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ORIGINAL CONTRIBUTION

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Morphology and deformation behaviour of SBS/PS blends: a combined microscopic and spectroscopic study

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Abstract Correlation between morphology and micromechanical deformation behaviour of blends consisting of a lamellae-forming linear styrene/butadiene block copolymer and polystyrene homopolymer (hPS) was studied by different microscopic techniques (transmission electron microscopy and scanning electron microscopy) and rheo-optical Fourier transformed infrared spectroscopy. Attributable to a change in morphology from well-ordered lamellae to a distorted one, a transition in deformation mechanism from homogeneous plastic flow of the lamellae to formation of local craze-like deformation zones was observed on addition of hPS. The latter led to a drastic reduction in elongation at break. An abrupt depression in the degree of orientation of the polystyrene (PS) and the polybutadiene (PB) phases in the blends suggested that the failure occurs at the interface between the added hPS and PS blocks of the block copolymer.

Keywords Polystyrene-block-polybutadiene-block-polystyrene block copolymer · Morphology · Micromechanical mechanism · Crazes · Electron microscopy

Introduction

Block copolymers belong to the heterogeneous soft matters, in which the molecules self-assemble into an array of periodic nanostructures via intramolecular phase separation [1]. The periodicity of these structures lies in the same order as the gyration radius of the corresponding macromolecules. The type and the size-scale of these structures are controlled by various parameters such as molecular weight, composition, molecular architectures etc. [1, 2, 3, 4, 5, 6, 7]. A precise control of these structures enables the tailoring of their mechanical properties over a wide range [8, 9, 10].

The phase morphology of heterogeneous polymer systems like block copolymers and their blends is usually characterised by transmission electron microscopy (TEM) and scattering techniques such as small angle X-ray scattering (SAXS), small angle neutron scattering (SANS) etc. [1, 11, 12, 13, 14, 15]. Earlier studies focused on the equilibrium behaviour of blends consisting of a diblock copolymer and a homopolymer. Recently, investigations on block copolymer/homopolymer mesoblends and binary graft copolymer/homopolymer blends were reported [16, 17]. Such studies are of great scientific importance as they provide an insight into the thermodynamics and phase behaviour of these polymers. However, the equilibrium structures are of less practical significance. In addition, for technical applications, it is important to use the styrene/diene block copolymers, in which both the ends of the flexible diene molecules are anchored by glassy components [e.g., polystyrene-block-polybutadiene-block-polystyrene (SBS) triblock copolymer]. The latter is essential for the mechanical stability of the component chains

[8]. Furthermore, the molecular weight should be high enough to ensure the strength of the resulting materials, but not so high as to worsen the rheological properties.

The SBS triblock copolymers are often mixed with general-purpose polystyrene (GPPS) to reduce price and to optimise mechanical properties. The samples are prepared via common processing techniques such as extrusion, blow moulding, injection moulding etc. An important aspect that has to be taken into account in this respect is the molecular weight of the added polystyrene homopolymer (hPS) relative to that of the polystyrene (PS) block of the copolymer (discussed in detail by Hamley in [1]). The tendency to macrophase-separation increases as hPS molecular weight increases. Low molar mass hPS is more soluble with the block copolymer but does not contribute positively to the mechanical properties of the mixtures. On the other hand, hPS with higher molecular weight tends to separate into macroscopic domains leading to a loss of transparency and deteriorated mechanical properties Thus, optimum processing conditions are critical in designing application-relevant physical properties of such blends.

It should be noted that the nature and orientation of resulting nanostructures of block copolymer systems can be markedly altered by changing the processing conditions. For example, the impact of external forces such as shear, electric field etc. leads to a large range of non-equilibrium morphologies. Consequently, the materials show morphological features and mechanical properties quite different from those of the equilibrium state.

A great deal of work has been carried out on phase behaviour of binary blends consisting of styrene/diene diblock copolymer and homopolymers (e.g., hPS) [1]. In previous studies by our research group, details on the deformation micromechanisms in blends comprising styrene/butadiene star block copolymer and hPS were reported [18, 19]. Special emphasis was put on the impact of morphology on the deformation behaviour of these systems [18]. However, there has been no in-depth systematic study leading to detailed understanding of the structure-property correlation in binary SBS/hPS blends, especially using samples prepared by common processing techniques, as yet. In this work, we report on the phase morphology and deformation behaviour of blends consisting of a linear SBS triblock copolymer and general-purpose hPS.

Materials and methods

Materials and sample preparation The characteristic data of the materials used are indexed in Table 1. The copolymer used in this work was an asymmetric linear SBS triblock copolymer having PS outer blocks of different molecular weights (the molecular weight ratio is approximately 5). The total PS volume content was 74%. The block copolymer was synthesised by butyllithium initiated sequential living anionic polymerisation. After the polymerisation of the longer outer PS block, styrene and butadiene monomers were simultaneously added into the reaction mixture in order to introduce a tapered interface. Then, a final charge of styrene monomer was added to produce the second outer PS block. The hPS was GPPS prepared by radical polymerisation.

Table 1 Characteristic data of the samples used. Number average (M_n) and weight average (M_w) molecular weights determined by gel permeation chromatography

Sample code	M_n (g/mole)	M_w/M_n	PS content (Vol.%)
SBS	82,000	1.15	74
hPS	82,000	2.03	100

After mixing the blend components in an extruder, tensile bars were prepared by injection moulding. The mass and the mould temperature were 225 °C and 45 °C, respectively. The blends were prepared with 20, 40, 60, 80 wt% of hPS.

