



Morphology and micromechanical behavior of binary blends comprising block copolymers having different architectures

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Abstract

Morphology and deformation behavior of binary blends comprising styrene/butadiene block copolymers (polystyrene content, $\Phi_{PS} \sim 0.70$) having different molecular architectures were studied by means of transmission electron microscopy and tensile testing. In contrast to the binary diblock copolymer blends discussed in literature, the phase separation behavior of the blends investigated was found to be strongly affected by asymmetric molecular architecture. The blends showed macrophase separated grains, in which the structures resembled the microphase morphology of none of the blend components. Unlike the classical rubber-modified or particle-filled thermoplastics, neither debonding at the particle/matrix interface nor the particle cavitation was observed in these nanostructured blends. The microdeformation of the blends revealed plastic drawing of polystyrene lamellae or PS struts dispersed in rubbery matrix and orientation of the whole deformation structures along the strain direction.

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1. Introduction

Block copolymers are of particular practical significance. By virtue of connectivity of dissimilar homopolymer chains via a covalent linkage, these heterophase polymers undergo intramolecular phase separation and form ordered ‘microphase separated’ structures. The periodicity of these structures lies in the same order as the gyration radius of the copolymer molecules, much smaller than the wave length of light, hence assuring the transparency of the products [1].

Polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) triblock copolymers are used as thermoplastic elastomers [2]. Their significance from the practical point of view lies in the fact that the transparent heterophase polymers having a wide range of mechanical properties can be achieved by simply changing the composition and hence the nature of phase morphology [1,2]. However, it has been known for some time that a modification in their molecular architecture

at constant composition has a dramatic influence on their microphase separation phenomena, and consequently on their mechanical properties [3–6].

The experimental results discussed in our recent paper [5] strongly suggested that architectural modification in block copolymer systems, especially via asymmetric molecular conformation, may open new possibilities of controlling self-assembly processes in these nanostructured materials. As a result, without changing the net chemical composition, a variety of microphase separated structures were achieved. The modification of molecular architecture has shown to overcome the constraint of the classical picture of the block copolymer phase behavior to change the composition in order to control the self-assembled nanostructures and, hence, has provided new variables in designing materials based on heterogeneous polymers.

Different authors have performed comprehensive studies on block copolymer blends and described their solubility limits (discussed in detail by Hamley in Ref. [1]). In particular, the influence of the molecular weight ratio (r) and relative composition of the copolymers have been addressed [6–9]. It was shown that macrophase separation occurs, if the value of r is greater than 10, forming regions

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of lamellar domains with different periods. In contrast, if the value of $r \leq 5$, the blend components were found to be mixed in molecular level. Recently, Hashimoto et al. by studying the phase behavior of binary diblock copolymer blends in the range $5 \geq r \leq 10$, demonstrated that a partial demixing of the blend components may occur at certain composition range [7]. The investigations were extended to non-lamellar morphologies too [1,8,9].

In spite of a great deal of works on phase behavior of diblock copolymers and their blends, only limited works have been carried out concerning the influence of morphology on the mechanical properties of these nanostructured materials. In particular, a systematic study of structure–property correlation of the binary blends of triblock structures and their derivatives is still missing.

Recently, we investigated the fracture toughness behavior of binary blends consisting of a star shaped and a linear triblock copolymer by instrumented Charpy impact testing. Dynamic crack resistance concept (R -curves) was employed to characterise the toughness of the binary blends [10,11]. An addition of a small amount of a thermoplastic elastomeric linear block copolymer to a highly asymmetric lamellae forming star block copolymer was found to result in a strong increase in crack toughness. The drastic increase in the resistance against crack initiation and propagation was attributed to the shift in deformation mechanism from microvoid coalescence to shear flow [10]. However, the micromechanical deformation behavior leading to the toughness enhancement was not well understood. For the precise understanding of the micromechanisms of toughness enhancement in binary block copolymer blends, which is important for the microstructural construction of tailor made polymers, the correlations between the phase separation behavior and its effect on the deformation mechanisms should be systematically studied. In this communication, we report the morphology and micromechanical behavior of binary blends of styrene/butadiene block copolymers that were used to study the fracture toughness behavior earlier [10,11] by putting particular emphasis on the effect of asymmetric architecture of one of the blend partners.

