

Mechanical properties of weakly segregated block copolymers: 1. Synergism on tensile properties of poly(styrene-*b*-*n*-butylmethacrylate) diblock copolymers

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Abstract

Mechanical properties of poly(styrene-*b*-*n*-butylmethacrylate) diblock copolymers, PS-*b*-PBMA, with different lengths of the polystyrene block were investigated. The copolymers display a composition range where the tensile strength of the block copolymers exceeds the values of the corresponding homopolymers. At a PS-content of 74 vol% not only the tensile strength but also the strain at break is higher than that of pure polystyrene. Furthermore, the absorbed energy shows a maximum at a polystyrene content of 29 vol%. This composition reveals a morphology of hexagonally packed PS-cylinders which turns out to be effective for the increase of toughness in PS-*b*-PBMA diblock copolymers. The improved properties of PS-*b*-PBMA diblock copolymers are discussed with respect to a possible correlation and synergism between phase behaviour, morphology, deformation mechanism, and interface formation. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Mechanical behaviour of polymer materials is especially interesting for technical applications, but also relevant for other properties of polymers (e.g. optical, electrical, thermal etc.). The combination of various polymers into blends can lead to materials with improved mechanical properties. The enhancement of toughness in rubber-modified materials or polymer blends depends on their morphology. For high impact polymers it is well known that the impact properties of homopolymers can be improved by the incorporation of a dispersed elastomeric phase. This effect is caused by multiple crazing of multiple cavitation with shear yielding, which is macroscopically shown by the phenomenon of stress-whitening [1,2].

In contrast to polymer blends in block copolymers various ordered morphologies in a size scale of typically 10–100 nm were observed. Block copolymers show usually a macroscopical grain structure, with grain sizes of 1–10 μm .

Such materials will exhibit therefore isotropic properties in the case of an absence of macroscopic orientations. The morphologies of block copolymers have been the subject of many experimental studies. In poly(styrene-*b*-isoprene), PI-*b*-PI, diblock copolymers the following morphologies are reported: BCC-spheres, hexagonally packed cylinders, ordered bicontinuous double diamond (OBDD) and lamellar structures [3–6]. In the weak segregation limit the perforated layers and the cubic bicontinuous structure ('gyroid') was found [7–9]. Commonly used thermoplastic elastomers (TPE) like poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers, PS-*b*-PB-*b*-PS, are important for technical applications. TPE consists of a hard block (crystalline or glassy) and a rubbery soft block. The thermoplastic elastomer Kraton[®] (Shell Oil Co.) is such a material consisting of glassy PS blocks and a rubbery PB middle block [10]. Whereas PS-*b*-PB diblock copolymers with a PB-matrix show only a very small tensile strength the presence of bridged midblock conformations in PS-*b*-PB-*b*-PS (SBS) triblock copolymers can display an improved mechanical strength [11]. The deformation behaviour of the PS-cylinders in SBS triblock copolymers at higher

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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	$10^{-3} \times M_n$ copolymer (M_w/M_n) ^a	Φ_{PS} block ^b	Morphology (TEM)
SBM 9	412,0 (1,03)	0.09	PS-spheres
SBM 15	406,8 (1,05)	0.15	PS-spheres
SBM 29	246,0 (1,04)	0.29	PS-rods
SBM 40	212,1 (1,05)	0.40	Perforated PS-lamellae
SBM 55	534,0 (1,06)	0.55	Lamellae
SBM 67	450,0 (1,05)	0.67	Lamellae
SBM 74	463,0 (1,03)	0.74	Lamellae/PBMA-cylinder
SBM 83	383,1 (1,04)	0.83	PBMA-spheres

^aSize exclusion chromatography (SEC), values are based on the PS standards^b¹H-n.m.r.

strains has been intensively investigated by various methods [12–15].

Recently, Russell and co-workers [16,17] reported data concerning the phase behaviour of poly(styrene-*b*-butylmethacrylate) PS-*b*-PBMA, diblock copolymers. It was shown that PS-*b*-PBMA diblock copolymer melts show a microphase separation upon heating. These diblock copolymers exhibit both an upper critical order transition (UCOT) and a lower critical order transition (LCOT). In a previous paper [18] we reported the morphologies of this diblock copolymer system depending on polystyrene content and molecular weight.