Electron microscopy The phase-separated morphologies of the samples before and after deformation were studied by means of TEM (200 kV TEM, Jeol JEM 2010). Ultrathin sections (ca. 70 nm thick) for the TEM were prepared using a Leica Ultramicrotome. In order to compare the morphology of the samples, the sections for the TEM were always taken from the similar locations (ca. 0.25 mm beneath the surface at the middle of the bar). Prior to the electron microscopic investigation, the butadiene phase was selectively stained by osmium tetroxide (OsO_4).

Fracture surface of the specimens broken in tensile tests were analysed by scanning electron microscope (SEM) (Jeol JSM 6300). The fracture surfaces were sputter-coated with an approximately 10 nm gold layer before the SEM examinations.

Tensile testing Injection-moulded tensile specimens according to ISO 527 were strained at a cross-head speed of 50 mm/min using a universal tensile machine (Zwick) at room temperature (23 °C). At least ten specimens of each sample were tested.

Fourier-transformed infrared spectroscopy The deformation of individual phases at the molecular level under uniaxial strain was monitored by means of Fourier-transformed infrared spectroscopy (FTIR) spectroscopy. Orientation of each component was measured in terms of the degree of orientation (*f*) by evaluating their characteristic absorption bands using Eq. 1.

$$f = \frac{R-1}{R+2} \cdot \frac{R_0+2}{R_0-1} \quad (1)$$

where $R_0 = 2\cot^2\psi$ is the dichroic ratio of perfectly aligned chains oriented parallel to the draw direction and ψ is the angle between the direction of the vibrational transition moment and the polymer chain axis.

$$R = \frac{A_{//}}{A_{\perp}} \quad (2)$$

R in Eq. 2 is the dichroic ratio while $A_{//}$ and $A_{\perp}$ stand for absorbance of light polarised parallel and perpendicular to the strain direction, respectively.

For FTIR investigations, films approximately 40 μm thick were prepared by pressing the granules of the block copolymer samples. The films, with dimensions of 20×10 mm, were successively stretched in a special tensile device integrated to an IR spectrometer (Perkin Elmer FTIR spectrometer S2000 equipped with a MCT detector). Spectra in the range 700–3,500 cm^{-1} were examined.

Results and discussion

Morphology of SBS triblock copolymer/hPS blends

The equilibrium morphology of the triblock copolymer was characterised in our previous papers by scanning force microscopy [20, 21]. Here, we address briefly the block copolymer morphology as revealed by TEM in the solution-cast film and an injection moulding.

The block copolymer shows a lamellar arrangement of the microphase-separated structures (Fig. 1). The lamellae have an average spacing of about 31 nm in both solution-cast and injection-moulded samples.

The lamellae in the solution-cast film (Fig. 1a) have random alignments. One occasionally sees “kink boundaries” as well. The microphase-separated structures have no preferential orientation. In contrast, the injection-moulded sample (Fig. 1b) reveals a well defined alignment of the lamellae along the flow direction as a result of shear stress acting during the process of injection moulding.

Representative TEM images of the injection-moulded SBS/hPS blends are presented in Fig. 2. The addition of hPS to the SBS block copolymer leads to a distortion of the lamellar morphology. As in the pure block copolymer, the microphase-separated structures are oriented along the injection direction.

As discussed in the literature [11, 12, 13, 14, 15] and introduced earlier, the phase behaviour of the block copolymer/homopolymer mixtures is governed by the relative length of the hPS chains and the PS block chains of the block copolymer (i.e., the molecular weight ratio, *r*). There is an interplay between microphase separation and macrophase separation, and which effect predominates depends on the relative molecular weight and the composition of the mixture (discussed in detail by Hamley in [1]).

