Asymmetric PS-*block*-(PS-co-PB)-*block*-PS Block Copolymers: Morphology and Deformation Behaviour of Star Block Copolymer/PS Blends

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ABSTRACT

The morphology and deformation behaviour of blends comprising an asymmetric styrene/butadiene star block copolymer and polystyrene homopolymer (hPS) were investigated by means of transmission electron microscopy (TEM) and uniaxial tensile testing. The hPS samples used had a wide range of molecular weights. In spite of the high polystyrene content, the star block copolymer exhibited a morphology consisting apparently of a rubbery matrix, attributable to its asymmetric architecture and presence of PS-co-PB as soft rubbery blocks. In the blends, depending on the molecular weight and modality of the added hPS and on the composition of the mixtures, different morphologies (ranging from microphase-separated and macrophase-separated ones to a combination of both of them) were observed. Consequently, it was possible to tailor the tensile mechanical properties based on the nature of the nanoscopic morphology of the star block copolymer/PS blends.

KEYWORDS

SBS block copolymers, blends, morphology, mechanical properties, micromechanisms, electron microscopy

INTRODUCTION

Polymer blends are a big component of current scientific research and technology. The principal motivation in this respect is to enhance the desired properties of the individual homopolymers or even to achieve novel properties at attractive costs. Generally, the behaviour of polymer blends depends on the degree of mixing of the components and their mutual interaction. However, the vast majority of polymer pairs are immiscible because of their small change in entropy gain upon mixing. For such polymer blends the mixing and subsequent fabrication procedures are crucial to performance since they determine the interfacial adhesion as well as the final morphology [1].

On the other hand, two immiscible constituents can be chemically linked together to form a block copolymer with fine uniform microdomains whose dimension extend up to tens of nanometers, which is explicitly smaller than the domain size in polymer blends (usually in the order of 1 μm). By suitably controlling the molecular architecture of the macromolecular chains and molecular weight of each constituent, the block copolymers possessing well-defined morphologies endowed with a wide range of thermal and mechanical behaviour can be tailored [2-8].

Styrene/diene block copolymers (e.g., polystyrene-*block*-polybutadiene-*block*-polystyrene, SBS triblock copolymer) are of particular interest, in which both the ends of the flexible diene molecules are anchored by glassy components. This is essential for the mechanical stability of the component chains [6]. Furthermore, the molecular weight should be high enough to ensure the strength, but not too high to worsen the rheological properties.

Generally, the block copolymer nanostructures that are formed in the solid state are of practical interest. In classical sense, these structures, which are responsible for different kinds of micromechanical mechanisms and mechanical behaviour, are adjusted by changing the relative composition of the chemically linked chains.

Further options for the fine-tuning of block copolymer nanostructures are provided by blending and processing [2,6,9-11]. Three-component block copolymers and their derivatives form an additional variety of microphases, which may allow novel routes to developing materials having new property profiles [5,11,12]. It has been known for some time that the modification of molecular architecture may significantly alter their phase behaviour and opens up new possibilities of morphology control in these copolymers [13-17].

The morphology of SBS triblock copolymers with different molecular architectures and block interface has been intensively investigated [2,16,17]. It was found that the phase behaviour of the triblock copolymers does not fit into the well-known phase diagram of styrene-butadiene diblock copolymers. In spite of nearly equivalent chemical composition (about 70 vol. % of styrene), the investigated SBS block copolymers showed significantly different morphologies. Thus, besides the total phase volume ratio, the asymmetric architecture and the interfacial structure between the incompatible blocks determine the morphologies and mechanical properties of these materials.

Via architectural modifications of block copolymers, limitation of altering composition (e.g., in an AB diblock) to achieve a particular morphology can be overcome. Simultaneously, these new morphologies and new routes to control block copolymer nanostructures pose new challenges to clarify their complex structure-property correlations.

The aim of this paper is to study the morphology and deformation behaviour of blends comprising an asymmetric styrene/butadiene star block copolymer and polystyrene homopolymer (hPS) at low hPS concentration (less than 50 wt.-%). Polystyrene homopolymers having widely varying molecular weight values were used. Special emphasis has been put on the influence of molecular weight and dispersity of the PS homopolymer added.