In this study the mechanical properties of PS-*b*-PBMA diblock copolymers depending on the PS-content and the morphology will be presented.

2. Experimental

2.1. Polymerization procedure

All polymerizations were carried out in carefully flamed glass reactors in THF as the solvent at -78°C under an argon atmosphere using syringe techniques. After several cycles of degassing the styrene from calcium hydride the monomer was introduced into the reactor by condensation under reduced pressure. THF was condensed from oligometric 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 with a syringe. The living anions were terminated by adding methanol after another 30 min. Then, the polymer was precipitated in a 7/3 methanol/water mixture at -30°C , washed and dried in vacuum for several days.

2.2. Sample preparation

All samples were dissolved in toluene. 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.

2.3. Characterization

Measurements with size exclusion chromatography (SEC) were carried out using a Knauer-SEC with a RI/Viscodetector and a PS standard linear column. The volume fraction of the diblock copolymers were estimated by ¹H-n.m.r. The molecular weights, compositions and morphologies of the diblock copolymers used in this study are summarized in Table 1.

The dynamic elastic and loss shear moduli, G' and G'' , were determined with a Rheometrics RDAII using the temperature step mode and a frequency of 1 Hz.

Ultrathin sections (50 nm) were cut at room temperature using glass knives in a Ultramicrotome (Reichert) equipped with a glass knife. The polystyrene blocks were stained with RuO₄ vapour. Electron microscopic observations have been performed with a Jeol 2000 FX (Eindhoven) and a BS500 (Halle) transmission electron microscope operated at 80 kV. Tensile tests were performed using a universal testing machine (Zwick 1425) at a strain rate of $1.6 \times 10^{-4} \text{ s}^{-1}$. The sample dimensions of tensile bars had a thickness of 0.5 mm and a total length of 50 mm. The toughness of the diblock copolymers were estimated as absorbed energy from the stress–strain curves.

3. Results and discussions

3.1. Morphology and phase behaviour

PS-*b*-PBMA diblock copolymers with an overall molecular weight of $M_n > 200 \text{ kg/mol}$ and various polystyrene contents have been synthesized in order to investigate the correlation between morphologies and mechanical properties.

The dynamic mechanical analysis proved a partial miscibility for diblock copolymers with asymmetrical compositions. Investigations of PBMA performed by Heijboer [19] have shown that near the α -relaxation a strong β -relaxation is due to the rotation of the butyl ester side group. The dependency of the glass transition temperatures on the PS volume fraction are shown in Fig. 1. In the case of strong

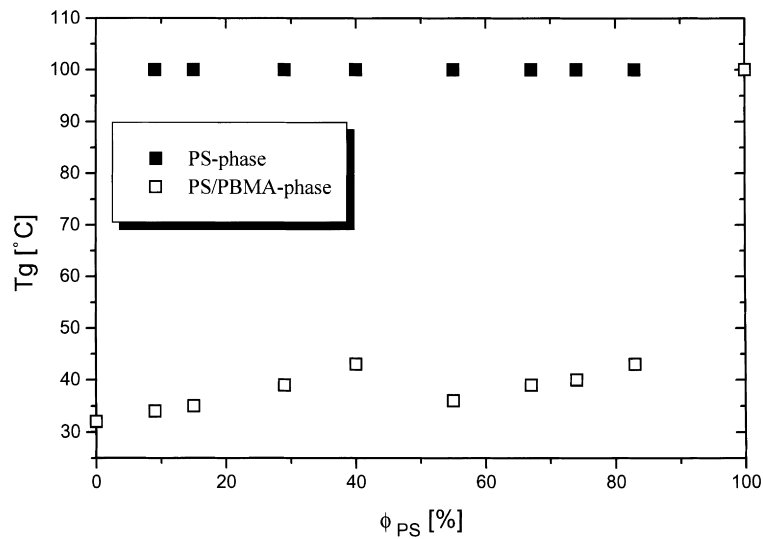


Fig. 1. Dependence of the glass transition temperature on the volume fraction ϕ_{PS} .