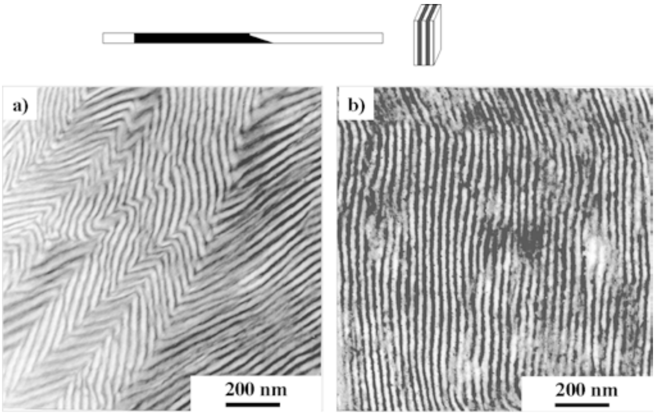


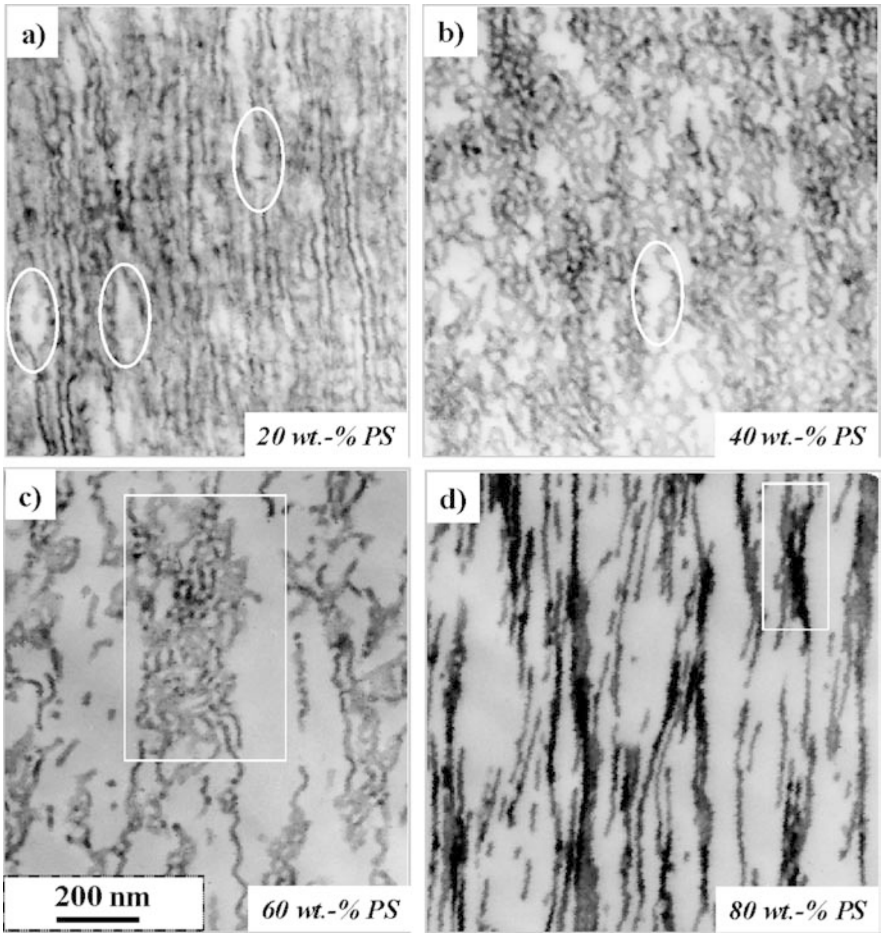
Fig. 1a, b Transmission electron microscopy (TEM) micrographs showing the microphase-separated morphology of the SBS triblock copolymer. **a** Solution-cast film. **b** Injection-moulded sample. Molecular architecture and morphology of the block copolymers (schematic) are presented at the *top*

Feng et al. investigated the miscibility of blends based on the hPS and SBS block copolymers [22, 23] and reported that the miscibility of the blends depends solely on the molecular weight of the homopolymer and the molecular weight ratio (*r*). If the molecular weight of the added hPS is too large (greater than that of the corresponding block of the block copolymer), the majority of the hPS chains cannot penetrate deeply into the block domains of the block copolymers. In this case, the hPS and the block copolymer form separate phases. A similar situation exists in the blends studied in the present work (see Table 1). The longest PS block of the block copolymer has a molecular weight of approximately 50,000 g/mole while the number average molecular weight of the hPS samples is higher (82,000 g/mole). The hPS has a very wide molecular weight distribution. However, the majority of hPS added to the copolymer should macrophase-separate under equilibrium conditions (for details see [18, 24, 25]). One may, nevertheless, anticipate that a part of the low-molecular-weight fraction of the hPS chains might be dissolved by the PS block chain.

The equilibrium morphology of the SBS/hPS blends used in this study was discussed elsewhere [24]. In accordance with our studies on star block copolymer/PS blends [18, 19, 26], macrophase separation between the SBS and hPS was observed [24].

The macrophase separation between added hPS and the block copolymer is strongly suppressed in the

Fig. 2a–d Representative TEM micrographs showing the morphology of the injection-moulded block copolymer/polystyrene (PS) blends: the homopolymer PS content is indicated; injection direction vertical



injection-moulded samples (Fig. 2) leading to a more homogeneous structure. The latter results from the high shear stress during processing via injection moulding and rapid cooling from the melt. Under these circumstances, the melt has not enough time to relax to develop the equilibrium morphology. At lower hPS concentration, the PS lamellae seem to swell locally leading to the formation of regions with thicker PS domains (areas inside white circles in Fig. 2). At higher hPS content, hPS forms the matrix embedding the microphase-separated block copolymer inclusions (areas inside white rectangles in Fig. 2). With increasing hPS content, the lamellar structure of the block copolymer is continuously destroyed.

In the case of a compatible block copolymer/homopolymer blend, one would expect a continuous widening of the PS lamellae with increasing hPS content [11, 12, 13]. However, this was not the case in the investigated blends, which clearly represent an incompatible system as discussed above.

The results discussed so far are in line with those obtained on the basis of thermal methods [24]. Using different microscopic techniques and dynamic mechanical analyses of the present system, we concluded that the chains of hPS and SBS block copolymer are not compatible. The large mismatch in the molecular weight of the PS block in the block copolymer and the hPS chains was regarded as the main cause of the observed incompatibility

Because the polymer blends studied were processed by injection moulding, in which the melt is subjected to a large shear deformation and cooled rapidly to a temperature well below the glass transition temperature of either phase, the structures formed deviate far from equilibrium ones.

Owing to a molecular weight larger than that of the PS block of the block copolymer, the hPS chains cannot distribute uniformly during processing, giving rise to lateral widening of the PS lamellae. As a result, an inhomogeneous morphology results, in which regions rich in PS or block copolymer are formed as demonstrated by our recent studies on blends of a star block copolymer and hPS.