2. Experimental section

Synthesis of the block copolymer used has been described by Knoll and Nießner [12]. Binary blends of a star block copolymer (ST2-S74) and a linear triblock copolymer (LN4-S65), both based on styrene and butadiene, are used in this study. The characteristics of the block copolymers are given in Table 1. The sample films approximately 0.5 mm thick were cast from solution using toluene as solvent. The solvent was allowed to evaporate slowly over a period of about a week. The resulting films were dried for several days at 23 °C and annealed at 120 °C for 48 h in a vacuum oven in order to allow the formation of well ordered structures. Tensile specimens having a total

Table 1

Characteristics of the blend components; styrene as hard outer block in LN-S654 is 32 vol% while the middle statistical block contains about 50 vol% styrene

Blend component	M_n (g/mol)	M_w/M_n	Φ_{styrene}	Morphology (TEM)
ST2-S74	109,200	1.69	0.74	Lamellae
LN4-S65	116,000	1.20	0.65	PS domains in random PS-co-PB matrix

length of 50 mm were punched out of the solution cast films. The blends contain 20, 40, 60 and 80 wt% of LN4-S65.

Morphological details of the samples were examined using a transmission electron microscope (200 kV TEM, Jeol, JEM 2010). The butadiene phase was selectively stained by osmium tetroxide (OsO_4) prior to the transmission electron microscopy (TEM) imaging. Ultrathin sections of each sample were prepared by using a Leica Ultramicrotome.

In order to determine the macroscopic mechanical behavior, the tensile specimens were subjected to uniaxial tensile testing at a cross-head speed of 50 mm/min using a universal tensile machine at 23 °C.

3. Molecular architecture and morphology of block copolymers

Details of the morphology of the block copolymers used may be found in Refs. [5,12]. Fig. 1 shows the TEM micrographs of solution cast films of star block (Fig. 1(a)) and linear block copolymer (Fig. 1(b)). Molecular structure and morphology of respective polymers are schematically represented at the top of each micrograph. Star block (ST2-S74) and triblock (LN4-S65) copolymers reveal the morphologies consisting of alternating lamellae and randomly distributed cylinders, respectively. The star block

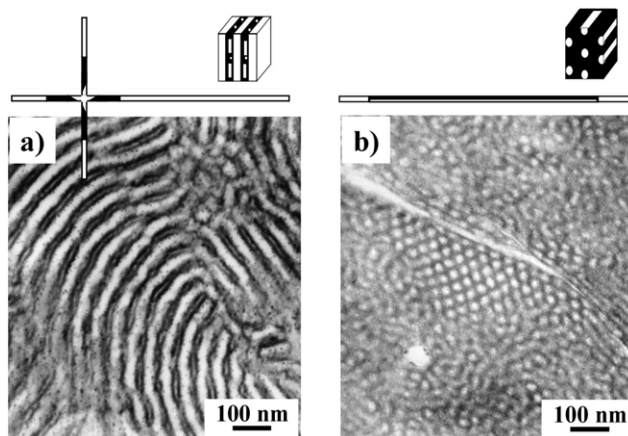


Fig. 1. Representative TEM images of solution cast block copolymer samples: (a) star block copolymer and (b) linear triblock copolymer; OsO_4 staining; scheme of molecular architecture of the copolymers is given at the top of each micrograph; PS and PB phases are represented by white and black colours, respectively.

copolymer has a peculiar ‘two-component three-phase’ morphology consisting of alternating layers of PS and PB, the latter layers embedding fine cylinder-like domains (see Fig. 1(a)). Note that the domain spacing in the star block and the triblock copolymer is about 40 and 25 nm, respectively.