segregated block copolymers, which form a sharp interface between the blocks, neat phases are expected. However, for PS-*b*-PBMA diblock copolymers, the glass transition temperature only 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 Figs 1–3 for two unsymmetrical diblock copolymers. For both samples the glass transition temperature of the

PBMA-block is higher than those of pure PBMA. Pure PBMA displays a glass transition temperature of 31°C (measured at a frequency of 1 Hz). On the contrary, 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) to 39°C. To explain this phenomenon we have to assume an asymmetrical phase diagram for PS-*b*-PBMA diblock copolymers. An

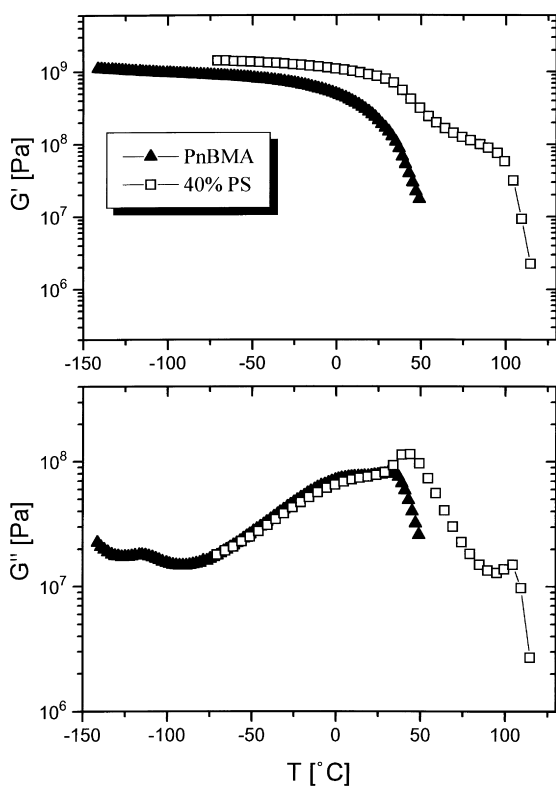


Fig. 2. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for SBM40 ($\phi_{PS} = 0.40$, $M_n = 212$ kg/mol) and pure PBMA ($M_w = 363$ kg/mol) measured at a frequency of 1 Hz.

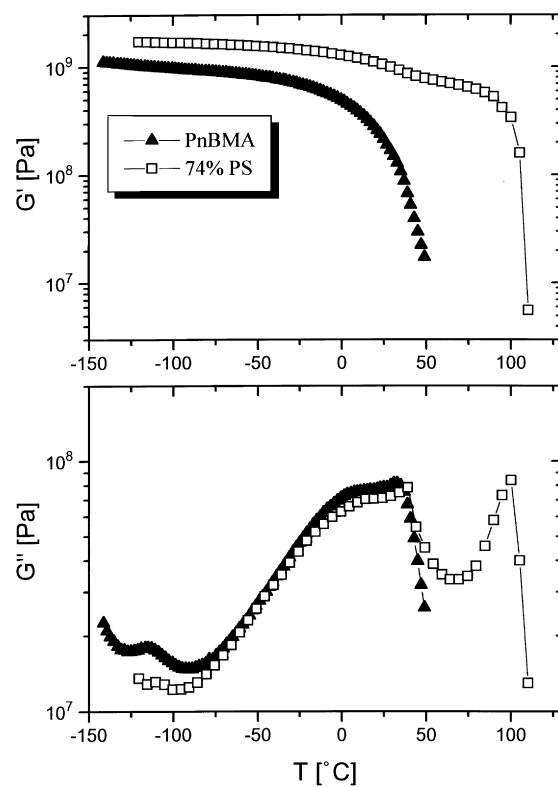


Fig. 3. Dependence of storage modulus (G') and loss modulus (G'') on the temperature for SBM74 ($\phi_{PS} = 0.74$, $M_n = 463$ kg/mol) and pure PBMA measured at a frequency of 1 Hz.



