical structures at 83% PS show almost the same properties as those of pure PS.[11,28] In contrast, block copolymers with LAM/HEX (samples SBM72 and SBM74) and HEX (sample SBM76) structures show improved mechanical properties at all measured strain rates compared to those of pure PS. For example, the tensile strength for a block copolymer with 72% PS increased up to 68 MPa at a strain rate of $\dot{\epsilon} = 5.5 \times 10^{-2}$ s^{-1}, which is about 50% higher than that of pure PS at the same strain rate (Figure 11).

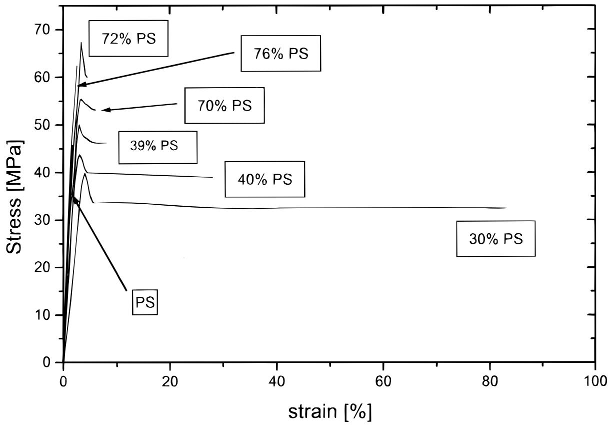

Figure 11. Stress−strain curves for diblock copolymers depending on volume fraction of PS at a strain rate of $\dot{\epsilon} = 5.5 \times 10^{-2}$ s^{-1}.

As already shown in Figure 5, the tensile strength also exceeds the value of pure PS at small strain rates, which means that the synergistic effect on tensile strength is clearly attributed to phase behavior and interface formation and does not depend on strain rate.

In contrast to the properties at lower strain rates, the maximal tensile strength was observed already at a PS content of 72% (sample SBM72; LAM/HEX) due to the premature failure of block copolymers with 76% PS (Figures 5 and 11). This means that the maximum of tensile strength is shifted to higher PBMA contents with increasing strain rates, which is similarly true for rubber toughened polymers where the toughness values decrease at very high strain rates.[2]

As shown in Figure 11, for sample SBM30 (30% PS) an interesting property profile was observed. The strain at break extends to about 80%, which is much higher than with all the other samples, and the tensile strength is only about 10% smaller than that of pure PS. This can be due to the steep increase of yield stress of samples with PBMA matrix with increasing strain rate. A morphology consisting of hexagonally packed PS cylinders (sample SBM30) thus seems to be very effective for a combination of a high tensile strength and toughness. Diblock copolymers with bicontinuous structures show a much steeper increase of yield stress with increasing strain rates than observed for other morphologies. This leads to a tensile strength at high strain rates which is even higher than that of pure PS, which is a surprising result if one takes into account that the PS content of sample SBM39 is only 39%. Whereas the tensile strength of sample SBM35 (hexagonally packed PS cylinders; HEX) and SBM40 (HPL) is smaller than that of pure PS and SBM39 (39% PS; bicontinuous) at all measured strain rates, their strain at break is much

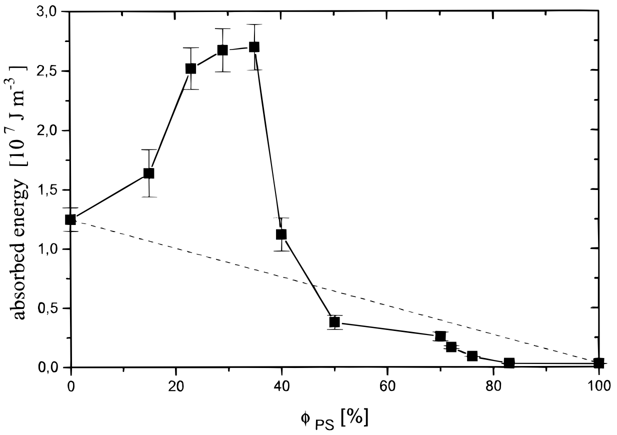

Figure 12. Dependence of absorbed energy on volume fraction of PS at a strain rate of $\dot{\epsilon} = 5.5 \times 10^{-2}\ \mathrm{s}^{-1}$.