To summarise this section, the morphology of the investigated system is largely controlled by processing of the blend components. The resulting morphologies

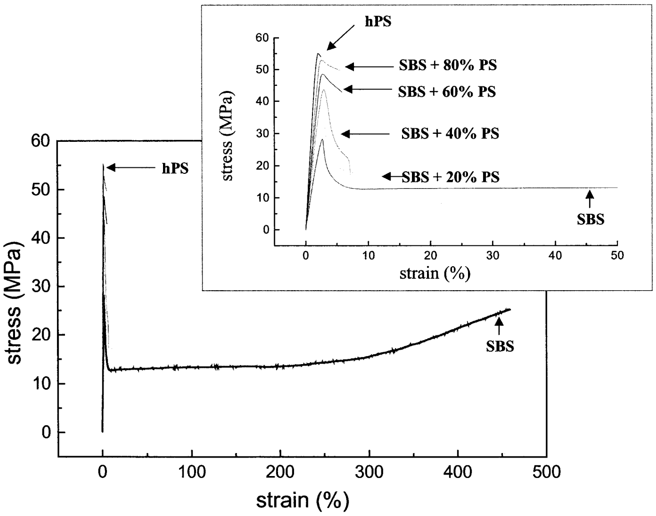


Fig. 3 Stress-strain curves of the investigated blends; injection-moulded tensile specimens according to ISO 527 were strained at room temperature (23 °C) at a rate of 50 mm/min. *PS* Polystyrene. *SBS* polystyrene-block-polybutadiene-block-polystyrene, *hPS* homopolymer PS

consist mainly of nanostructures, the macroscopic phase separation being suppressed during processing.

Mechanical properties

The stress-strain behaviour of injection-moulded blends is presented in Fig. 3. Young's modulus and yield stress are plotted in Fig. 4 as a function of composition (hPS percent weight, Φ_{hPS}). At a first glance it can be seen that the elongation at break drops drastically from over 400% to about 11% when 20 wt% hPS is added to the SBS triblock copolymer. Similar behaviour was observed in the blends of star block copolymer and GPPS [19]. However, the drop in the strain at break in the blends with star block copolymer was significantly lower than that with the linear triblock copolymer. As can be derived from Fig. 4, important macroscopic properties such as Young's modulus and yield stress change almost linearly with the blend composition. The increased overall PS content makes the samples more resistant against plastic deformation, thereby increasing the yield stress. As PS at room temperature is a polymer glass, its addition to the block copolymer increases the amount of stiff material. As a result, the measured value of Young's modulus shows a linear dependence on the added hPS content.

The surprisingly large drop of elongation at break observed for an hPS content of 20 wt% may be correlated with the strong incompatibility between the homopolymer and the block copolymer. A macroscopic stress whitening was observed in the investigated blends during tensile testing, indicating the formation of localised deformation zones. The added hPS was found to be separated, mainly in the form of thick PS layers (results not shown here; thickness in the range of 200 nm). Even at the lower hPS concentration the lamellar morphology was destroyed. The premature fracture of the thick PS layers and crack initiation and propagation from regions of weak physical binding might have been the cause of a drastic change in the elongation at break.

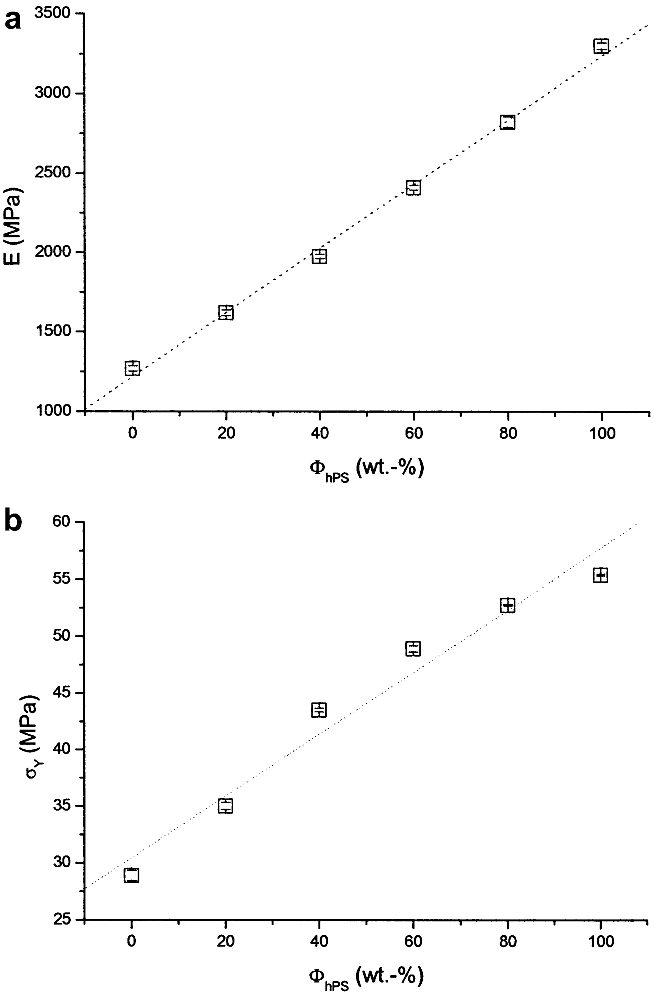


Fig. 4a, b Young's modulus (**a**) and yield stress (**b**) of the blends as a function of composition; injection-moulded bars were tested at room temperature (23 °C) at a rate of 50 mm/min

The SBS block copolymers having lamellar morphology (e.g., in this study) with a molecular weight of circa 100,000 g/mole show a good level of strength and ductility. A polystyrene-block-polybutadiene (SB) diblock copolymer having similar morphology and possessing identical molecular weight shows poor mechanical properties. As addressed by a recent study, the presence of an AB diblock content in ABA triblock copolymers leads to worsening of mechanical strength even without altering the nature of microphase-separated structure [27]. In the light of those findings, one can deduce that a particular microphase morphology is a necessary, but not an adequate, condition for a specific mechanical behaviour.