Fig. 4. TEM micrograph of SBM29 ($\Phi_{PS} = 0.29$, $M_n = 246$ kg/mol) with hexagonally packed PS cylinders (stained with RuO_4).

asymmetric phase composition is expected, and an essentially pure polystyrene matrix phase together with a PS/PBMA mixed phase may exist. This asymmetry of phase composition could have a pronounced effect on the mechanical properties. A broadening of the interface between PS and PBMA at higher temperatures was observed by neutron reflectometry, confirming our assumption of a partial miscibility of PS-*b*-PBMA diblock copolymers [20]. The



Fig. 5. TEM micrograph of SBM40 ($\Phi_{PS} = 0.40$, $M_n = 212$ kg/mol) with perforated lamellae of PS. The perforated lamellar structure with parts of the sample cut perpendicular through the perforated lamellae and parts cut through lamellae plane are shown (stained with RuO_4).



Fig. 6. TEM micrograph of SBM67 ($\Phi_{PS} = 0.67$, $M_n = 450$ kg/mol) with lamellar morphology (stained with RuO_4).

phase behaviour of PS-*b*-PBMA diblock copolymers is still under discussion and needs further investigation.

Our previous investigations [18] have shown that in the case of PS-*b*-PBMA diblock copolymers with high molecular weights microphase separated morphologies with spherical, hexagonal (Fig. 4) and lamellar structures exist depending on the PS-block length. More detailed investigations show the existence of a perforated lamellar structure (HPL) at a PS-content of 40% (Fig. 5).

In Fig. 5 one example of the morphology consisting of perforated lamellae of PS is shown. The figure shows very clearly that parts of the sample are cut perpendicularly through the perforated lamellae and other parts are cut through the lamellar plane. In both directions view holes in the stained PS-layers exist. However, it is difficult to determine from these pictures whether the holes in the PS-layers are organised in a regular (hexagonal or tetragonal) fashion. This, however, does not seem to be relevant for the mechanical properties as described below. A perforated lamellar structure for samples with high PS-content was not found. Whereas in PS-*b*-PI the transition to hexagonal

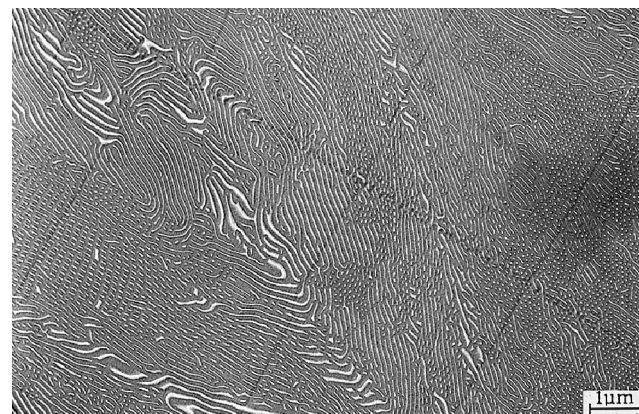


Fig. 7. TEM micrograph of SBM4 ($\Phi_{PS} = 0.74$, $M_n = 463$ kg/mol). The coexistence of ordered areas of lamellar structures and hexagonally packed PBMA cylinders can be found in this sample (stained with RuO_4).