EXPERIMENTAL

Materials

The important characteristics of the samples studied are collected in table 1. The details on the structure, rheological properties and morphology of the star block copolymer (named hereafter as ST3) may be found elsewhere [10]. The block copolymer provided by the BASF, Ludwigshafen was synthesised by butyl-lithium initiated living anionic polymerisation. The copolymer molecule has approximately 4 asymmetric arms, one of which is much longer than the others. The longest arm is styrene-rich while the shorter ones are butadiene-rich [2,9,10]. Each arm has an $S_1(S/B)S_2$ structure. Asymmetric star (see Fig. 1) was prepared by joining the living $S_1(S/B)S_2$ chains (where S/B stands for a PS-co-PB random copolymer; the polystyrene blocks S_1 and S_2 are of unequal lengths) using oligofunctional coupling agent. The total polystyrene content of the copolymer studied was 74 vol.-%. The ratio of longer to shorter outer PS blocks is sufficiently higher than 1 ($S_1/S_2 \gg 1$) and the molecular weight of the longest PS block lies in the range of 50,000 – 70,000 g/mole.

Two different types of hPS samples were used for microscopic examinations: PS015 ($M_w = 15,100$ g/mole and $M_w/M_n = 1.29$), and PS190 ($M_w = 190,000$ g/mole and $M_w/M_n = 2.3$). The one has a molecular weight much smaller than that of the longest PS outer block of the star block copolymer while the second one has an M_w higher than that of all the PS blocks.

Sample Preparation

All the samples were prepared by solution casting from 3% (weight/volume) solution each in toluene by allowing the solvent to evaporate over a period of about a week followed by vacuum drying at 23°C for several days and finally annealing for 48 hours in a vacuum oven at 120°C. Some of the samples used for microhardness measurements were prepared by compression moulding.

Techniques

Macroscopic tensile tests were carried out using a universal tensile machine (Zwick 1425) at a crosshead speed of 50 mm/min. The total length and the thickness of tensile specimens were 80 mm and 0.5 mm, respectively. The distance between the crossheads of tensile machine was 50 mm. At least 6 specimens from each sample were tested.

The morphology of the samples was investigated by means of a *transmission electron microscope* (200 kV Jeol JEM 2010 and 120 kV Leo 912) using ultramicrotomed thin sections (~70 nm thick). Prior to the TEM inspection, the butadiene phase was selectively stained by osmium tetroxide (OsO₄).

Microindentation hardness (H) was calculated by measuring the residual impression produced by a Vickers diamond indenter onto the surface of the compression-molded sheets. An indentation time of 6 s and a load of 10 g were respectively used. The Vickers hardness is defined as [18]:

$$H = k \frac{P}{d^2} \quad (1)$$

where P is the applied load in N, d the diagonal of the impression in m, and k a geometric factor equal to 1.854. The H values were derived from an average of at least 10 indentations.

RESULTS AND DISCUSSION

Morphology of Star Block Copolymer/hPS Blends

Fig. 2 shows the morphology of the star block copolymer used (ST3) to prepare the binary blends with polystyrene homopolymer. The details on the phase behaviour of ST3 will be discussed elsewhere [19].

In agreement with our preceding studies on asymmetric block copolymers, the star block copolymer studied, deviates significantly from the classical block copolymer phase diagram. Instead of forming hexagonal arrangement of PB cylinders in the PS matrix, as demanded by its total composition (74 % PS), a co-continuous morphology comprising PS struts dispersed in a rubbery matrix is formed. The deviation from the classical block copolymer phase behaviour is substantiated by the presence of a PS-co-PB random copolymer as rubbery block, which contains a considerable part of polystyrene and hence increases the effective rubber volume fraction. The latter would favour the formation of a morphology corresponding to the structure of a diblock copolymer having lower PS content. This morphology looks very similar to the 'gyroid' phase observed in block copolymer systems. The shift of phase behaviour of the asymmetric block copolymers is in line with the recent postulation by Matsen [20], which allows even the incorporation of short outer chains into the middle block domains for certain asymmetries.