We mentioned earlier that the morphology of the injection mouldings studied here is far from equilibrium. Thus, care should be taken while describing the morphology formation in these non-equilibrium systems. Owing to the relatively low molecular weight of PS outer blocks of the triblock copolymer, the mechanical coupling (entanglements) between the added hPS and PS block is poor, which can be regarded as a reason for the poor mechanical properties of the SBS/hPS blends studied.

Micromechanical behaviour

The macroscopic mechanical properties of the SBS/hPS blends determined by the uniaxial tensile testing can be directly correlated with the structural changes due to mechanical loading. Details on the deformation behaviour of SBS/hPS blends using TEM have been discussed in our recent papers [18, 19, 25]. Particular emphasis was put on the impact of morphology and blend composition in these studies. In this paper, our goal is to correlate the deformation phenomena occurring on different length scales in such blends using microscopic and FTIR techniques. Thus, we concentrate on deformation behaviour of the pure block copolymer and a blend containing 40 wt% hPS. This is also the composition range usually recommended for producing injection-moulded parts from SBS/hPS mixtures. First, we analysed the micromechanical behaviour of these samples with the aid of SEM and TEM.

In Fig. 5, the dimensions of the selected tensile specimens after deformation are compared with that of an unstrained reference tensile bar. The width (and hence the cross) of the middle part of the deformed tensile bar of the pure block is much smaller than that of the reference sample, which reflects a high degree of plastic deformability of the block copolymer.

The deformation of test specimens took place via the formation of a neck and its subsequent elongation during tensile testing. The large stretching of the block copolymer tensile bar correlates well with its large elongation at break. In contrast, the blend broke in a brittle manner, in which the deformation was localised in a small region close to the fracture surface.

The study of deformation behaviour was extended by the analysis of fracture surface morphology by SEM, which provides information on the structural changes on a microscopic scale. The fracture surface morphology does not reveal all the details of micromechanical processes of deformation. However, the information gained may be helpful in understanding some macroscopic phenomena such as crack propagation mechanisms, and in following the micromechanical behaviour just before the specimen fracture. In Fig. 6 and Fig. 7 are shown the morphology of the fracture surface (and an area close to the fracture surface, Fig. 7) of a pure block copolymer and a blend containing 40 wt% hPS.

The ductile behaviour of the pure SBS block copolymer during uniaxial tensile testing is manifested in the fracture surface morphology as well. The fracture surface is characterised by a dense array of fibrillar structures enclosing large holes (Fig. 6). The origin of these holes, several tens of micrometres in diameter and several micrometres deep, is not clear. However, their growth may be regarded as a consequence of extremely high plastic deformation leading to a high ductility.

The morphology of the fracture surface (and the surface close to it) in SBS/40 wt% hPS appears to be entirely different from that of the pure block copolymer (Fig. 7). There are no pronounced holes and extensively drawn material on the fracture surface. The mode of crack propagation seems to be predominantly unstable, leading to a brittle fracture. There are often regions with “folded ribbon”-like structures, which might have been formed by the snap-back of the highly stretched material (Fig. 7c). Similar structures were observed in binary

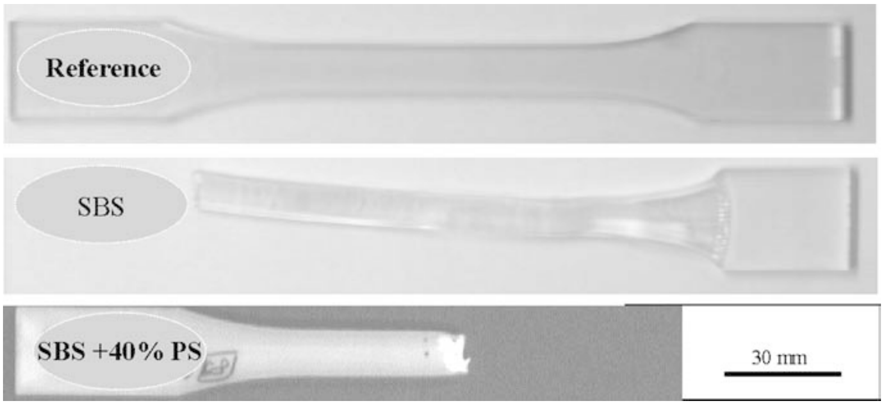


Fig. 5 Optical micrographs of the tensile bars of selected injection-moulded samples broken in tensile testing compared with an undeformed reference tensile specimen

block copolymer blends, which showed very tough behaviour under impact loading conditions [28]. Therefore, these structures seem to be correlated with tough material behaviour. It should be, however, noted that the dimension of these structures (a few micrometres) has no correspondence with that of the block copolymer nanostructures (several nanometres).

