

Morphology and Micromechanical Deformation Behavior of Styrene–Butadiene Block Copolymers. III. Binary Blends of Asymmetric Star Block Copolymer with General-Purpose Polystyrene

R. Adhikari,¹ G. H. Michler,¹ S. Goerlitz,¹ K. Knoll²

¹*Institute of Materials Science, Martin-Luther Universität Halle-Wittenberg, D-06099 Halle/Saale, Germany*

²*BASF–Aktiengesellschaft, Polymer Research, GKT/I-B1, D-67056 Ludwigshafen, Germany*

Received 2 September 2003; accepted 28 September 2003

ABSTRACT: The correlation between morphology, mechanical properties, and micromechanical deformation behavior of the blends consisting of an asymmetric styrene/butadiene star block copolymer (ST2-S74, total styrene volume content $\Phi_{PS} = 0.74$) and general-purpose polystyrene (GPPS) was investigated using transmission electron microscopy and uniaxial tensile testing. Addition of 20 wt % of GPPS to the block copolymer resulted in a drastic reduction in strain at break, indicating the existence of critical PS lamella thickness D_c . Above D_c lamellar block copolymers

displayed a transition from ductile to brittle behavior, substantiating the mechanism of thin layer yielding proposed for lamellar star block copolymers. The blends showed a variety of deformation structures ranging from classical crazelike zones to those with internal shearlike components. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1208–1218, 2004

Key words: block copolymers; mechanical properties; micromechanism; electron microscopy; thin layer yielding

INTRODUCTION

Blending of homopolymers represents a common technological means of combining their useful properties.^{1,2} However, this often leads to deterioration of the mechanical properties because of poor phase adhesion. Block copolymers, on the other hand, offer an excellent option of combining the mechanical properties of homopolymers that are linked covalently in the interfacial region. The chemical connectivity of the component chains leads to the formation of highly ordered microphase-separated structures with periodicity of 10–100 nm.^{3–5} Because the type and the dimension of these ordered structures control the mechanical properties of these nanostructured heteropolymers, morphology control in block copolymers has become an important facet of modern materials science and engineering.

Styrene/butadiene (SB) block copolymers are often used in combination with other homopolymers such as general-purpose polystyrene (GPPS). The blending

reduces the price and, at the same time, endows the brittle polystyrene (PS) with an increased toughness. It represents an important way of morphology control in block copolymers.

The ways in which the polymeric materials respond in microscopic and submicroscopic level toward the applied external stress determine their mechanical behavior.¹ Micromechanics is concerned with the reaction of individual macromolecules and microscopic structures (such as crystallites, lamellae, grains, etc.) toward the external load. Hence, it is desirable to understand precisely the micromechanical deformation behavior of polymeric materials to be able to adjust their macroscopic mechanical properties.¹

In the past, phase behavior and morphology of binary diblock copolymer/homopolymer mixtures have been intensively investigated.^{6–9} It has been demonstrated that the phase behavior of a binary block copolymer/homopolymer mixture is primarily governed by the length of homopolymer chains relative to the corresponding block of the block copolymer (i.e., the ratio $N_{\text{homo-A}}/N_{\text{block-A}}$, where $N_{\text{homo-A}}$ and $N_{\text{block-A}}$ represent the degree of polymerization of added homopolymer **A** and corresponding block **A** in the block copolymer **AB**, respectively). There is a competition between microphase and macrophase separation in a binary block copolymer/homopolymer blend. Which effect predominates depends on the blend composition, as well as the ratio $N_{\text{homo-A}}/N_{\text{block-A}}$.^{3,6–9} In such blends, the low molecular weight homopolymer is

Correspondence to: R. Adhikari (rameshwar.adhikari@iw.uni-halle.de).

Contract grant sponsor: Kultusministerium des Landes Sachsen-Anhalt.

Contract grant sponsor: Max-Buchner-Forschungstiftung; contract grant number: MBFSt 6052.

TABLE I
Overview of the Investigated Samples

Sample code	M_n (g/mol) ^a	M_w/M_n ^a
ST2-S74 ^b	109,000	1.69
GPPS ^c	93,600	2.03

^a Number-average (M_n) and weight-average (M_w) molecular weights determined by gel permeation chromatography (GPC) using PS calibration.

^b Star block copolymer having total polystyrene volume fraction $\Phi_{PS} = 0.74$.

^c General-purpose polystyrene prepared by radical polymerization.

solubilized within the corresponding block of the copolymer at low concentrations. As the molecular weight of homopolymer approaches that of the corresponding block of the block copolymer, it tends to segregate to the middle of the microdomains. Finally, if the molecular weight of the homopolymer is larger than that of the corresponding block of the block copolymer, macrophase separation tends to predominate. Likewise, increasing homopolymer concentration in the mixtures favors the macrophase separation.^{6–9}

In the investigation of phase behavior of SB block copolymers and their blends with homopolystyrene under thermodynamic equilibrium conditions, PS produced by anionic polymerization (which possesses a narrow molecular weight distribution) was used.³ In spite of the great academic significance of equilibrium morphology of the block copolymer/PS blends, these are seldom realized in practical cases. The morphologies produced in these materials prepared by common processing methods like injection molding, extrusion, and compression molding, on the other hand, are rather far from the equilibrium state. Moreover, PS is usually synthesized by radical polymerization and has a wide molecular weight distribution.

Compared with the study of morphology and phase behavior of block copolymer/homopolymer blends, less attention has been paid to the correlation between their morphology, mechanical properties, and micro-mechanical deformation behavior. In this article, we describe this correlation in binary blends of a highly asymmetric styrene/butadiene star block copolymer and GPPS using injection-molded samples.

EXPERIMENTAL

Materials

Important characteristics of the investigated samples are collected in Table I. The block copolymer chosen in this study was an asymmetric star block copolymer produced by BASF (designated as ST2-S74, volume fraction of PS, $\Phi_{PS} = 0.74$; BASF AG, Ludwigshafen,

Germany). The details on synthesis and morphology of this block copolymer can be found elsewhere.^{10–12} It has four asymmetric SBS arms (on average), one of which is much longer than the others. The longest arm is styrene-rich, whereas the shorter ones are butadiene-rich. GPPS used in this study prepared by radical polymerization has a wide molecular weight distribution (number-average molecular weight, $M_n = 93,600$ and polydispersity index = 2.03).