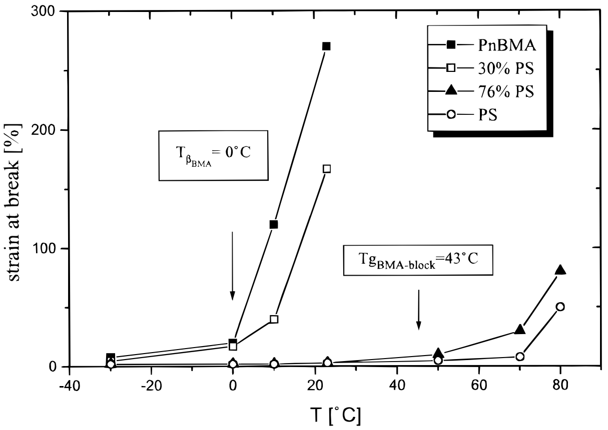

Figure 13. Dependence of the strain at break on temperature for diblock copolymers with different compositions and for pure PS and PBMA at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}\ \mathrm{s}^{-1}$.

higher than that of block copolymers with bicontinuous structures (SBM 39).

The absorbed energy, estimated from stress–strain curves, shows a maximum at 35% PS (Figure 12). At this composition hexagonally packed PS cylinders were found by TEM, confirming our previous observation at small strain rates that this morphology is responsible for improved toughness as compared to pure homopolymers of PS and PBMA.[11] A sharp decrease of absorbed energy occurs for perforated lamellae at 40% PS. Lamellar structures show a small absorbed energy (toughness) as compared to the morphologies in the composition range 25–40% PS. The generally higher absorbed energy of samples with hexagonally packed PS cylinders (25–35% PS) compared to that of perforated lamellar structures (HPL, 40% PS) may be attributed to a change of the deformation mechanism. For SBS triblock copolymers with hexagonally packed PS cylinder large deformations of the PS cylinder in the PB matrix are found which are responsible for their enhanced strength.[45,46]

In Figures 13 and 14 the influence of temperature on mechanical properties of block copolymers with different morphologies is shown. Due to the proximity of the glass transition temperature (T_g) of PBMA to room temperature, the tensile properties show a steeper dependence on temperature than usually observed for rubber toughened polymer. The properties of PBMA are strongly altered in the proximity of the glass transition at 31 °C due to the increased mobility of chains close to T_g. For temperatures smaller than −20 °C PBMA becomes brittle (Figures 13 and 14). The tensile strength of block copolymers shows a steep decrease, which is shifted by about 10 K to higher temperatures than observed for pure PBMA (Figure 14). This is attributed to the increased T_g of the PBMA-rich phase compared to that of pure PBMA due to the partial miscibility of PS and PBMA.[11] Also, the strain at break is strongly altered near T_g of the PBMA-rich phase (Figure 13). This means that the dependence of tensile properties on temperature for the block copolymers can be related to their dynamic–mechanical behavior. For diblock copolymers with LAM/HEX (72–74% PS) and HEX (76% PS) structures the tensile strength exceeds the value of pure PS also for higher temperatures up to about 70 °C. This means that LAM/HEX and HEX structures are also effective at higher temperatures due to different deformation mechanism as compared to those of pure PS.

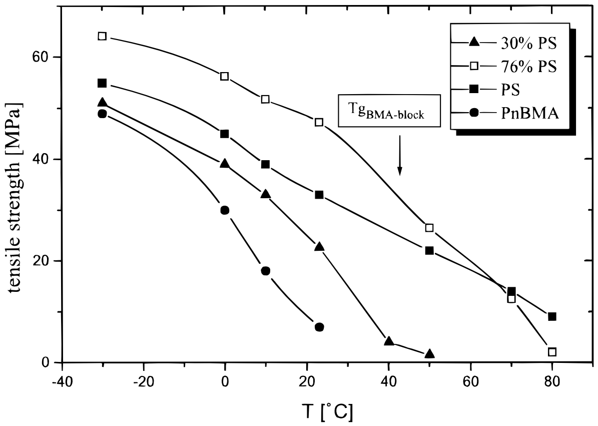

Figure 14. Dependence of the tensile strength on temperature for diblock copolymers with different compositions and for pure PS and PBMA at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4}\ \mathrm{s}^{-1}$.