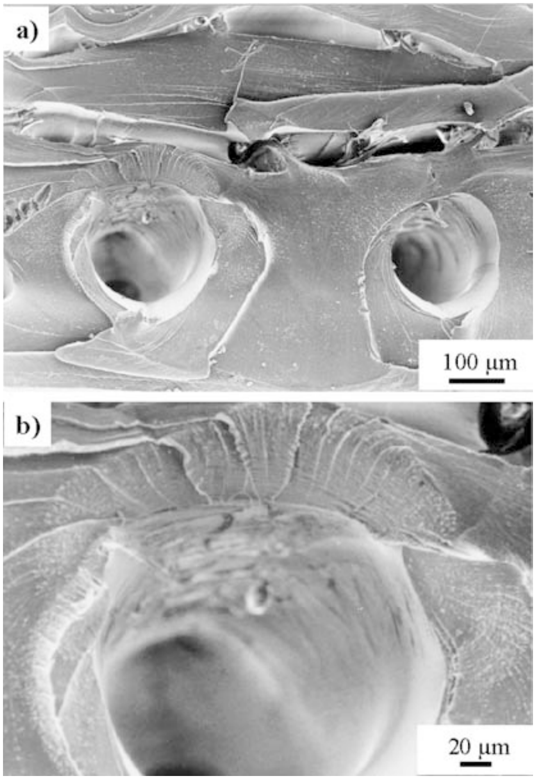
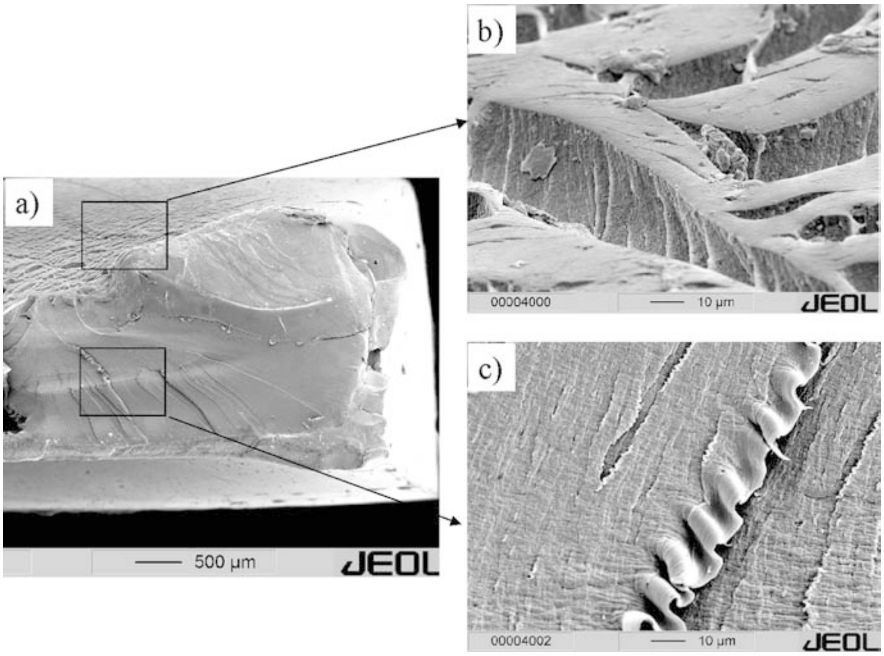


Fig. 6a, b Lower (**a**) and higher (**b**) magnifications of scanning electron microscope (SEM) micrographs showing the deformation structures of the SBS triblock copolymer; fracture surface of the tensile specimens strained at a rate of 50 mm/min at 23 °C

Most conspicuously, the specimen surface at the vicinity of the fracture surface is occupied by numerous cracks running down into the sample (Fig. 7b). These cracks suggest a surface-flaw-assisted crack initiation and propagation, resulting in brittle behaviour.

Deeper insight into the strain-induced structural changes was obtained by TEM analysis of the specimens deformed in tensile testing. TEM micrographs in Fig. 8 and Fig. 9 present the strain-induced structural changes of the pure SBS block copolymer and a blend with 40 wt% hPS, respectively. In Fig. 1 (b) and Fig. 8 (a) are TEM pictures of identical magnifications. The comparison of these micrographs makes it evident that after deformation both the lamellar thickness and long period in the SBS have been drastically reduced. The mean PS lamella thickness was reduced from about 15 nm to about 9 nm. The original lamellar structure of the block copolymer has been destroyed due to deformation. The PS lamellae appear to consist of alternating thicker and thinner regions, which are obviously formed by the large plastic yielding of the lamellae. The mechanism has been described in our previous paper as "thin-layer yielding" [25]. Similar necking and drawing of glassy PS lamellae was reported recently by Cohen et al. [29, 30] and previously by Hashimoto et al. as well [31, 32]. The necking and drawing of the glassy lamellae may be visualised as being analogous to the necking and drawing of the tensile specimen, and is the reason for the high ductility of the SBS triblock copolymer.

Fig. 7a–c Lower (**a**) and higher (**b**, **c**) magnifications of SEM micrographs showing the deformation structures of the SBS/40 wt% hPS blend; fracture surface of the tensile specimens strained at a rate of 50 mm/min at 23 °C



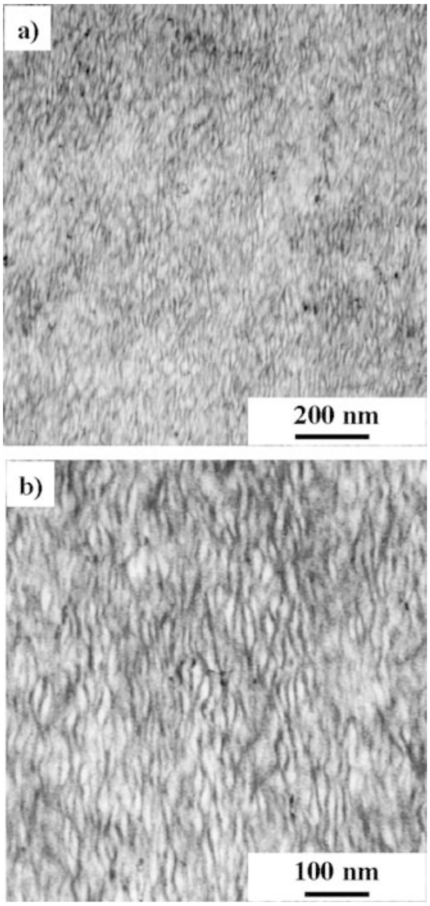


Fig. 8a, b Lower (**a**) and higher (**b**) magnifications of TEM images showing the deformation structures of the SBS triblock copolymer; deformation direction vertical; morphology of the undeformed sample in Fig. 1*b*