The star block copolymer (ST2-S74) was melt blended with GPPS in various weight ratios: 20, 40, 60, and 80 wt % GPPS. Tensile bars were produced by injection molding (mass temperature 225°C and mold temperature 45°C).

Tensile testing

Macroscopic tensile tests were carried out using a universal tensile machine at a crosshead speed of 50 mm/min at room temperature (23°C) using dogbone-shape tensile bars according to ISO 527. At least 10 specimens were tested to obtain good statistics of the measured value.

Electron microscopic methods

Morphological details of undeformed as well as deformed samples were examined using transmission electron microscopy (TEM, JEOL 200 kV; JEOL, Tokyo, Japan). For the TEM investigations, a small block of specimen taken from the middle of a tensile bar (e.g., side I in Fig. 1), approximately 0.25 mm below the surface, was trimmed to a pyramidal shape and immersed in an osmium tetroxide (OsO_4) solution for several days at room temperature (23°C) to selectively stain the butadiene phase. Ultrathin sections of the samples for TEM were cut from each block using a Reichert-Jung Ultracut-C Ultramicrotome (Vienna, Austria) operated at room temperature (23°C). Sections from strained samples were taken from the location close to the fracture surface. In every case, the sections were taken from side I of the tensile bar, as shown schematically in Figure 1. Lamellar long period and lamellar thickness were quantified from the trans-

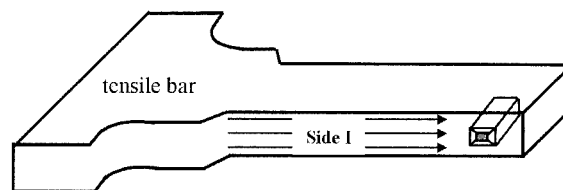


Figure 1 Scheme showing the location in the tensile bar from which the sections were taken for the TEM. The arrows indicate the direction of injection molding as well as the lamellar orientation.

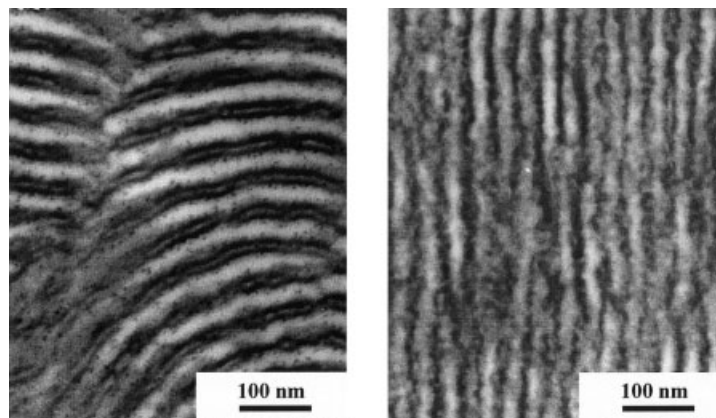


Figure 2 Morphology of the star block copolymer ST2-S74. Left: solution-cast film; right: injection-molded bar; injection direction vertical.

mission electron micrographs using a special image processing program and Fourier transformation.

RESULTS AND DISCUSSION

Morphology of star block copolymer/GPPS mixtures

Microphase-separated morphology of the star block copolymer (ST2-S74) used in this study was discussed comprehensively in parts I and II of this study.^{12,13} Here, we discuss briefly the morphology of solution-cast and of injection-molded ST2-S74 samples.

The TEM micrographs in Figure 2 depict the lamellar morphology of this sample showing alternating PS (white) and PB (dark) layers with PB lamellae embedding scattered PS domains about 6–9 nm in diameter. The PS and the PB lamellae, approximately 20 and 16 nm thick, respectively, were aligned in the direction of injection molding because of shear stress (Fig. 2, right). This typical morphology of the star block copolymer

has been referred to as a “two-component, three-phase” morphology.¹⁰

The morphology of the injection mold is qualitatively equivalent to that of the solution-cast sample (Fig. 2). However, it should be acknowledged that the nonequilibrium morphology of the injection mold is generally highly anisotropic, and this may vary depending on the depth of the sample from the surface and even across the length of the injection-molded bar because of the presence of different shear stress field along the sample cross section.¹⁴ To ensure a reasonable comparison, the specimens for microscopic investigations of each sample were always prepared from the identical locations of the injection-molded bars. Therefore the results presented in this article are rather qualitative, and we are aware of presenting the micrographs that are representative as far as possible.

As shown in Figure 3, ST2-S74/20 wt % GPPS blend possesses, like the pure block copolymer, the lamellar arrangement of microphase-separated PS and PB

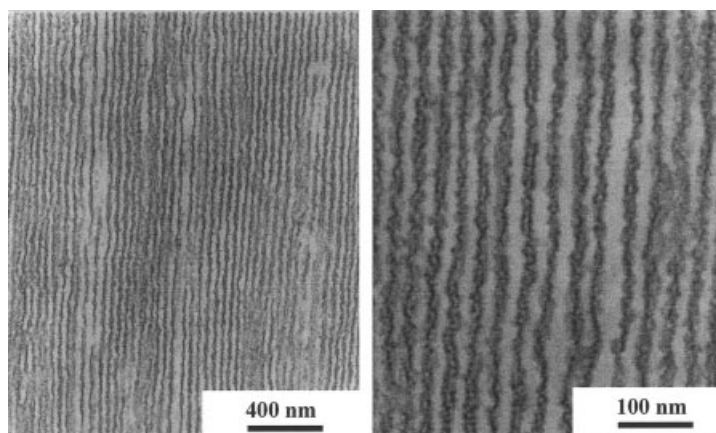


Figure 3 Lower (left) and higher (right) magnifications of TEM micrographs showing the lamellar structure of ST2 + 20% GPPS. Note that the PS lamellae are more continuous than in the pure star block copolymer.