Discussion

It was shown for rubber toughened polymers that different morphologies of those polymers can lead to improved mechanical properties due to different deformation mechanism as compared to those of homopolymers.[16] The mechanical properties of rubber toughened polymers as well as of polymer blends are strongly influenced by phase behavior and morphology (shape, size, and volume fraction of the dispersed phase). In rubber toughened polymers three principal deformation mechanisms are reported, which involve shear yielding, crazing, and rubber particle cavitation.[17–19] For polymer blends in some cases synergistic effects on tensile properties have been observed. Kim et al.[20] observed improved toughness and strength for ternary blends of ABS/PMMA/PC. This can be attributed to the preferential arrangement of the PMMA phase between the PC and SAN phases and an encapsulation of the dispersed PC phase. In this case, the higher interfacial adhesion between PC and PMMA causes the improved mechanical properties of this ternary blend. Generally, synergetic effects on tensile properties can be observed in miscible or partially miscible polymer blends.[21] For semicrystalline polymer blends synergetic effects on tensile properties are attributed to the reduced average spherulite size, the increased overall crystallinity, and the formation of intercrystalline links.[22]

In polymer blends interconnected structures can show improved mechanical properties compared to those of blends with dispersed morphologies. In those cases, the spinodal decomposition structure provides improved energy dissipation between dispersed phase and polymer matrix due to an interconnected network structure.[27] Comparing interconnected structures in polymer blends with bicontinuous structures in block copolymers, we can conclude that the enhanced energy dissipation between the phases should be responsible for their improved properties. Stress concentration at the PS-rich phase of the bicontinuous structure could lead to a large plastic deformation of this phase, which can enhance the tensile strength.

Whereas many incompatible polymer blends show a deterioration of mechanical properties due their weak interfacial adhesion, in block copolymers the properties are much better since the homopolymers are chemically coupled in the interfacial region.[1,2,8,17] In the case of PS-*b*-PBMA diblock copolymers the interface width is relatively broad due to the partial miscibility,[14,23] which has a pronounced influence on mechanical properties. In one of our previous papers[23] it was shown that a symmetrical diblock copolymer with a molecular weight of 248 300 g/mol possesses an interface width of 8.4 ± 0.2 nm at 151 °C, which is markedly larger than observed for poly(styrene-*b*-isoprene) diblock copolymers (PS-*b*-PI). The investigations of Bühler[32] have shown that a broadened interface in block copolymers can enhance the tensile strength, which is in accordance with our results. Usually one can assume that in the interfacial region a larger amount of defects results in a low interfacial strength. For diblock copolymers chain ends are localized preferentially in the middle of the respective components, and the chemically coupled chains in the interfacial region can enhance the strength as compared to the case of blends. It was shown by Bühler and Gronski[41] for block copolymers that an increasing interface width leads to an decreasing interfacial energy. This is connected with a decreasing stress concentration at the interface which is responsible for the increase of tensile strength. The total free energy of block copolymers in the strong segregation limit (SSL) is considered by two contributions—first the interfacial energy and second the contribution from the stretching of the chains that arises from the incompatibility of the components. Within the weak segregation limit (WSL) the microscopic density profile of the components is considered to vary sinusoidally in space, and the chains of the components are highly interpenetrating. It was shown by various authors that between the weak and strong segregation limits an intermediate segregation regime (ISR) between $12.5 < \chi N < 95$ can be indentified (crossover between ISR and SSL at $\chi N \approx 50$[42]), where the chains are stretched due to the coarsening of the density profile as χN is increased from the WSL.[43] The interface is broadened, and the junction points are not completely localized in the interfacial region. The χ parameter of PS-*b*-PBMA was determined for a partially deuterated block copolymer to $\chi = 0.0127 \pm 0.001$ at 120 °C, at which the samples were annealed.[48] Table 1 gives the value of χN for different samples. For sample SBM50 (50% PS) the value of χN is about 29, which means that this sample is in the intermediate segregation regime. In contrast, for sample SBM76, which shows the largest tensile strength, the value of χN is about 52. We can assume that samples with asymmetrical compositions are also intermediately segregated because for those compositions the value of $(\chi N)_{\text{critical}}$ increases as compared to that for symmetrical compositions.