As pointed out above, the styrene/butadiene block copolymers are often used in combination with polystyrene homopolymer (hPS). It is well known that the length of homopolymer chains (here hPS chains) relative to that of the corresponding block (here PS block) plays a vital role in the phase behaviour of these binary blends [5,8].

The low molar mass homopolymer, which is easily assimilated by the corresponding block domains, can be used to change the dimension of a given morphology and even to produce new morphologies corresponding to a different net composition. Hence, the method of blending with homopolymers can also be helpful to locate the position of a 'new' morphology in the phase diagram.

Fig. 3 illustrates the morphology of two different blends of ST3 with hPS having different molecular weights, each blend containing 20 wt.-% hPS. By comparing Fig. 3 with Fig. 2, three kinds of morphologies can be distinguished: microphase separated 'bicontinuous'

structure (Fig. 2), microphase-separated lamellar structures (Fig. 3a) and macrophase-separated morphology containing hPS particles embedded in the ST3 matrix (Fig. 3b).

The polystyrene samples differ in their molecular weights, as mentioned earlier. PS015 and PS190 have weight average molecular weights (M_w) of 15,000 g/mole and 190,000 g/mole, respectively. On the other hand, the molecular weight of the longest polystyrene block in the star block copolymer is in the range of 50,000-70,000 g/mole. Obviously, PS015 has shorter chains that can be easily accommodated by the longest PS blocks of the star molecules. Hence, an addition of 20 wt.-% of PS015 leads to the formation of a morphology corresponding to higher overall polystyrene content (lamellar morphology in Fig. 3a). Since the resulting morphology is a lamellar one (and the expected morphology for a block copolymer having lower PS content than for the lamellae is the 'gyroid' phase), the microphase separated structures observed in the pure ST3 can be considered as being, at least, very close to the 'gyroid' morphology.

The increase of the molecular weight of the added polystyrene results in an entropy loss and the hPS chains cannot diffuse anymore into the PS blocks of the block copolymer. Consequently, these hPS molecules tend to segregate towards the middle of the domains and finally, if the molecular weight is too high, these are even expelled out of the PS domains leading to the formation of macrophase-separated hPS particles dispersed into the matrix block copolymer. The molecular weight of the PS190 is obviously much higher than the corresponding block in the block copolymer. Hence, the added polystyrene predominantly forms the hPS particles leaving the morphology of the surrounding matrix unchanged (Fig. 3b).

Fig. 4 illustrates the morphology of ST3 and a mixture of PS015 and PS190 (their weight ratio is 1:1), the total composition of hPS being 40 wt.-%. The hPS used here is practically a bimodal mixture of homopolystyrene and the morphology of this blend is obviously a combination of those of Figs. 3a and 3b. The formation of this morphology may be

understood in terms of the discussion used for the explanation of morphology of blends of ST3 with individual hPS components.

In fact, the block copolymer employed is not a monodisperse system. As mentioned in the experimental section, the star shaped molecules were obtained by coupling the asymmetric triblock chains. As the coupling is a statistical process, one may anticipate that a random mixture of stars having different total composition can be formed. This would play an important role in the phase behaviour of the blends with polystyrene homopolymer. However, this is not the object of present study.

The results suggest that besides the molecular weight and total homopolymer concentration, the modality of the added hPS should be regarded as an important parameter on dealing with the morphology control in blends of a block copolymer and homopolymers.

Nevertheless, it is worth noting that the foregoing discussion in case of solution cast samples may not be valid for the mixtures produced by extrusion or injection/ compression moulding. Processing may dramatically alter the morphology of these binary blends. Particularly, in compression moulded ST3/hPS blends an entirely different type of morphology has been observed [21].

In contrast to the blends of a lamellar block copolymer and PS, in which predominantly layered morphologies prevail [22], the corresponding blends with ST3 reveal a typical ‘droplet-like’ morphology in the compression moulds as illustrated by TEM images given in Fig. 5 [21]. In layered systems, the microscopic deformation mode and the resulting mechanical properties are largely limited by the thickness of those layers [22]. On the contrary, in the present system with ‘droplet-like’ morphology, the ease of plastic deformation is enhanced and the ‘ductile-to-brittle’ transition is shifted to higher overall PS content [21].