TABLE II
Average PS Lamella Thickness D and the Lamellar Long period L Measured in TEM Micrographs of the ST2-S74/GPPS Blends

ST2-S74 (wt %)	GPPS (wt %)	D_{PS} (nm)	\bar{D} (nm)	L (nm)	\bar{L} (nm)
100	0	10–36	20	34–54	42
80	20	12–52	28	40–56	46
60	40	14–46	30	43–65	50
40	60	17–74	40	55–90	72
20	80	15–105	45	55–125	85

phases. Compared to the less-uniform PS lamellae of the pure block copolymer, the layers in this blend are quite continuous. Quantification of PS lamella thickness by image processing of the TEM micrographs reveals that the average thickness of the PS lamellae in ST2-S74/20 wt % GPPS is 28 nm (note that the average thickness of the PS lamellae in pure ST2-S74 was 20 nm), whereas the thickness of the PB lamellae changes insignificantly (see also Table II). The PB phase still embeds scattered PS domains.

Careful inspection of low-magnification images of the sample ST2-S74/20 wt % GPPS in Figure 4 reveals two distinct regions: one of them contains more polystyrene and appears lighter (PS-rich regions, Fig. 4) and the other contains lesser polystyrene or more block copolymer (bc) and appears darker (bc-rich regions, Fig. 4). Both regions possess a lamellar structure. The PS lamellae in the former are obviously thicker than those in the latter. There are even regions of thick stripes of polystyrene layers. The appearance of these regions with different local PS content in the blend with 20 wt % PS indicates that the added polystyrene homopolymer is unevenly distributed in the corresponding block of the star block copolymer. The appearance of thick stripes of polystyrene layers further suggests that the added GPPS would macrophase-separate under equilibrium conditions.

Uneven distribution of the added GPPS in the corresponding block domains of ST2-S74 was further demonstrated by high-voltage electron microscopic (HVEM) examination of these blends.¹⁵ In the semi-thin sections about 500 nm thick, the presence of lamellar stripes, containing higher (lighter) and lesser (darker) amounts of styrene, was observed, which also confirmed the uneven distribution of the added GPPS in the PS blocks of ST2-S74 in agreement with the present results. It should be noted that the uneven distribution of the added polystyrene, especially the formation of thick polystyrene layers that are exclusively the homopolystyrene, is also a result of chance mixing caused by processing.

Representative micrographs of samples containing 40, 60, and 80 wt % of GPPS are given in Figure 5. These micrographs reveal the following features as discussed below.

1. The PS lamellae become increasingly more continuous in the blends in contrast to the split lamellae of the pure block copolymer ST2-S74 (compare with Fig. 2, right). Simultaneously, the thickness of the PS lamellae increases with the GPPS content in the blends, whereas the thickness of the PB lamellae changes only insignificantly (see also Table II). Actually, the thickness of the PB lamellae also increases slightly, which may suggest that part of the added polystyrene (i.e., the low molecular weight fraction of added GPPS) might have been mixed to the butadiene phase. Furthermore, the continuity of the PB lamellae along the injection-molding direction decreases at higher GPPS concentration as the PB lamellae takes the form of “elongated PB islands” [Fig. 5(b), (c)]. The reduction in the length of the PB lamellae may be partly compensated by an increase in their thickness.

At higher GPPS content ≥ 60 wt %, the PS lamellae fuse together, and polystyrene practically forms the matrix [Fig. 5(b), (c)]. The PS domains scattered in the PB phase persist irrespective of the blend composition.

2. Despite the presence of a few unusually thicker PS layers (thickness up to a few hundred nanometers; e.g., see Fig. 3), no particle–matrix morphology typical of most polymer blends is observed in the star block copolymer/GPPS blends (Fig. 5). This is the reason that the investigated blends are almost as transparent as the star block copolymer itself. The dimension of heterogeneity in these blends lies well below the wavelength of visible light, and thus too small to scatter light.

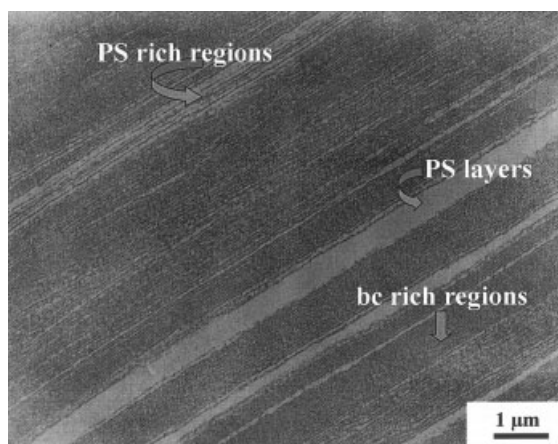


Figure 4 Low-magnification TEM micrograph of the sample ST2 + 20% GPPS.