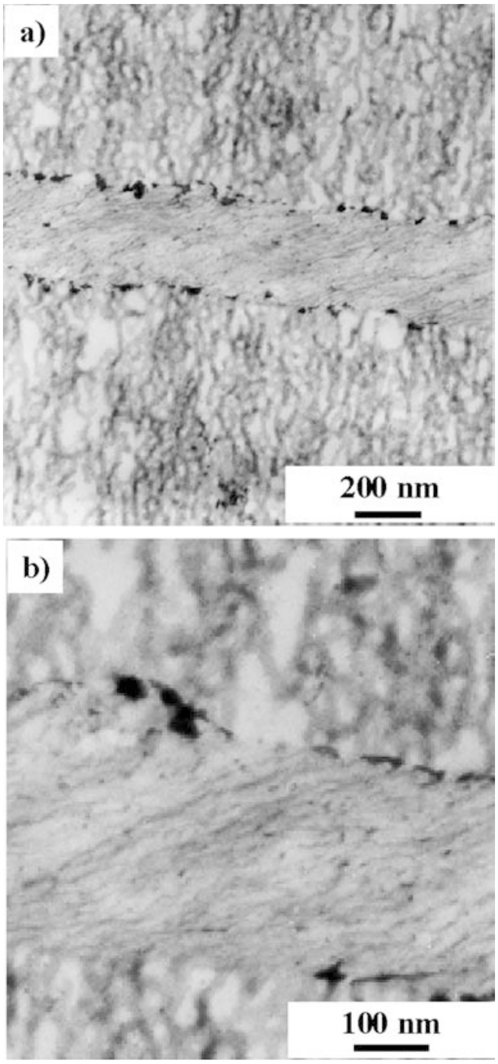


Fig. 9a, b Lower (**a**) and higher (**b**) magnifications of TEM images showing the deformation structures of the SBS/40wt% hPS blend; deformation direction vertical; morphology of the undeformed sample in Fig. 2b

It has been already discussed that the strain at break was drastically reduced when 20 wt% hPS was added to the SBS block copolymer. The reason lies in the fact that, in contrast to the pure block copolymer, a pronounced localisation of deformation was observed in all the blends. It is obviously associated with a change in deformation mode. As can be read from the stress-strain diagram of the blends (Fig. 3), the blends showed ductile failure accompanied by necking and drawing of the tensile specimens up to 40 wt% hPS. However, the macroscopic strain is limited by the localisation of deformation in a small region.

The strain-induced structural changes in a blend containing 40 wt% hPS is shown by TEM micrographs of the yielded region close to the fracture surface in Fig. 9. Craze-like deformation bands were observed perpendicular to the principal stress axis. The sharp edged craze-like band in Fig. 9 shows the fine fibrillar structures, consisting of both PS (grey regions) and polybutadiene (PB) (dark regions) phases. The fibrillar structures are slightly inclined to the deformation direction signalling the tendency towards the shear deformation. Such deformation structures were observed in the blend of star block copolymer with PS as well [25, 26]. A dense deposition of the OsO_4 (dark spots) at edges of these deformation bands suggests the formation of microvoids at the boundary between deformed material and the undeformed one.

The extremely fine structure of the fibrils inside the deformation band is an indication of a very ductile local deformation of the sample. However, macroscopic strain of the specimens is limited by the localisation of deformation. Eventual failure might occur by the growth of microvoids formed at the boundary of these deformation zones leading to cracks and crack propagation.

To summarise the results of microscopic examination via TEM, the premature failure of tensile specimens of SBS/hPS blends resulting in a very small strain at break was an expression of an extremely local nature of deformation. The latter should be connected with the molecular parameter viz. the molecular weight differences between the hPS and PS outer blocks of the block copolymer. The incompatibility of the added hPS may lead to a microvoid formation at the boundary between the PS block and hPS chains that acts as a precursor of catastrophic crack propagation.

Molecular orientation behaviour

The degree of orientation of individual phases in the block copolymer and a blend (SBS/40 wt% hPS) is plotted as a function of nominal strain in Fig. 10. Infrared (IR) absorption bands at wavenumbers 967 cm^{-1} and 1,028 cm^{-1} were selected for the quantitative evaluation of orientation of PB and PS phases, respectively. The band at 967 cm^{-1} was attributed to the out-of-plane wagging vibration of *trans* CH = CH double bonds [33], and its transition moment angle was recognised to be perpendicular to the chain axis [34]. On the other hand, the absorption band at 1,028 cm^{-1} was attributed the ν_{18a} in-plane CH bending mode vibration of the aromatic ring [35]. This vibration possesses a dipole moment vector perpendicular to the chain axis [35]. A detailed account of the orientation behaviour of styrene/butadiene block copolymers with different morphologies may be found in [36].