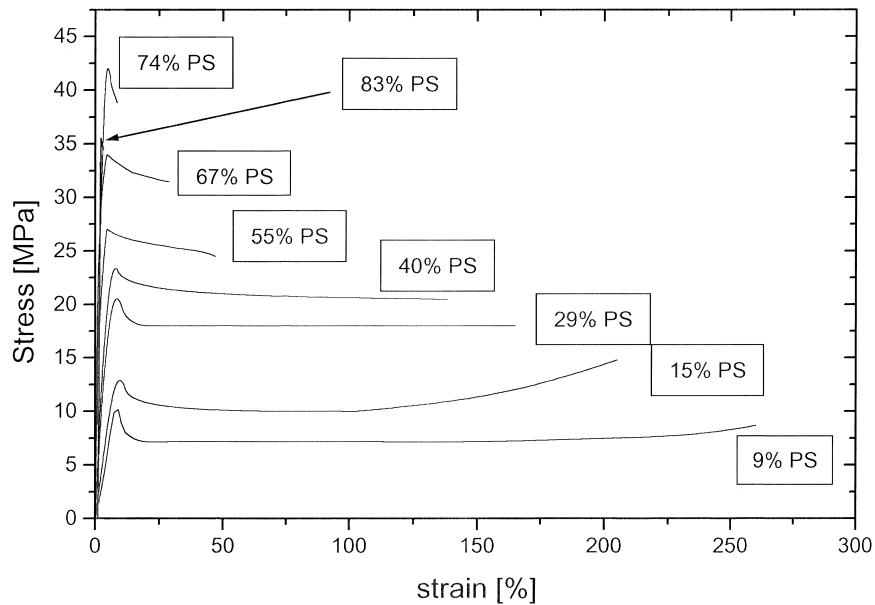


Fig. 8. Stress–strain curves for diblock copolymers depending on the PS-volume fraction at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

structures was observed at approximately 70% PS [21], in our block copolymer system a direct transition from lamellar structures to a lamellar/hexagonal (LAM/HEX) structure was found at 70% PS (Figs 6 and 7). This structure reflects a coexistence of ordered areas of lamellae and hexagonally packed PBMA-cylinders and cannot be expected from Leibler's theory, which is based on equal polymerisation degrees and segment length of the homopolymers. However, in the case of PS-*b*-PBMA diblock copolymers the polymerisation degrees as well as the segment length of PS and PBMA are different. Furthermore, in the weak segregation limit, the differences of free energies for different structures are very small, which makes it difficult to achieve equilibrium morphology for samples with high molecular-weights.

A further increase of PS-content up to 83% PS leads to a

change into spherical structures [18]. A morphology of hexagonally packed cylinders could not be observed at high polystyrene contents. The hexagonal structure may exist in the uninvestigated composition range $0.74 < \Phi_{\text{PS}} < 0.83$. This would imply, that the composition range of the hexagonal structure on the PS-rich side of the phase diagram would be smaller than for PS-*b*-PI.

3.2. Mechanical properties

In contrast to rubber-modified polymers and thermoplastic elastomers (TPE) both blocks, polystyrene (PS) and poly(*n*-butylmethacrylate) (PBMA), are thermoplastic materials. This is the reason for the thermoplastic behaviour of PS-*b*-PBMA diblock copolymers also for small PS-contents.

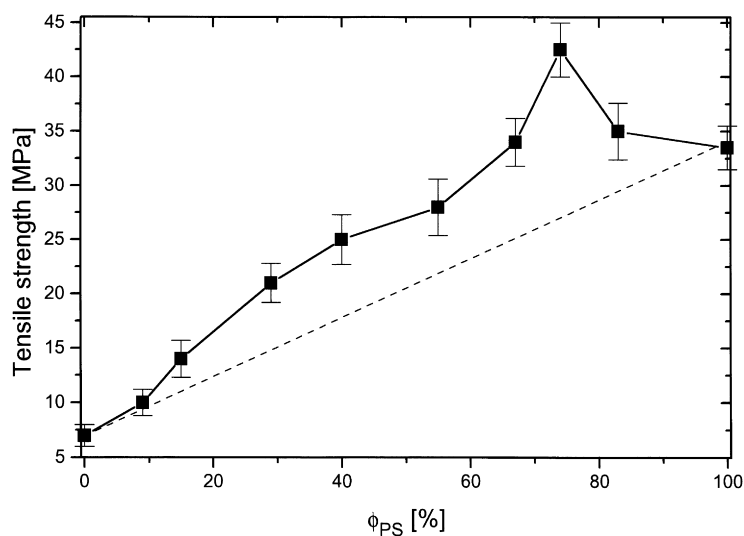


Fig. 9. Dependence of tensile strength on the volume fraction Φ_{PS} for diblock copolymers at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