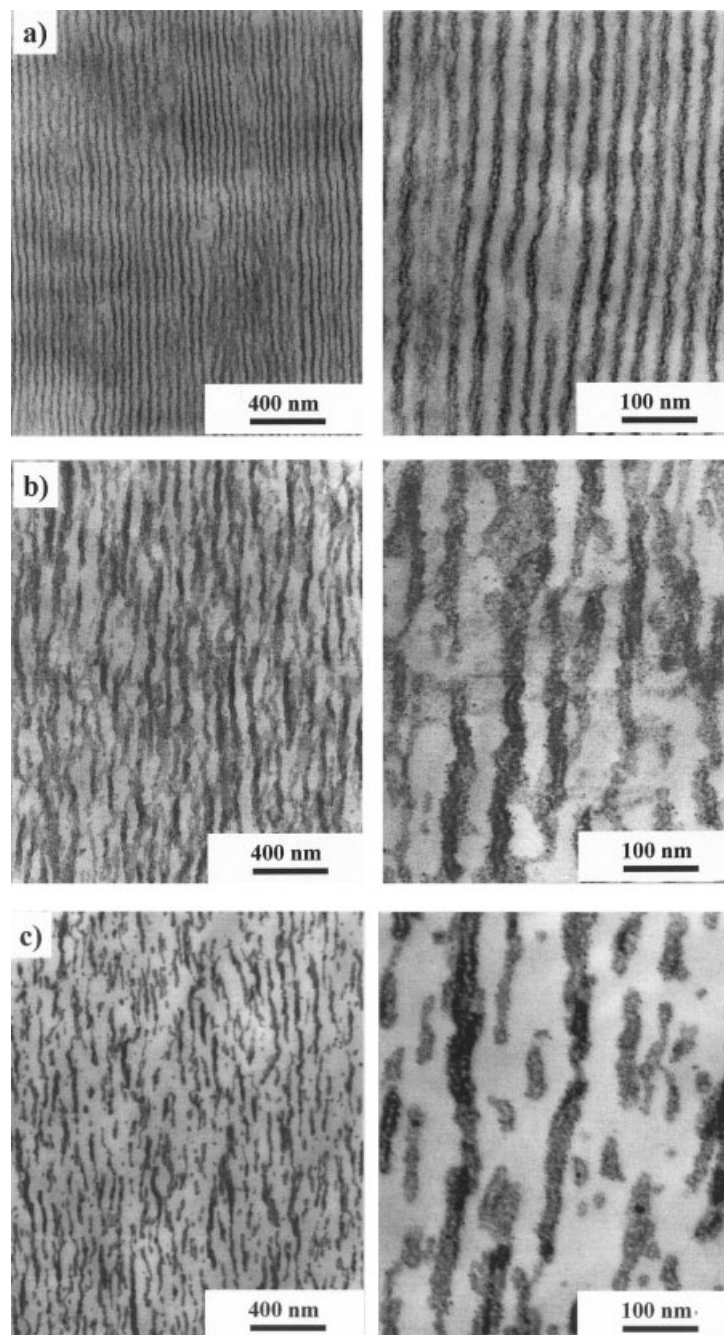


Figure 5 Lower (left) and higher (right) magnifications of TEM micrographs showing the morphology of injection-molded ST2/GPPS blends: (a) 40% PS, (b) 60% PS, and (c) 80% PS; injection molding direction vertical.

3. The microstructures are always oriented in the flow direction as a result of the shear forces operating in the injection-molding process.

As the PS lamellae fuse to form PS matrix at higher GPPS content (>40 wt %), it becomes more difficult to accurately measure the thickness of the PS lamellae. However, it is still possible to evaluate the thickness of PS strands that still assume "lamellar form." As determined by the image processing of the TEM micro-

graphs, the thickness of the PS lamellae D_{PS} as well as the long period L (see Table II) in the blends show a parallel increase with GPPS content. A continuous increase in both D_{PS} and L in the blends with ascending PS homopolymer content clearly suggests that the major part of the added GPPS is accommodated by the PS blocks of the star block copolymer.

Several authors have reported macrophase separation in binary blends containing block copolymers. Recently, Yamaoka^{16,17} studied the morphology and

toughness behavior of the blends of K-Resin 05 and a statistical copolymer of poly(methyl methacrylate) and polystyrene (PMMA-*co*-PS) using compression-molded samples and concluded that a macrophase separation between the blend components takes place. Previous works of Löwenhaupt and Hellmann¹⁸ on poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA/PS) have also shown the macrophase separation of added PS if the molecular weight of the PS was larger than that of the corresponding block of PS-*b*-PMMA diblock copolymer. Macrophase-separated poly(vinyl methyl ether) (PVME) domains were observed by Hashimoto et al.¹⁹ in a binary blend consisting of PVME and a styrene/butadiene star block copolymer. In part I of this study,¹² we also reported a macrophase separation of the GPPS in star block copolymer matrix under equilibrium conditions. It should be noted that the morphology of the injection-molded block copolymer/polystyrene blends is obviously far from equilibrium. Therefore, the conclusions drawn about the phase behavior of block copolymer/homopolymer blends by studying them under thermodynamic equilibrium cannot directly be translated in the samples investigated in this work.

Unlike under equilibrium conditions, in which the block copolymer and the added polystyrene undergo macrophase separation, the injection-molded blends displayed the microphase separation of the incompatible phases (i.e., the phase separation was not extended over a macroscopic scale). Obviously, the latter may be regarded as processing induced microphase separation. It is known from the literature that the structure formation in polymer mixtures is strongly influenced by processing parameters.^{14,20} Processing may significantly alter the phase behavior of the block copolymer systems by providing the new routes to novel morphologies.²¹

The compatibility of the added polystyrene homopolymer with the star block copolymer can be attributed to the complex asymmetric architecture of the copolymer. As mentioned earlier in the experimental section, the star molecules are made up of four asymmetric arms (on average), one of which is much longer than the others. The longer arm possesses a terminal PS block with a molecular weight in the range of 70,000–90,000 g/mol. The polystyrene blocks in the copolymer molecules are practically polydisperse, as are the polystyrene homopolymer molecules added to prepare the blends. Hence, it is quite reasonable that a considerable amount of higher molecular weight fraction of the GPPS can be added to the longest terminal polystyrene blocks of the block copolymer molecules. Meanwhile, the smaller PS blocks are also able to dissolve a part of the low molar mass fraction of the added PS. Furthermore, the macrophase separation in the injection molds is mainly suppressed by the rapid cooling of the melt. On cooling the melt very quickly,

the microphase-separated structures are frozen in, and the molecules do not have enough time to assume thermodynamically the most favorable morphology.

Mechanical properties

The stress–strain curves of ST2-S74/GPPS blends recorded at room temperature (23°C) are presented in Figure 6(a). Elongation at break, yield stress, and Young's modulus are plotted as a function of blend composition in Figure 6(b)–(d), respectively. As evident from Figure 6, the elongation at break decreases drastically when ST2-S74 is blended with 20 wt % of GPPS. Yield strength and Young's modulus increase almost linearly, which is attributed to the increasing overall polystyrene content. An abrupt change in elongation at break for the blend (at 20 wt % GPPS) suggests a transition in deformation mechanism (discussed later).