This means that all investigated samples in this study are intermediately segregated, which is confirmed by the measured high value of the interface width.[23] As recently described elsewhere, the temperature dependence of χ for PS-*b*-PBMA diblock copolymers is relatively small and can be described as[48]

$$\chi = (0.0243 \pm 0.0004) - (4.56 \pm 0.169)/T \qquad (2)$$

This leads us to the conclusion that the PS-*b*-PBMA diblock copolymers used in this study are also intermediately segregated at other investigated temperatures. In contrast, block copolymers with molecular weights of about 130 kg/mol are weakly segregated, where it is interesting to investigate the influence of the state of order (WSL or disordered) on mechanical properties.[12] It should be kept in mind that deuteration also changes the thermodynamics slightly if we compare deuterated and nondeuterated samples. This effect is believed to be relatively small, and we assume that it is not important for our discussions. Furthermore, χ also could show a dependence on composition, which, however, is also not included in our discussion.

Block copolymers generally show different deformation mechanisms as compared to those for homopolymers, because the microphase separated morphologies in the nanometer scale are too small to initiate crazes.[24] The investigation of Argon and co-workers shows[25] that in PS-*b*-PB diblock copolymers a cavitation mechanism can be observed for different morphologies. More recently, the deformation of block copolymers with cylindrical, spherical, and lamellar structures was studied.[44−46] Polis and Winey observed kink band formation in poly(styrene-*b*-ethylene propylene) diblock copolymers by applying steady shear strain.[47] For PS-*b*-PBMA diblock copolymers we observe narrow zones of large deformated lamellae in a symmetrical diblock copolymer by applying simple tension at room temperature. In those deformation zones lamellae of various directions are aligned into the direction of the applied stress by rotation mechanisms of the lamellae. The internal structure of the deformation zones consists of large deformed craze fibrils of PS and PBMA. The PBMA lamellae can easily cavitate because of their low modulus. The stress concentration at the PS lamellae leads to large deformation of PS. The same mechanism was observed by Argon in PS-*b*-PB diblock copolymers[25] and is discussed as a cavitation mechanism. In contrast, with PS-*b*-PBMA diblock copolymers the existence of asymmetrical phase compositions as found by dynamic—mechanical analysis could have a pronounced influence on tensile strength.[14,15] From these previous results we conclude that an essentially pure PS matrix and a PS/PBMA mixed phase may exist. The mixed phase could increase the critical cavitational stress as compared to that of PB, which then could be responsible for the improved tensile strength. Furthermore, the existence of a broadened interface leads to an improved interfacial strength which can improve the tensile strength. The details of the deformation mechanisms of PS-*b*-PBMA diblock copolymers have been described elsewhere.[15]

Also, the Young's modulus can be influenced by the morphology. In the case of a bicontinuous structure the networklike nature of the structure can improve the Young's modulus. As shown in Figure 8, the tensile strength and Young's modulus of the bicontinuous structure are improved as compared to that of other morphologies in the composition range 30−50% PS. Different models for elastic constants of composites including the Reuss, Voigt, and Takayanagi models cannot give a reliable description of the properties of our system with complex morphologies because they only include the elastic constants of the respective homopolymers, the volume fraction, and the Poisson's constant but do not consider the morphologies of the polymers.[29] Furthermore, we do not know the real values of the modulus of the phases. First, we have not found neat phases but a mixed PS/PBMA phase and a pure PS phase. On the other hand, the modulus of structures in the nanometer scale could differ from those of bulk materials. Therefore, we cannot predict the dependence of the Young's modulus on composition from these models.

The improvement of tensile strength of PS-*b*-PBMA block copolymers in the composition range 72−76% PS (Figure 5) could be described by the decrease of stress concentration at the broadened interfacial region. The increased critical cavitational stress is due to the existence of a mixed PS/PBMA phase and a pure PS matrix. On the other hand, the particular phase composition is due to the intermediate segregation which is responsible for a high strength of the matrix as compared to a possible existence of A-rich and B-rich phase compositions in other partially miscible systems.