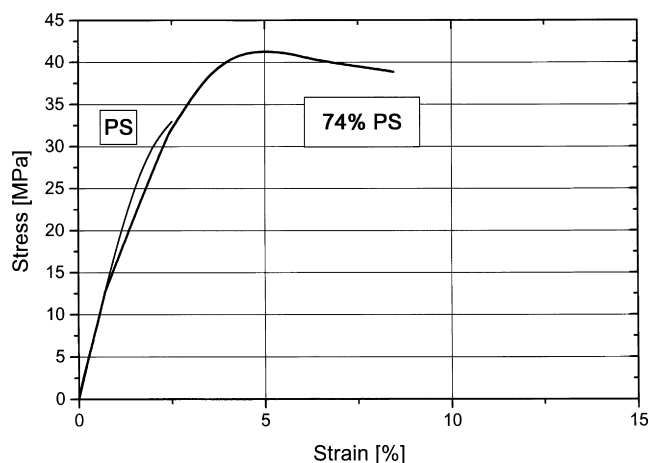


Fig. 10. Stress–strain curves for pure polystyrene ($M_w = 315$ kg/mol) and SBM74 ($\Phi_{PS} = 0.74$, $M_n = 463$ kg/mol).

A strong increase of tensile strength with increasing PS-content was found. In contrast to the low molecular weight diblock copolymers [22] we found at 74% PS a maximum of tensile strength (Figs 8 and 9), which is about 20% higher than that of pure PS. This synergism of tensile strength was found in the composition range between 70% and 80% PS content [23], which was not observed for other diblock copolymers. In the case of block copolymers consisting of polystyrene and polybutadiene only triblock copolymers with a rubbery middle block can show a higher tensile strength. The tensile strength of PS-*b*-PBMA diblock copolymers is for all compositions higher than the linear relationship (dashed line in Fig. 9).

The increase of the PS-content up to 67% leads to a tensile strength, 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. This means that the spherical structure at 83% PS is connected with a decrease of tensile strength and the deformation process should be almost the same as that of pure PS.

In Fig. 10 the stress–strain behaviour of a diblock copolymer with 74% PS is compared with that of 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. Further, the Young's modulus of the block copolymers as indicated by the slope of the stress–strain curves at small strain shows almost the same value as for pure PS. This leads to the conclusion that an increasing PBMA content up to about 25% can lead to an increasing strain at break and tensile strength combined with a high stiffness (Young's modulus).

Many investigations have shown that the mechanical properties of polymers depend on test conditions, geometry and morphology of the used polymer. Investigations of various polymers show that mechanical properties measured in uniaxial compression tests are different from those measured in simple tensile tests. Polystyrene is a ductile

polymer if it measured in compression tests [24]. In contrast to this, polystyrene is brittle in simple tensile tests due to the premature failure. The main problem is that stress concentrations around cracks, notches and other geometrical features act to localize the deformation, often to the extent of causing brittle fracture [25]. The PS-*b*-PBMA block copolymers as well as the homopolymers used in this study were measured in simple tensile test. It should be mentioned that all samples used in this study were prepared from solvents (see sample preparation) and cannot directly be compared with commercially manufactured materials. Such materials show in most cases a large degree of anisotropy in mechanical properties, which we tried to avoid [26].

The synergetic effect of tensile strength should be discussed as a complex correlation between phase composition, interface formation, morphology and deformation processes. The complex morphology at a polystyrene content of 74% PS, which displays a coexistence of lamellar and hexagonal rod-like structures, may be discussed as one reason for the improved mechanical properties compared to that of pure PS. The partial miscibility of PS and PBMA, which leads to an essential pure PS-phase coexisting with a PS/PBMA mixed phase has pronounced effect on the mechanical properties. The mixed phase can increase the critical cavitation stress quite comparable to block copolymers with a rubbery block [27].

The investigations of polymer blends during several decades have shown that mechanical properties can be improved in the case of strong interfacial adhesion between components [28–31]. The toughness of homopolymers can be enhanced up to one order of magnitude by adding small amounts of elastomers. Toughened polymers may be distinguished by using different criteria, including composition, morphology, and the toughening mechanism [32]. Rubber toughening of glassy polymers involves three principal irreversible deformation mechanisms: shear yielding, crazing and rubber particle cavitation. Rubber toughening has proved to be so effective that the technology has been extended to almost all commercial glassy thermoplastics, including polystyrene, poly(methyl methacrylate), poly(vinyl chloride) and polycarbonate [1,2,33]. In rubber toughened polymers the enhancement of toughness compared to the unmodified homopolymers is generally connected with a decrease of tensile strength and stiffness. There are few polymer blends where synergetic effects in their mechanical properties are reported. Most of these polymer blends involve semicrystalline polymers. Poly(2,6-dimethyl-1,4-phenylene oxide)/polystyrene, polypropylene/high-density polyethylene and polybutene/polypropylene blends are examples for polymers which show synergetic effects on the mechanical properties [34,35]. In semicrystalline polymers the enhancement of mechanical properties can be attributed to the reduced average spherulite size, increased overall crystallinity and the formation of intercrystalline links. Synergism or positive deviation in