A well-defined yield point appears during the tensile deformation of the pure block copolymer ST2-S74 [Fig. 6(a)]. After the yield point, the stress declines rapidly (strain softening), reaches a minimum, and again increases slowly (strain hardening). This sample undergoes fracture at a strain and stress of 257% and 20 MPa, respectively. Macroscopically, the deformation occurs by necking and drawing of the specimen.

The yield point is visible in some ST2-S74/GPPS blends as well. However, they show only strain softening. With increasing GPPS content the extent to which the neck can elongate (drawing of the tensile bar) decreases and the tendency of the brittle fracture increases. Additionally, the blends exhibit a macroscopic stress whitening that indicates the formation of the local deformation zones such as crazes. The stress whitening becomes pronounced up to a GPPS content of 40 wt %, and becomes less distinct with increasing GPPS content because of extreme localization of the deformation zones.

Micromechanical deformation behavior

The mechanical behavior of polymeric materials is governed by underlying micromechanical processes of deformation and fracture. Hence, the mechanical properties of the samples characterized by the macroscopic tensile test may be directly correlated with the strain-induced deformation structures.

Figures 7 and 8 show the deformation structures observed in injection-molded ST2-S74 and its two different blends with the GPPS, respectively. In the pure star block copolymer (Fig. 7), the deformation mechanism is homogeneous deformation of the lamellae, whereas the formation of local crazelike deformation zones predominates in the blends (Fig. 8).

In pure block copolymer ST2-S74 (Fig. 7), homogeneous deformation of PS and PB lamellae results in a

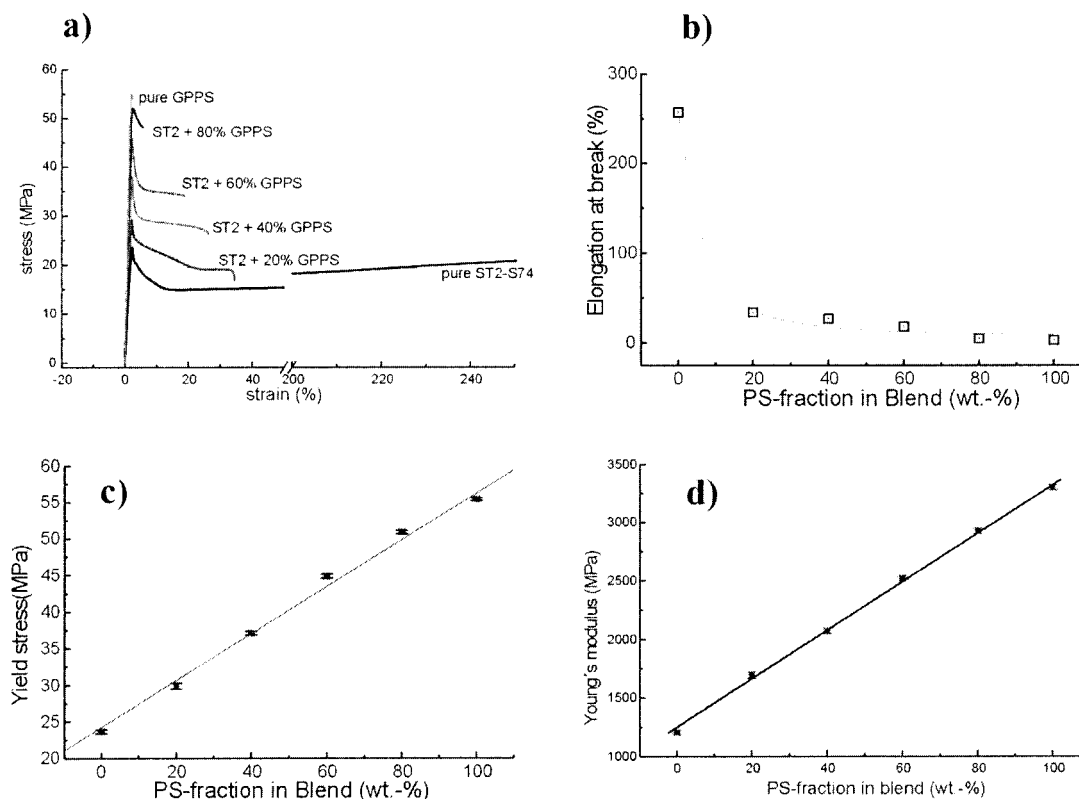


Figure 6 Mechanical properties of the star block copolymer/GPPS blends determined by tensile testing at 23°C according to ISO 527: (a) stress–strain curves, (b) elongation at break, (c) yield stress, and (d) Young's modulus as a function of blend composition.

reduction in lamellar thickness (see e.g., Fig. 9) and the long period by more than 50% [compare Fig. 7 (right) with Fig. 2 (right)]. No locally confined deformation zones were observed, which can be correlated with the absence of stress whitening during the tensile experiment.

In ST2-S74, the PS lamellae show necking and drawing, which may be accompanied by the subsequent

chain orientation. Drawing of the lamellae occurs in manner analogous to that of the whole tensile specimen. This microscopic plastic flow of PS lamellae (yielding of thin PS layers), called “thin layer yielding,” depends strongly on the thickness of the PS as well as the adjacent PB layers.¹² The plastic drawing of glassy polystyrene lamellae in SBS block copolymer systems was reported earlier by Hashimoto et al.^{22,23}

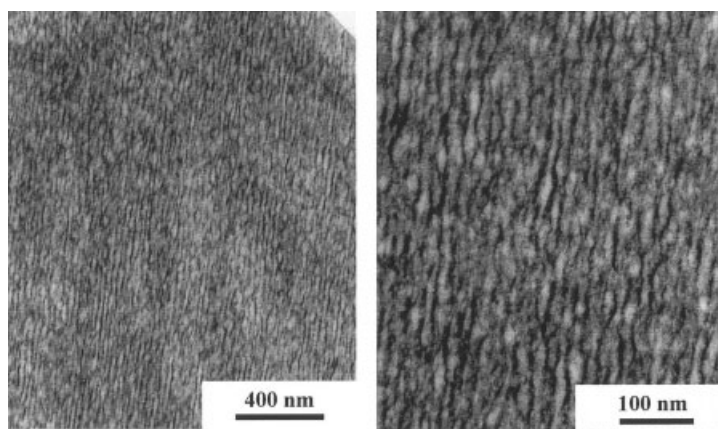


Figure 7 Lower (left) and higher (right) magnifications of TEM images showing the deformation structures in ST2-S74; deformation direction is vertical.