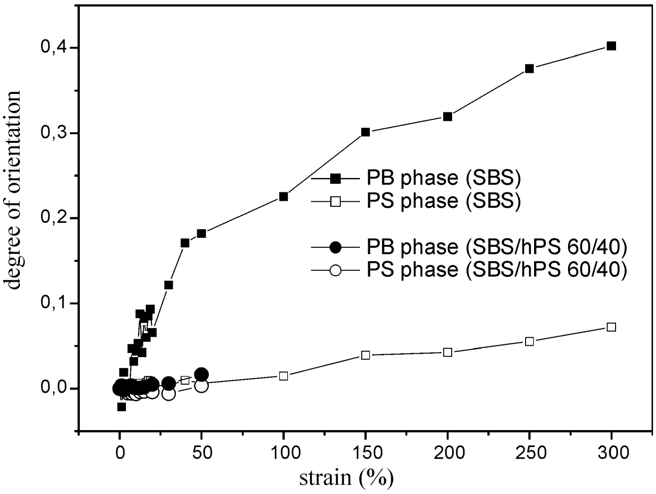


Fig. 10 Degree of orientation of the individual phases [PS and polybutadiene(*PB*)] in the SBS triblock copolymer and an SBS + 40% hPS blend measured by Fourier-transformed infra red spectroscopy

The direct comparison of the orientation behaviour of SBS and that of its blends with hPS (Fig. 10) makes it evident that both PS and PB phases in the former orient more strongly than that in the latter. The higher degree of orientation also dictates a higher degree of deformation in the individual components. The degree of orientation of the soft PB phase in the SBS block copolymer was significantly higher than that of the glassy PS phase (for detail see [36]). In contrast, both the constituents in the blend studied show almost no orientation.

As mentioned earlier the well-defined lamellar morphology of the parent SBS triblock copolymer appears to be strongly disturbed in the blends with hPS. In the case of good compatibility between the added hPS and the block copolymer, one would expect, depending on the molecular weight of the added hPS relative to that of the PS block, either continuous widening of PS lamellae or transition to a morphology corresponding to a higher PS content. In the present case, since the blends represent a relatively incompatible system due to the higher molecular weight of hPS chains than of PS block, the hPS chains are not strongly coupled with the PS blocks. Thus, the boundary between the hPS and PS block chains may be regarded as “weak points”. As a result, the applied stress acts neither in the PS nor in the PB phase but at these points. As a consequence, microcracks which might have formed at the weak sites grow to cause a premature failure. Hence, none of the phases (neither PS nor PB) in the blends undergoes significant molecular orientation.

Whether the poor coupling between the hPS and PS block chains lies behind the poor orientation of the individual phases in the investigated blends can be checked by analysing the selective orientation behaviour of a pure block copolymer having comparable chemical composition. The blend presented in Fig. 10 has a total PS content of about 84 wt%. The degree of orientation of this blend is compared with that of an SBS triblock copolymer (named SBS-75 here) containing 75 wt% PS in Fig. 11. The latter has a cylindrical morphology comprising PS matrix [20]. The detail of the molecular orientation behaviour of this copolymer is described elsewhere [36]. The constituents in the copolymer SBS-75 orient rather strongly, which arises from the presence of stable molecular coupling and entanglements. In this case, the applied stress, which acts directly in the PS matrix upon uniaxial loading, causes an even higher orientation in the PS phase than in the SBS copolymer dealt with in this work.

Conclusions

The results discussed in this paper can lead to the following conclusions.

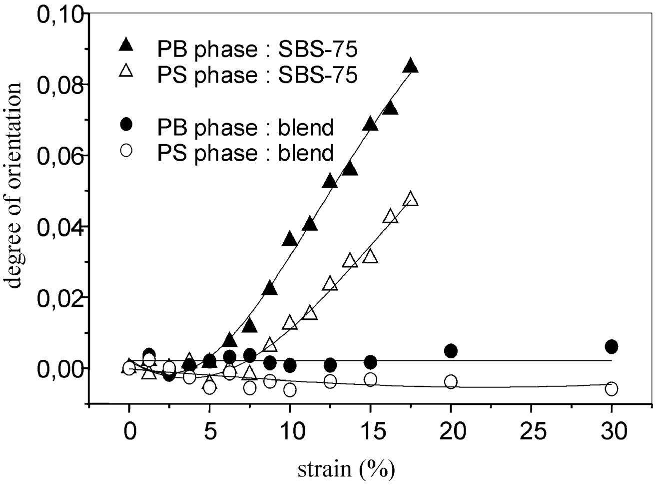


Fig. 11 Degree of orientation of PS and PB phases of the blend studied (total PS content ~ 84 wt%) compared with that of an SBS triblock copolymer having PS matrix (SBS-75; total PS content ~75 wt%)

-1. Morphology: in contrast to the well-ordered lamellar morphology of injection-moulded SBS triblock copolymer, a distorted morphology was observed in the blends. The macrophase separation of the blend components was suppressed by rapid cooling of the melt and high shear stress of the injection moulding process.

-2. Mechanical and micromechanical behaviour: in uniaxial tensile testing, the SBS/hPS blends behaved in a brittle manner even at a low hPS content, while the pure block copolymer showed a highly ductile behaviour. Yield stress and Young's modulus changed almost linearly with composition. The brittle behaviour of the blends was associated with an extreme localisation of deformation in craze-like zones. The premature failure of the blends can be attributed to the poor compatibility between the hPS molecules and PS blocks of the copolymer due to large difference between the molecular weight of added hPS and that of PS block of the copolymer.

-3. Molecular orientation behaviour: the degree of orientation of the soft PB phase in the SBS block copolymer was significantly higher than that of the glassy PS phase. Nevertheless, a remarkable degree of orientation was noticed in the glassy phase as well. In contrast, the degree of orientation in both the phases was nearly zero in SBS/hPS blends. This effect may be attributed to the premature failure at the boundary between hPS chains and PS block chains resulting from a poor coupling between them.

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