Mechanical and Micromechanical Properties

a. Stress-strain Behaviour

Provided that the rubbery centre PB block is chemically bound to the outer glassy PS blocks, the mechanical behaviour of microphase-separated styrene/butadiene systems is mainly governed by their morphologies. Thus, due to the formation of a wide range of morphologies, a variety of mechanical properties was observed.

Figure 6 shows the stress-strain curves of the block copolymer and blends studied. The blends of ST3 with polystyrene contain 20 wt.-% of PS015 and PS190 each. The deformation of each sample is characterised by the presence of a yield point and a considerable plastic deformation zone. Most interesting is the fact that the elongation at break of the two blends is notably smaller than that of the star block copolymer.

The ST3 sample exhibits a ductile behaviour since it elongates up to several hundred percent. A closer inspection of the curves for ST3 reveals the presence of two well-defined yield points at about 4% and 20% strain. In order to assure that the existence of these two distinct yield points in the star block copolymer, various experiments were performed by using the samples by prepared by different methods and loading under different conditions. The phenomenon of ‘double yielding’ has been discussed only in semicrystalline polymers (such as polyethylene) yet. Thus, the presence of two distinct yield points in the star block copolymer makes its tensile deformation to resemble that of low density polyethylene (LDPE) discussed in the literature (discussed in detail in [23]).

As expected, owing to the higher overall PS content, the addition of PS015 to ST3 (PS015 content = 20 wt.-%) giving the lamellar morphology of Fig. 3a leads to a rise in the stress level for every strain. The decrease in strain at break suggests that the homopolymer chains, accommodated by the PS block domains of the block copolymer, may act as weak points, which may eventually lead to the premature fracture of the specimens. The fact that two distinctly separated yield points of the star block copolymer do not appear in the blend having

microphase-separated lamellar morphology, suggests that the ‘double yielding’ behaviour of ST3 could be associated to its special morphology.

With addition of PS190 to ST3, the stress level again decreases and the elongation at break increases relatively to that of ST3/PS015 blend. The stress level in this blend is, nevertheless, higher and the elongation at break smaller than that of ST3. In this sample, the added PS190 increases the overall PS content in the system leading to an increase in the stress. In contrast, the presence of the ST3 matrix (see Fig. 3b) tends to reduce the stress level allowing a more homogeneous deformation. As a consequence, the stress-strain curve of this sample falls in between that of ST3 and ST3/20 wt.-% PS015 blend.

b. Structure-Microhardness Correlation

Additional information on the micromechanical properties of polymeric materials can be gained from microhardness measurements. The microindentation hardness technique has found in recent years widespread application in polymer research [18]. The technique has been increasingly used in the characterisation of homopolymers, polymer blends and copolymers. The influence of different molecular parameters (molecular weight, branching degree etc.) on the morphology of semicrystalline polymers, the role of the glass transition temperature in amorphous polymers [24-27] and the relevance of the chemical architecture in systems having microphase-separated morphology has been examined in preceding studies using the microhardness technique [28-30]. In particular, the microhardness behaviour of triblock and star block copolymers, binary block copolymer blends and blends containing hPS has been the object of recent studies [28-30]. The relevant finding here is that microhardness is not determined by the phase constitution of the block copolymers but mainly by the nanostructure of the components, i.e., by the morphology.

To study the influence of the morphology of the block copolymer systems on their microhardness behaviour, binary blends of ST3 and hPS having different molecular weights were studied. The results obtained are shown in Fig. 7. The amount of ST3 was kept 80 wt.-% in each case.