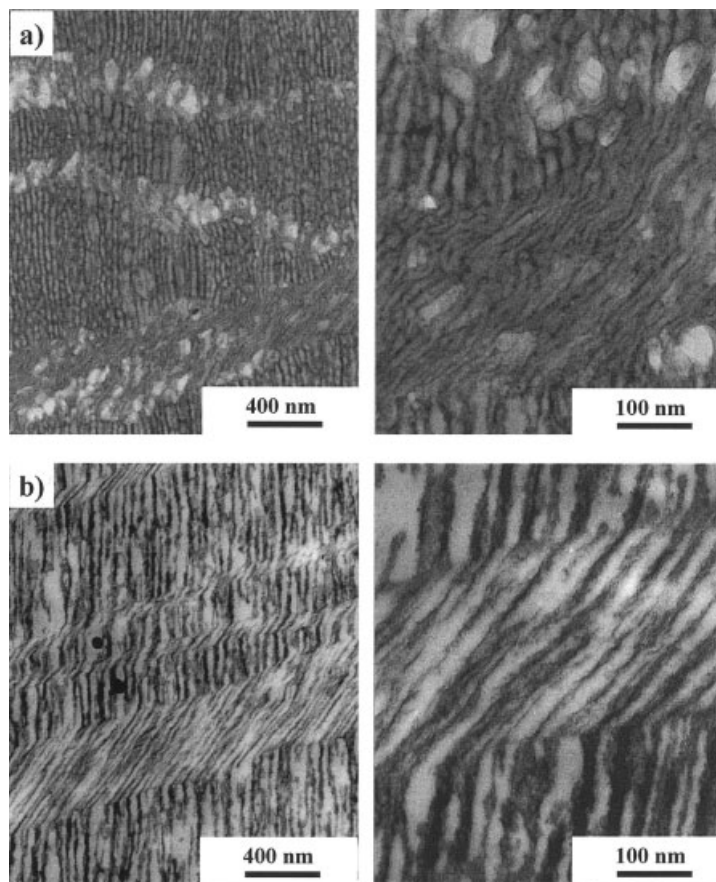


Figure 8 Lower (left) and higher (right) magnifications of TEM images of ST2/GPPS blends showing crazelike deformation zones; deformation direction is vertical: (a) 20% PS and (b) 60% PS.

and more recently in SBS block copolymer by Cohen et al.²⁴ This homogeneous plastic flow of the PS lamellae is the reason for the observed surprisingly high elongation at break in ST2-S74. That the toughness of the polymeric materials can be largely increased by control of the microstructure was demonstrated in independent studies by Wu,²⁵ van der Sanden,²⁶ and Baer et al.^{27,28} in other systems.

Deformation structures in the selected blends of the star block copolymer with polystyrene homopolymer are given in Figure 8. Pronounced cavitation leading to the formation of wide but relatively short, local crazelike zones occurs at 20 wt % GPPS [Fig. 8(a)]. The macroscopic elongation at break was found to decrease from 257% (in pure ST2-S74) to some 34% (in a blend with 20 wt % GPPS) as a consequence of the change in deformation mechanism.

The microvoids and highly stretched PS lamellae appear in the deformation bands [Fig. 8(a)]. The macroscopic elongation of the sample, however, is limited by the local nature of deformation. The deformation zones look similar to the crazes observed in thermoplastics and their rubber-modified grades.¹ The PS lamellae in the deformation zones are extremely stretched ($\lambda > 4$) and partly separated by microvoids

and partly by stretched PB lamellae. The observed macroscopic strain at break of 34% in this sample [see Fig. 6(b)] is contributed almost alone by the stretched PS lamellae in these deformation bands.

The transition in deformation mechanism from homogeneous plastic deformation (in pure block copolymer; Fig. 7) to the formation of the local crazelike deformation zones [in the blends; Fig. 8(a)] is obviously reflected in an abrupt change in macroscopic behavior of the tensile specimens and can be correlated with the morphology of the investigated samples. In particular, the deformation mechanisms in the samples with layered structures can be dictated by the thickness of the glassy PS layers. For example, Figure 10 compares the distribution of PS lamellae in the pure star block copolymer and a blend containing 20 wt % polystyrene. It can be easily recognized that the transition from homogeneous plastic flow of the PS lamellae (e.g., Fig. 7) to the formation of local deformation zones [e.g., Fig. 8(a)] occurs when the thickness of polystyrene lamellae reaches a value of about 30 nm. This observation provides strong support to the mechanism of thin layer yielding discussed in Michler et al.¹²

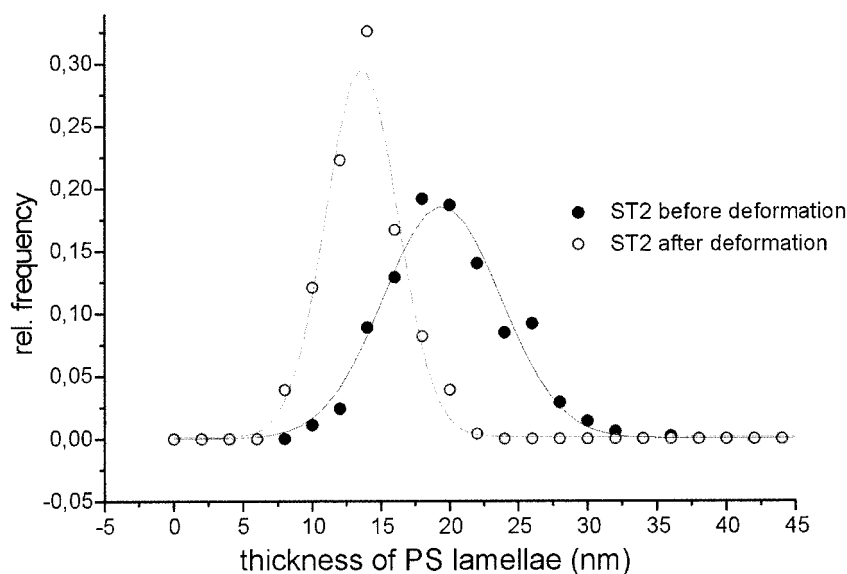


Figure 9 Distribution of PS lamella thickness in ST2-S74 before and after deformation determined by evaluating the corresponding TEM micrographs.