The understanding of the stiffness mechanism of sample SBM76 is complex, and actually we can only speculate about the possible reasons. One influence could be the enhanced stiffness of components in the nanometer scale and the unknown influence of the stretched chain conformation on the Young's modulus. Second, the shape of the morphology of sample SBM76, consisting of hexagonally packed PBMA cylinders in a PS matrix, could have an influence on the local stress level at small strains, which could also influence the moduli. For a first phenomenological and qualitative understanding one could compare the storage shear modulus of SBM76 and pure PS. For sample SBM76 the storage shear modulus is larger than that of pure PS near room temperature. One should take into account that at very small deformations the shear modulus is correlated to the Young's modulus $G = E/[2(1 + \nu)]$, where ν is the Poisson constant. One can assume that $E \approx 3G$ (for $\nu \approx 0.5$, which is true for many polymers), which is fulfilled for many polymers. For sample SBM76 we measured a storage shear modulus of 1.3 GPa at 25 °C and can calculate then 3.9 GPa for the Young's modulus, which is a relatively good approximation of our experimental data. For pure polystyrene the Young's modulus is about 3 GPa, which is lower than the value observed for sample SBM76. It was shown for bicontinuous structures that the storage shear modulus is much higher than observed for other morphologies such as spheres, cylinders, and lamellae.[26] In the case of sample SBM76 the existence of a PS matrix could be important for the improvement of the Young's modulus. It is obvious in Figure 7 that the Young's modulus only deviates significantly from the linear dependence (dashed line in Figure 7) for PS contents higher than 70%. There a transition from lamellar to structures with a PS matrix was observed.

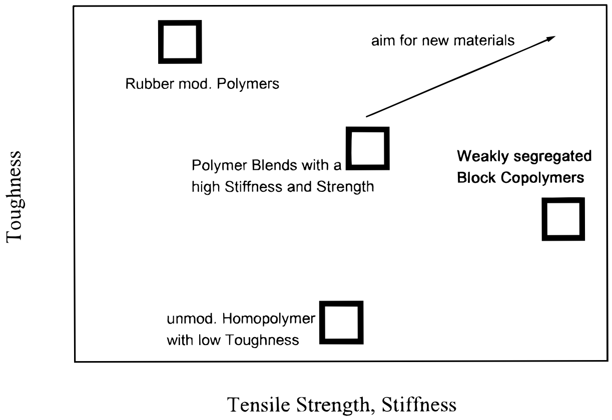

Figure 15. Qualitative dependence of toughness on tensile strength and stiffness for different polymeric systems which show the aim for the property profile of weakly segregated block copolymers.

Conclusions

From combined structural and mechanical investigations it is clearly shown that the segregation state (weak or intermediate segregation), the microphase separated morphologies, their size in the nanometer scale, the interface formation, and chain conformation have a pronounced influence on the mechanical properties of block copolymers. Block copolymers with molecular weights of $M_n > 200$ kg/mol show synergetic effects on tensile strength at 70−80% PS content, Young's modulus at 76% PS content, and absorbed energy at 30−40% PS content. Whereas disordered structures are generally connected with a deterioration of most mechanical properties,[12] the different morphologies of block copolymers have a pronounced influence on tensile properties in a small composition range. It was demonstrated that bicontinuous structures (39% PS) lead to an enhanced tensile strength which exceeds the value of pure PS at higher strain rates. In contrast, block copolymers with spherical structures (at a PS content of 83% PS) show almost no influence on the mechanical properties at all measured strain rates, which is in good agreement with the investigations performed by Argon and co-workers[31] on PS-*b*-PB diblock copolymers with spherical structures. For block copolymers with 72−76% PS content the tensile strength exceeds the value of the homopolymers also at higher strain rates and temperatures, demonstrating that the mechanical properties are improved over a wide application range.

The new concept of using weakly segregated block copolymers as thermoplastic materials with improved mechanical properties has demonstrated the potential for the creation of new polymeric materials based on block copolymers. It is qualitatively shown in Figure 15 how most of the interesting tensile properties such as tensile strength, stiffness, and toughness (absorbed energy) of weakly segregated block copolymers are improved as compared to those of the respective homopolymers. Especially, a strong improvement of tensile strength and Young's modulus is found in our system which usually is not observed for rubber toughened polymers and most of the polymer blends. However, the toughness of PS-*b*-PBMA diblock copolymers is still much lower than obtained for rubber toughened polymers and several polymer blends, especially at lower temperatures due to the high T_g of the PBMA block. The most interesting properties of weakly segregated block copolymers are their high tensile strength and stiffness combined with a good toughness at higher temperatures. In contrast to SBS triblock copolymers, the investigated PS-*b*-PBMA block copolymers are intermediately segregated (or weakly segregated for molecular weights of about 130 kg/mol[12,14]), which is the reason for some of the observed properties.

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