Each star molecule has approximately four arms in average and possesses a highly asymmetric architecture, i.e. the outer PS arms are of unequal length; and the ratio of longer/shorter polystyrene blocks is rather high ($r \geq 6$), the longest block having a molar mass of approximately 70,000 g/mol. The middle polybutadiene block of each arm is tapered to the inner PS core of the molecule. The star molecules are produced by coupling of asymmetric SBS arms, and since the latter is a random process, the star block copolymer contains a mixture of stars having different number of arms and different compositions (see Ref. [12] for more information on synthesis).

The linear block copolymer (Fig. 1(b)) has symmetric PS outer blocks, each block having a molecular weight of about 18,000 g/mol. The middle block is made up of a random copolymer of polystyrene and polybutadiene (PS-*co*-PB) [12].

4. Results and discussion

In the investigated composition range, the binary blends exhibited the coexistence of lamellar grains and regions consisting of PS domains, i.e. the grains containing different morphologies (microphase separated structures) were themselves macrophase separated. TEM image of a blend consisting of 60 wt% LN4 and 40 wt% ST2 is shown in Fig. 2. A part of the lamellar region is magnified in inset. Two regions are evident in the TEM image: one with a macrodomain (dispersed) possessing lamellae structure

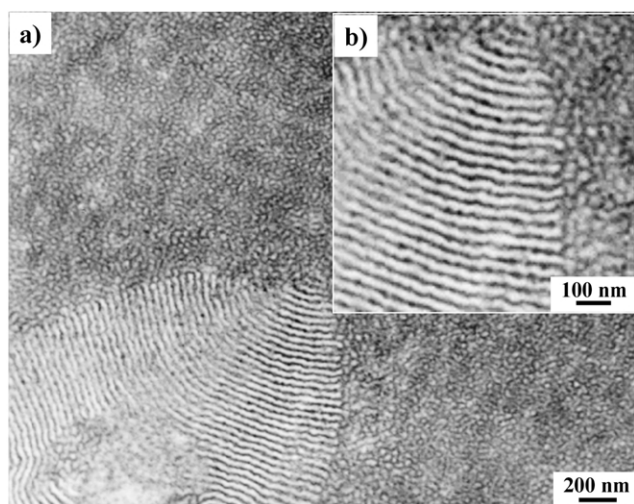


Fig. 2. Representative TEM micrograph showing the morphology of a blend consisting of 60 wt% LN4 and 40 wt% ST2; the inset shows the higher magnification of a part of lamellar grain; the magnification in Fig. 1(a) and this figure (inset) can be directly compared.

and the another one that forms the matrix. The latter appears to consist of a co-continuous network of soft (dark in TEM image) and hard (bright) phases. At the first glance, it may be guessed that the macrophases are formed by separation of the molecules of the blend components ST2 and LN4. However, the microphases inside them are characteristics of neither of the blend components.

It should be noted that the pure star block copolymer consists of alternating layers of PS and PB phases similar to that shown in inset of Fig. 2. Additionally, the PB lamellae of star block copolymer contained cylinder-like domains embedded in them [5,12] (see Fig. 1(a)). This two-component three-phase morphology characteristic of the pure star block copolymer is not found in the lamellar grain in the blend (Fig. 2). A closer inspection of the TEM images lead to three important questions, that have to be answered on the basis of molecular architecture of the block copolymers:

- Cause of evolution of macrophase separated grains.
- Disappearance of PS domains that were initially present inside the PB lamellae of the star block copolymer (e.g. see Fig. 1(a)).
- Formation of co-continuous matrix morphology.

The formation of non-uniform morphology (macrophase separation of the blend components) is clearly the indication of the fact that the block copolymer molecules are not compatible to each other. Note that both the block copolymers have nearly identical molecular weight (ca. 100,000 g/mol, Table 1). In the light of the conclusions drawn by the study of binary diblock copolymer blends [6–9], no macrophase separation should occur because the value of molecular weight ratio (r) is close to unity. Obviously, the demixing of the block copolymer molecules is associated with asymmetric architecture of the star block copolymer.