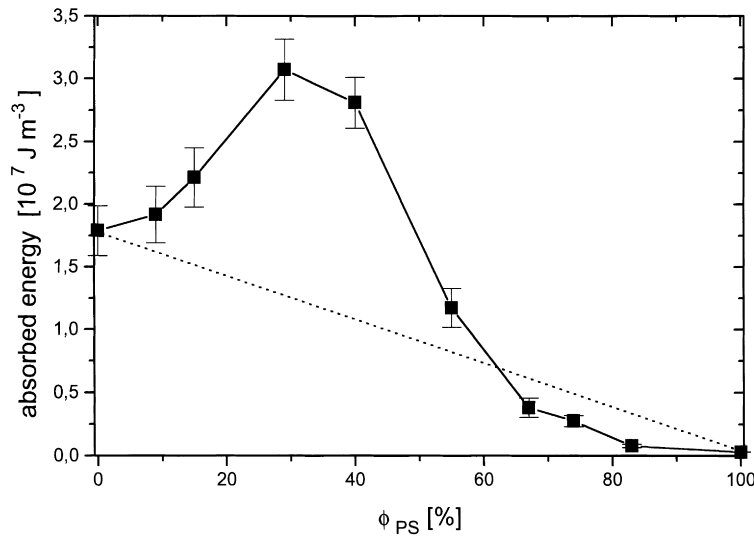


Fig. 11. Dependence of absorbed energy on the volume fraction ϕ_{PS} for PS-*b*-PBMA at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

mechanical properties is generally observed in miscible or partial miscible polymer blends.

For block copolymers quite different ordered structures exist in the nm-scale (spheres, cylinders, lamellae), which cannot be found in polymer blends. The deformation mechanisms are different to those of homopolymers, and provide reasons for the improvement of mechanical properties of block copolymers as compared to pure homopolymers. In the case of PS-*b*-PBMA diblock copolymers the partial miscibility and interface formation has a pronounced influence on the mechanical properties and deformation processes.

For PS-*b*-PBMA diblock copolymers a maximum of absorbed energy, estimated from the tensile stress–strain curves, were found. The dependence of absorbed energy on the PS content is shown in Fig. 11. A maximum of absorbed energy at a PS content of 29% was observed,

corresponding to a morphology of hexagonally packed PS-cylinders found by TEM (Fig. 4). The strain at break and the absorbed energy are rapidly decreased at a PS content of 55% (Figs 11 and 12). For diblock copolymers with 40% PS a morphology consisting of perforated lamellae and with a polystyrene content of 55% PS lamellar morphologies were observed by TEM (Figs 5 and 6). This could lead to the conclusion that the perforated lamellar structure is more effective for an enhancement of toughness than lamellar structures. In this study the absorbed energy was discussed only for small strain rates of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$, but the mechanical properties at higher strain rates will be discussed elsewhere [36].

The Young's modulus (stiffness) shows almost a linear dependence on the PS content at small PS-contents. For diblock copolymers with lamellar structures at a PS content of 67% a steeper increase of stiffness than a linear