The localization of deformation at the regions of higher polystyrene content (i.e., PS lamellae having thickness in the range ≥ 30 nm), resulting in a decrease in macroscopic elongation at break, was further supported by HVEM investigation.¹⁵ The HVEM micrographs of the strained semithin sections of the blends containing 20 and 40 wt % GPPS demonstrated that the formation of crazelike deformation zones was mainly localized at the strips of thick polystyrene layers. In particular, the mechanism of craze termination was observed in the HVEM.¹⁵ As the craze grew and reached the region of lower polystyrene content, the stress at the craze-tip could be relieved by the plastic deformation of the PS lamellae leading to an arrest of the advancing craze.

In several heterogeneous polymeric systems, including styrene/butadiene diblock copolymers and weakly segregated block copolymers, cavitation has been accepted as a dominating deformation mechanism where the plastic deformation of the brittle phase occurs by its micronecking and subsequent drawing.^{29,30} The micromechanism is characterized by the cavitation in the rubbery phase in such systems. A closer look at TEM micrographs in Figure 8(a) reveals that microvoid formation has occurred in the polystyrene phase at several locations, which is in agreement with the principle of thin layer yielding. Above a critical thickness D_c , PS lamellae cannot plastically flow and should undergo cavitation leading to the formation of crazelike zones.

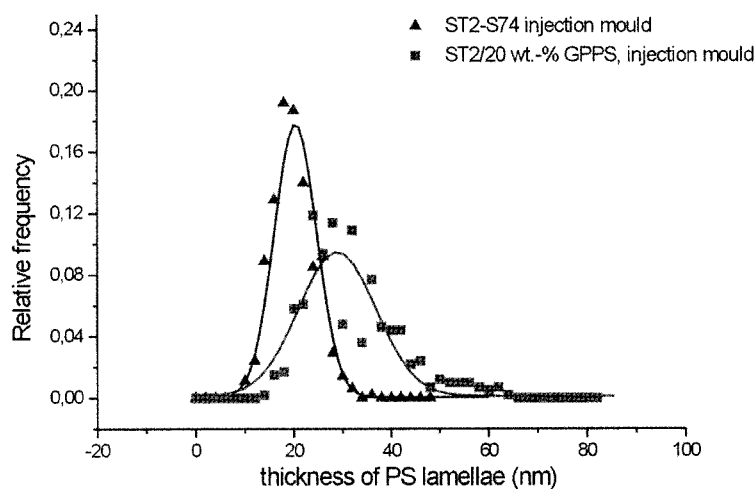


Figure 10 Distribution of PS lamella thickness in the star block copolymer and a blend containing 20 wt % GPPS.

At higher PS content, new kinds of deformation zones were observed by TEM [e.g., Fig. 8(b)]. Narrow, long, and sharp-edged deformation zones were found in the blends having GPPS content ≥ 40 wt % where the lamellae are simply kinked relative to the deformation direction (or the lamellae orientation direction).

Formation of such deformation bands [as those in Fig. 8(b)] in the block copolymers under tensile loading conditions has not been reported yet. The lamellae inside these bands are tilted at an angle of about 50° with respect to the strain direction. These bands resemble the kink bands observed recently by Polis et al.^{31,32} in a lamellar diblock copolymer under shear deformation. With respect to the orientation of the tilted lamellae with the loading direction, these bands resemble the classical shear bands as observed in glassy polymers.^{1,33} Relative to the orientation of the bands themselves, however, these structures look like crazes.

The lamellae in these crazelike zones are only slightly stretched, which results in much lower macroscopic elongation of the sample [Fig. 8(b)]. In contrast, the kink bands observed by Polis et al.^{31,32} in a lamellar diblock copolymer under shear deformation were formed simply by the rotation of lamellae and their thickness remained practically unchanged.

Lamellar rotation at the preferential slip planes have been mentioned as being responsible for kink-band formation by Polis et al.^{31,32} In our case, the mechanism of the evolution of the deformation bands with lamellae tilted at about 50° with the deformation direction, as if they were shear bands, is not clear and will be further investigated. In the line of recent studies on block copolymers having pentablock³⁴ or star architectures,³⁵ which showed a transition from crazing to shear deformation, so far it can only be assumed that those structures might have their origin in the tendency of star block copolymer systems toward shear deformation.

CONCLUSIONS

The results discussed in this article may be summarized as follows.

1. Injection-molded blends of the tapered styrene/butadiene star block copolymer with the general-purpose polystyrene (GPPS) showed no macrophase separation leading to the optically transparent product. The increase in the thickness of a part of the PS lamellae with increasing PS content solidly suggested the incorporation of the added PS to the polystyrene blocks of the star block copolymer. Furthermore, the added homopolystyrene distributed inhomogeneously

in the block copolymer, even leading to the formation of thick homopolystyrene layers.

2. Both the micromechanical and the mechanical behavior of the blends were strongly influenced by the total polystyrene content. A transition in deformation mechanism from the homogeneous plastic flow of PS lamellae to the formation of crazelike deformation zones was observed as the thickness of PS lamellae reached about 30 nm, supporting the mechanism of thin layer yielding proposed earlier.
3. At higher PS content, deformation structures revealed by the TEM resembled the "kink bands" observed recently in lamellar diblock copolymers subjected to shear deformation. These bands possessed the characteristics of both the crazes and shear bands.