The microhardness (H) of the star block copolymer having a morphology comprising co-continuous arrangement of glassy and rubbery phases (Fig. 2) shows a low value of 17 MPa. By adding a 20 wt.-% of hPS the H value increases to a level of about 28 MPa till the molecular weight of the added hPS is about 50,000 g/mole. The latter lies well below the molecular weight of the longest PS block of the block copolymer suggesting that the morphology formed in the blends at given concentration is predominantly microphase-separated (similar to that shown in Fig. 3a). Thus an increase of H in the blends with hPS and its constancy within the PS-molecular-weight range of 10,000 – 50,000 g/mole appears to correlate well with the change in microphase separated morphology from a rubbery matrix to a lamellar arrangement. The hardness increase observed when a morphology-transition takes place is consistent with our previous findings on microphase-separated block copolymer [28].

When the molecular weight of the added hPS is higher than about 50,000 g/mole, the H values drops slightly again to a level of about 24 MPa (Fig. 7). As discussed earlier, a shift from microphase separation to the macrophase separation occurs in the block copolymer/homopolymer blends as the hPS molecular weight approaches that of the corresponding copolymer block. In this case the matrix-morphology of the blends would resemble the one presented in Fig. 2. Nevertheless, the H values are higher than those of pure ST3, attributable to the presence of PS particles dispersed in block copolymer matrix (e.g., in Fig. 3b). Thus a decrease in microhardness is a direct indication of a macrophase separation of the blend components forming a ST3 matrix whose H value is smaller than that for a lamellar morphology. Microhardness can be consequently used as a simple and straightforward method to evaluate the phase behaviour of nanostructured polymer blends.

The existing correlation between the microhardness and the microphase-separated structure of the block copolymer systems is further substantiated by the study of compression moulded ST3/PS190 blends. Fig. 8 shows the plot of measured microhardness values against the PS190 content. In the plot, two different regions for the hardness increase can be distinguished: from 0 up to 40 wt.-% PS190, the H values increase slowly and beyond 50 wt.-% PS190, H rises rapidly.

It is known from earlier studies on amorphous polymers that the microhardness increases with the glass transition temperature (T_g) [18]. In the present case, addition of PS190 increases, of course, the overall PS content, which leads to an H rise. However, the T_g values remain practically constant at all compositions. Therefore, two different regions corresponding to a slower and a more rapid H increase with PS content suggest that there is an inherent influence of the blend's morphology and the corresponding nanomechanical deformation processes on the hardness value.

If we recall the morphology of the samples, actually the transformation of soft-phase-rich morphology to the existence of the hard PS matrix begins at a PS content of 50 wt.-%. Below 50 wt.-% PS, where the typical 'droplet-like' structures predominate (see Fig. 5) and the blends show a high degree of plastic deformation, lower H values are measured. For higher hPS concentrations, owing to the presence of the hard matrix, the formation tendency of localised deformation zones with microvoids increases. Thus, the steep increase in H values demarcates not only a transition in the microscopic morphology of the blends, but also the resulting microdeformation mechanisms under the influence of the load applied.

c. Deformation micromechanism studied by TEM

The deformation micromechanisms of lamellar forming styrenic block copolymers have been documented in earlier [31,32] and more recent studies [15-17,33-35]. The intensive plastic deformation of glassy PS lamellae in oriented styrene/butadiene block copolymer was observed in asymmetric lamellar block copolymers [33], which was also reported earlier by Hashimoto et al. on unoriented films. It is well established that during plastic deformation shearing and kinking processes occur prior to the destruction of the glassy lamellae. At higher strains, formation of 'fish-bone structure' ('chevron morphology') characterised by a four point SAXS pattern was observed [31,32]. Recently Cohen and co-workers reported that during deformation parallel and perpendicular to the lamellar orientation, a destruction of lamellar structure and formation of 'chevron' morphology, respectively occur [34].

In a preceding study, we have discussed the deformation mechanisms in blends of a star block copolymer and polystyrene homopolymer by changing the molecular weight and concentration of polystyrene homopolymer [35]. It was shown that deformation micromechanism of these systems strongly depends on the nature of the morphology. In the present paper, only a brief account of the deformation behaviour of a ternary blend (discussed in Fig. 4) is given. Further details will be given in a coming publication.

Fig. 9 shows the strain induced structural changes in a blend of ST3 and 40 wt.-% PS (PS being a 1:1 mixture of PS015 and PS190). The thin section for TEM studies was prepared from bars deformed in the tensile test (sectioning close to the fracture surface).