The stars containing only shorter arms are butadiene-rich while those containing one or more longer PS blocks are polystyrene-rich. Since the ratio of larger to shorter PS block in ST2 is more than 6, these might phase-separate even on consideration of conclusions drawn for binary diblock copolymer blends in literature.

The fact that the shorter PS arms of the star molecules have the length ($M_n \sim 10,000$ g/mol) in the same range as the PS outer blocks of the linear block copolymer LN4 ($M_n \sim 18,000$ g/mol), those PS block may form common domains leading to the co-continuous domains, which appear as matrix in the binary blend (Fig. 2). In particular, the PB-rich stars (i.e. those containing mostly the shorter PS arms) form common domains with the LN4 molecules. The longer outer PS blocks of the star molecules, which are several times larger than the shorter ones of the star block copolymer and also that of the linear copolymer. This results in the lamellar grains in the ST2/LN4 blends (e.g. dispersed phase in Fig. 2).

That the cylinder-like PS domains embedded in the PB lamellae of the ST2 (see Fig. 1(a)) vanish in the blends, suggests that those domains were formed initially in part by shorter PS blocks of the star molecules. In the blends, since the PB-rich stars containing the shorter PS blocks are mixed with LN4 molecules, the PS core of each star molecule is not enough to form separate PS domains embedded in the PB lamellae. Hence, the PB lamellae in the lamellar macrophase in the blend (Fig. 2) lack two-component three-phase morphology typical of the pure star block copolymer [5]. Consequently, the PB layers in the ‘lamellar grain’ is thinner than that in the pure star block copolymer (compare Figs. 1(a) and 2(b)). This notion is substantiated by the decrease of mean lamellar spacing (L) in the lamellar grain in the blend (Fig. 2(b), $L = 35$ nm) relative to that of the pure star block copolymer (Fig. 1(a), $L = 40$ nm).

That the system investigated represents a partially miscible one is further supported by a linear dependence of soft phase glass transition temperature in the blends with composition [13]. Additionally, the mechanical deformation behavior as characterised by the tensile testing (e.g. the parameters such as yield stress, strain at break and tensile strength, etc.) changes continuously [11,13]. Stress–strain curves of some of the samples is given in Fig. 3.

The pure star block copolymer shows the behavior similar to that of lamellar semicrystalline polymers such as high density polyethylene (ductile behavior). After an elastic deformation of the tensile specimen, a clear yield point (yield stress ~ 13 MPa) appears at a strain of about 8%. The yield point represents the deformation stage when the localised necking and subsequent drawing result in a slight drop in stress. On further drawing of the tensile specimen, the stress level remains nearly constant up to about 150% strain. It was shown that the lamellar microdomains undergo ‘micronecking’ and subsequent plastic flow in an analogous manner on the microscopic scale [17]. At higher strains, the gradual rise in stress is correlated with the orientation of highly drawn lamellae and respective chains (orientation hardening). The sample undergoes fracture at a strain of about 330%.

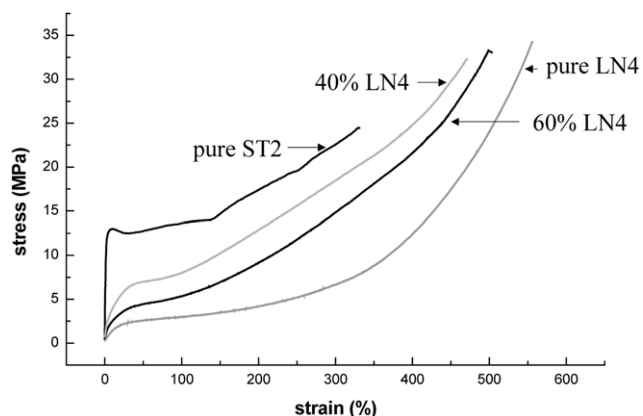


Fig. 3. Stress–strain curves of some of the investigated samples; tensile testing at a rate of 50 mm/min at 23 °C.