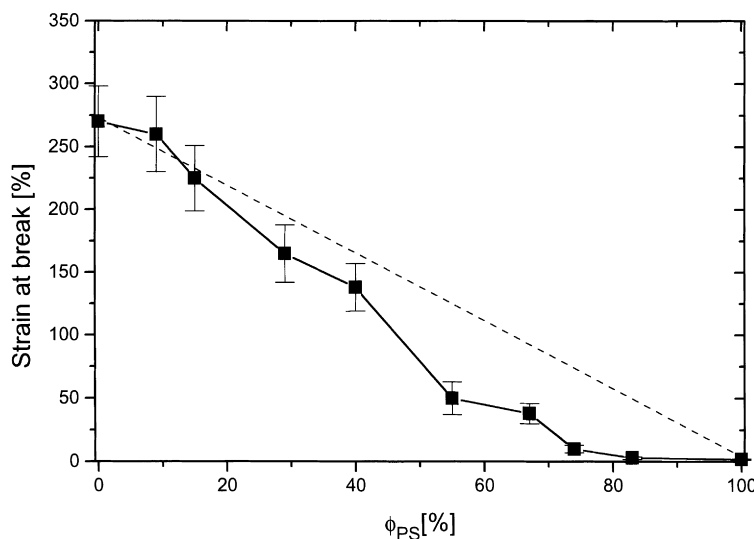


Fig. 12. Dependence of strain at break on the volume fraction ϕ_{PS} for PS-*b*-PBMA diblock copolymers at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

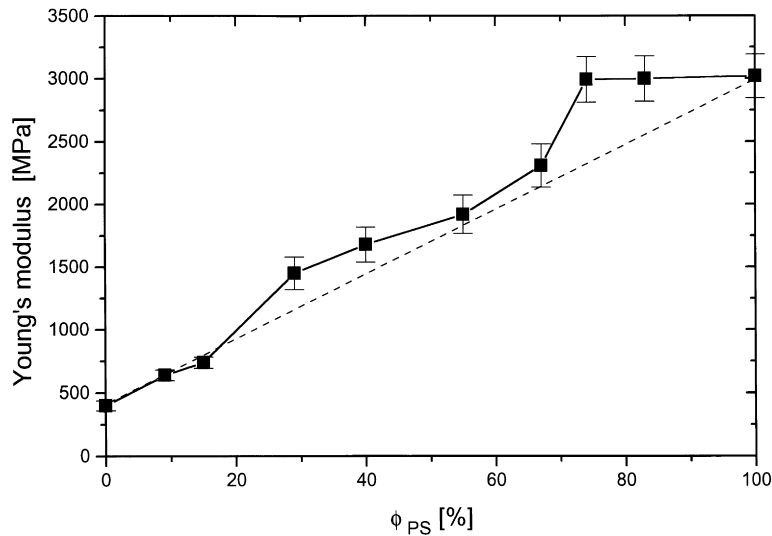


Fig. 13. Dependence of the Young's modulus on the volume fraction ϕ_{PS} for PS-*b*-PBMA diblock copolymers at a strain rate of $\dot{\epsilon} = 1.6 \times 10^{-4} \text{ s}^{-1}$.

dependence on the PS content was observed. A further increase of the PS content up to 74% leads to a Young's modulus, which is almost the same as pure PS, shown in Fig. 13. That means that the LAM/HEX-morphology at this composition leads to a high tensile strength as well as a high stiffness.

The coexistence of lamellar and hexagonally packed cylinders at 74% PS seems to be very effective for an improvement of mechanical properties. Whereas in the case of thermoplastic elastomers only triblock copolymers like SBS can lead to a higher tensile strength, an improvement of the mechanical properties were observed in our case study for PS-*b*-PBMA diblock copolymers and PBMA-*b*-PS-*b*-PBMA triblock copolymers [23]. For PS-*b*-PBMA diblock copolymers the relatively large width of the interface between PS and PBMA, which was measured by neutron reflectometry and TEM [20], the morphologies at the nanometre scale and the deformation process, which is very different from pure PS are reasons for their good mechanical properties [27].

3.3. Conclusions

It was demonstrated that the important mechanical properties like tensile strength, absorbed energy and Young's modulus (stiffness) are strongly influenced by the phase behaviour, microphase separated morphologies and interface formation of PS-*b*-PBMA diblock copolymers. Using weakly segregated block copolymers as thermoplastic materials with a high tensile strength and stiffness it is demonstrated that an improvement of the mechanical properties based on block copolymers is possible. Further investigations of the dependence of the mechanical properties of PS-*b*-PBMA diblock copolymers on molecular weight and strain rate are in progress [36,37]. A better understanding of the deformation process and possible synergetic effects in

weakly segregated block copolymers may offer further possibilities for a further design and optimisation of the mechanical properties of block copolymers.

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