Similar to the block copolymer/PS blends studied earlier microvoids are formed at the pole regions of stiff PS particles [33,35] at the initial stage of deformation. The microvoids after growing to critical sizes lead to the fracture of the specimens.

One may expect that during the deformation process the lamellar matrix would undergo plastic deformation (accompanied by micronecking and yielding [15,33,35]). The microvoids might become larger enabling a further large plastic deformation of the surrounding matrix.

The combination of these mechanisms (microvoid formation at the particle poles and large yielding of the surrounding lamellar matrix) would contribute to enhance the overall toughness of the block copolymer/PS blend. In this way, the use of a bimodal hPS instead of a single molecular weight PS with an asymmetric block copolymer would provide a new way of toughness modification of nanostructured systems.

CONCLUDING REMARKS

1. The phase and deformation behaviour of the block copolymer/hPS blends as revealed by TEM and uniaxial tensile testing is found to be strongly influenced by the molecular weight and modality of the added hPS.
2. Different morphologies ranging from microphase-separated to macrophase-separated ones (and a combination of both of them) have been evidenced. Thus, it is possible to tailor the tensile properties of the block copolymers based on the nature of their nanoscopic morphology.
3. The microhardness indentation technique is found to be very sensitive to the morphological changes in the nanophase-separated block copolymer systems.

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FIGURE CAPTIONS

Figure 1. Scheme showing the structure of the star block copolymer used; the dark and white colours stand for polybutadiene and polystyrene phases, respectively.

Figure 2. Lower (left) and higher (right) magnifications of TEM images of the star block copolymer showing co-continuous like morphology; osmium tetroxide staining makes the butadiene-rich phase appear dark.

Figure 3. Lower (left) and higher (right) magnifications of TEM images of the blends consisting of block copolymer and hPS: a) ST3 + 20 wt.-% PS015 and b) ST3 + 20 wt.-% PS190, osmium tetroxide staining makes the butadiene-rich phase appear dark.

Figure 4. Lower (left) and higher (right) magnifications of TEM images of ST3/40 wt.-% hPS, hPS contains 1:1 weight ratio of PS015 and PS190, osmium tetroxide staining makes the butadiene-rich phase appear dark.

Figure 5. TEM micrograph of a compression moulded ST3/PS190 blends: a) 30 wt.-% PS190 and b) 80 wt.-% PS 190; osmium tetroxide staining makes the butadiene-rich phase appear dark.

Figure 6. Stress-strain curves of the samples studied; tensile testing at 23°C at a cross head speed of 23°C.

Figure 7. Microhardness of some of the ST3/hPS blends as a function of hPS molecular weight; each blend contains 20 wt.-% hPS; the dotted line is only meant to guide the eye.

Figure 8. A plot of H versus PS190 content plot for ST3/PS190 blends measured using compression moulded samples

Figure 9. A TEM micrograph showing the deformation structures at initial stage of plastic deformation at the vicinity of PS particles in a ST3/40% hPS blend (hPS contains 1:1 weight ratio of PS015 and PS190), the strain direction is indicated by a white arrow; osmium tetroxide staining makes the butadiene rich phase appear dark.

Table 1. The characteristics of the materials used.

samples	$^{\S}M_w$ (g/mol)	$^{\S}M_w/M_n$	$^{*}\Phi_{PS}$	remarks
ST3	180,000	1.91	0.74	Structure similar to ST1, each arm with $S_1(S/B)S_2$ structure ($S_1 \neq S_2$), S/B is a random copolymer of PS and PB [10]
PS015	15,100	1.29	1.00	PS homopolymer
PS190	190,000	2.30	1.00	PS homopolymer

§ number average (M_n) and weight average (M_w) molecular weight determined by gel permeation chromatography using PS calibration

* total styrene volume content determined by Wijs double bond titration procedure

500

PS

PS

PS

PS

stress (MPa)

0 5 10 15 20 25 30

0 50 100 150 200 250 300 350 400

50

100

150

200

250

300

350

400

strain (%)