On the other hand, the linear block copolymer (LN4), owing to its morphology comprising dispersed PS domains in the rubbery matrix, exhibit predominantly rubber–elastic deformation and a large degree of strain recovery [5] typical of thermoplastic elastomer or a cross-linked rubber. At about 20% strain, a shoulder appears in the stress–strain curve, which is comparable with the yield point of the thermoplastic polymer. A successive fragmentation of the glassy PS domains begins at this point. The sample deforms in a homogeneous manner and shows an ultimate strength and strain of 34 MPa and 550%, respectively.

The stress–strain curves of the blends lie in between that of the pure components. It should be noted that a well-defined yield point is missing in the block copolymer blends. The absence of pronounced yield point (Fig. 3) is partly correlated with random orientation of microdomains in the matrix before deformation. In fact, the strain–strain curves of the blends investigated resemble qualitatively that of the pure linear block copolymer LN4. It implies that the mechanical behavior of the blends is predominantly controlled by the co-continuous matrix. With respect to the ultimate stress, the blends reach the value of pure triblock copolymer. However, the stress level at each strain of the blends increases with lamellar block copolymer content. The macrophase-separated lamellar grain may act, indeed as filler in the bicontinuous rubbery matrix.

Closer insight into the micromechanism of the blend can be gained by the analyses of strain induced structural changes in a binary blend. Fig. 4 shows the typical TEM micrographs of a blend containing 60 wt% LN4.

Comparative analyses of the TEM micrographs of Fig. 4 with that of Fig. 2 reveal that considerable structural changes have taken place in the blends due to tensile deformation that can be listed as follows:

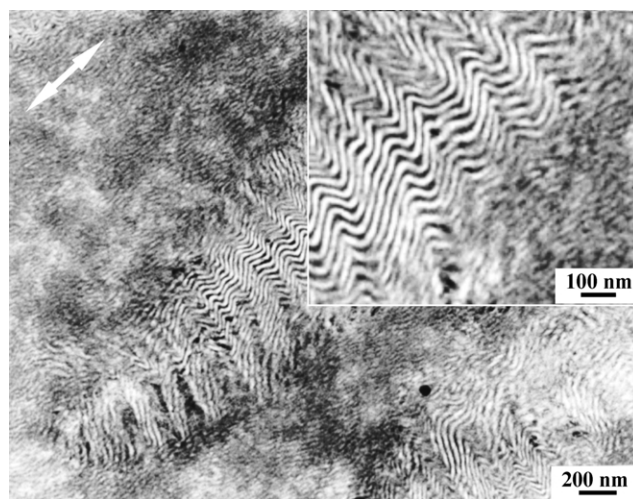


Fig. 4. Representative TEM micrograph showing the morphology of a blend consisting of 60 wt% LN4 and 40 wt% ST2 after tensile deformation; OsO_4 staining; deformation direction indicated by an arrow; the inset shows the higher magnification of a part of a deformed lamellar grain.

- (a) The isotropic matrix comprising the co-continuous-like hard and soft phases has turned into an anisotropic array of plastically drawn filaments, all aligned parallel to the deformation direction. Each filament takes a uniformly thick worm-like form.
- (b) The boundary between the lamellae and the co-continuous matrix phase is intact and there is no sign of failure at the interface.
- (c) The lamellar macrophase assume an elliptical shape extended towards the deformation direction, a sign of very high deformation, with a major part of the grain being made up of the lamellae aligned towards the strain direction. The lamellae are plastically deformed leading to the formation of wavy structures. The latter look-like ‘fish-bone’ structures observed in lamellar block copolymers formed under perpendicular deformation [14]. The lamellar long period in the wavy regions is higher than in the regions where the layers are straight and aligned along the strain axis.

The observations mentioned above lead to the conclusion that the matrix consisting of the co-continuous hard and soft phases is plastically deformable and controls predominantly the deformation behavior of the blend. Hence, the blend shows a behavior similar to that of the pure linear block copolymer. The lamellar ‘grains’ act as the ‘filler’ and enhances the strength of the polymer blend.