The formation of crazelike deformation zones with shearlike components is not fully understood and will be further investigated. Future studies should also be concentrated on the influence of block copolymer architecture on the phase behavior and micromechanical behavior of the block copolymer/PS blends. Determination of exact critical thickness and its dependency on the temperature and strain rate is under way.

This research was funded by the Kultusministerium des Landes Sachsen-Anhalt (Project: Neue Funktionswerkstoffe auf der Grundlage schwachentmischter Blockcopolymere). The authors thank Prof. W. Grellmann (Institut für Werkstoffwissenschaft, Halle) for making the tensile testing possible. R.A. acknowledges the research scholarship from the Max-Buchner-Forschungstiftung (MBFSt 6052).

References

1. Michler, G. H. *Kunststoff-Mikromechanik-Morphologie, Deformations- und Bruchmechanismen*; Carl Hanser Verlag: Munich, 1992.
2. Bucknall, C. B. In *The Physics of Glassy Polymers*; Haward, R. N., Young, R. J., Eds.; Chapman & Hall: London, 1997; Chapter 8, p 363.
3. Hamley, I. W. *The Physics of Block Copolymers*; Oxford Science Publications: Oxford, UK, 1998.
4. Bates, F. S.; Fredrickson, G. H. *Phys Today* 1999, 2, 32.
5. Bates, F. S.; Fredrickson, G. H. In *Thermoplastic Elastomers*, 2nd ed.; Holden, G., Legge, N. R., Quirk, R. P., Schroeder, H. E., Eds.; Hanser Publishers: Munich, 1998; Chapter 12, p 336.
6. Hasegawa, H.; Hashimoto, T. In *Comprehensive Polymer Science*, Suppl. 2; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: London, 1996; p 497.
7. Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* 1994, 27, 6532.
8. Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* 1992, 25, 2645.
9. Hashimoto, T.; Tanaka, T.; Hasegawa, H. *Macromolecules* 1990, 23, 4378.
10. Adhikari, R.; Michler, G. H.; Huy, T. A.; Ivankova, E.; Godehardt, R.; Lebek, W.; Knoll, K. *Macromol Chem Phys* 2003, 204, 488.

11. Knoll, K.; Nießner, N. *Macromol Symp* 1998, 132, 231.
12. Michler, G. H.; Adhikari, R.; Lebek, W.; Goerlitz, S.; Weidisch, R.; Knoll, K. *J Appl Polym Sci* 2002, 85, 683.
13. Adhikari, R.; Michler, G. H.; Lebek, W.; Goerlitz, S.; Weidisch, R.; Knoll, K. *J Appl Polym Sci* 2002, 85, 701.
14. Fabis, B. F. In *Polymer Blends, Vol. 1: Formulation*; Paul, D. R., Bucknall, C. B., Eds.; Wiley-Interscience: New York, 2000; Chapter 16, p 501.
15. Ivankova, E.; Adhikari, R.; Michler, G. H.; Weidisch, R.; Knoll, K. *J Polym Sci Part B: Polym Phys* 2003, 41, 1157.
16. Yamaoka, I. *Polymer* 1996, 37, 5343.
17. Yamaoka, I. *Polymer* 1998, 39, 1081.
18. Löwenhaupt, B.; Hellmann, G. P. *Polymer* 1991, 32, 1065.
19. Hashimoto, T.; Izumitani, T.; Ono, K. *Makromol Chem Macromol Symp* 1995, 98, 925.
20. Meijer, H. E. H.; Govart, L. E. *Macromol Chem Phys* 2003, 204, 274.
21. Lodge, T. P. *Macromol Chem Phys* 2003, 204, 265.
22. Hashimoto, T.; Fujimora, M.; Saito, K.; Kawai, H.; Diamant, J.; Shen, M. In *Advances in Chemistry Series: Multiphase Polymers*; Cooper, S. L., Estes, G. M., Eds.; American Chemical Society: Washington, DC, 1979; p 257.
23. Kawai, H.; Hashimoto, T.; Miyoshi, K.; Uno, H.; Fujimura, M. *J Macromol Sci Polym Phys* 1980, 17, 427.
24. Cohen, Y.; Albalak, R. J.; Dair, B. J.; Capel, M. S.; Thomas, E. L. *Macromolecules* 2000, 33, 6502.
25. (a) Wu, S. *Polymer* 1985, 26, 1855; (b) Wu, S. *J Appl Polym Sci* 1988, 35, 549.
26. van der Sanden, M. C. M. Ph.D. Thesis, Technical University, Eindhoven, The Netherlands, 1993.
27. Ebeling, T.; Hiltner, A.; Baer, E. *J Appl Polym Sci* 1998, 68, 793.
28. Kerns, J.; Hsieh, A.; Hiltner, A.; Baer, E. *Macromol Symp* 1999, 147, 15.
29. Schwier, C. E.; Argon, A. S.; Cohen, R. E. *Polymer* 1985, 26, 1985.
30. Weidisch, R.; Ensslen, M.; Michler, G. H.; Arnold, M.; Buddhe, H.; Höring, S.; Fischer, H. *Macromolecules* 2001, 34, 2528.
31. Polis, D. L.; Winey, K. I. *Macromolecules* 1998, 31, 3617.
32. Polis, D. L.; Smith, S. D.; Terrill, N. J.; Ryan, A. J.; Morse, D. C.; Winey, K. I. *Macromolecules* 1999, 32, 4668.
33. Young, R. J. *Introduction to Polymer Science*; Chapman & Hall: London, 1989.
34. Ryu, C. Y.; Ruokolainen, J.; Fredrickson, G. L.; Kramer, E. J.; Hahn, S. F. *Macromolecules* 2002, 35, 2157.
35. Weidisch, R.; Laatsch, J.; Michler, G. H.; Arnold, M.; Schade, B.; Fischer, H. *Macromolecules* 2002, 35, 6585.