At large deformations, the whole dispersed lamellar grain should have rotated to the deformation direction so that the plastically deformed matrix-filament also aligns strongly towards the strain axis. It is similar to the alignment of lamellar grains [15] and subsequent drawing of constituent layers [5,16,17] in pure styrene/diene lamellar block copolymers as reported in earlier studies. As a result, lamellar normals align perpendicular to the strain axis at increased deformation. Finally, all the lamellae orient parallel to the strain direction.

As a consequence of predominantly elastic deformation of the co-continuous matrix, a large part of deformation energy is stored as elastic energy, which upon specimen fracture, can be readily supplied to the dispersed lamellar macrophase due to a good adhesion between the phases. This energy might have been used to make the lamellae snap back and turn into wavy structures as observed in Fig. 4. As a result, the more flexible rubbery phase in the lamellar grain is permanently deformed leading to an increased lamellar spacing in the wavy regions.

A reliable evidence of plastic deformation of the domains (including glassy lamellae and the mixed phase) can be obtained by quantifying the change in thickness of the domains in the blends without deformation and after tensile testing. Such an evaluation was made by quantifying the TEM micrographs of a blend containing 40 wt% LN4. Each kind of the domains were measured, both in the matrix and the dispersed lamellar macrophase. It was found that that thickness of the hard domains decreased from 15–30 nm

(average 20 nm) to 6–20 nm (average 13 nm) due to tensile deformation. The strong decrease in overall thickness of the PS domains after tensile deformation demonstrates a large degree of permanent irrecoverable plastic deformation in the glassy polystyrene phase. This fact illustrates that, in addition to the lamellar domains, glassy domains in co-continuous morphology undergo plastic deformation as suggested by Thomas et al. in a neat SIS triblock copolymer containing *Gyroid* morphology [18]. The homogeneous plastic deformation of lamellar styrene/butadiene systems was described by a ‘thin layer yielding’ mechanism [17].

In addition, the formation of plastically deformed strands of polystyrene in the matrix of strained blend sample substantiates the assumption that the co-continuous phase has been formed by the partial mixing of the star and the triblock copolymer molecules. Such an extensive drawing was not observed in the pure linear triblock copolymer used in this study [19,20].

The deformation mechanisms of the binary blends can be represented by the following stages.

1. Elastic deformation of the matrix followed by the plastic drawing and alignment of drawn filaments.
2. Rotation of the whole lamellar grain and then the lamellae towards strain direction with subsequent lamellar orientation at higher deformation.
3. Supply of elastically stored energy from the matrix to the lamellar macrophase upon sample fracture and following the formation of wavy structures.

One of the most interesting features observed in the micromechanical behavior of the binary polymer blends studied that deserves mentioning is the difference in the deformation around the dispersed phase. Usually, depending on the adhesion between the particles and the matrix, debonding around the dispersed particles or the cavitation of the particles are observed in classical polymer blends [21]. Neither of these phenomena were observed in the present system. In addition, the binary block copolymer blends studied were characterised by very high plastic deformation of both the matrix and the dispersed phase. This means that the deformation micromechanisms observed in the conventional polymer blends cannot be directly applied in the nanostructured block copolymer blends.

5. Conclusions

We have studied the morphology and micromechanical deformation behavior of binary blends consisting of styrene/butadiene block copolymers (polystyrene content, $\Phi_{PS} \sim 0.70$) having different molecular architecture. The blend components were a highly asymmetric star block copolymer and a symmetric linear triblock copolymer. In contrast to the behavior of binary diblock copolymer blends discussed in literature, the blends investigated showed

macrophase-separated grains, in which the structures resembled the microphase morphology of none of the blend components. In the microscopic scale, the sample revealed an alignment of the whole deformation structures towards the strain direction accompanied by a plastic drawing of polystyrene lamellae or PS struts dispersed in rubbery matrix in these nanostructured binary blends. Unlike the polymer blends having matrix/particle morphology, neither debonding at the particle/matrix interface nor the particle cavitation was observed.

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