

Relationship between Nanostructure and Deformation Behavior of Microphase-Separated Styrene/Butadiene Systems

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ABSTRACT: The relationship between the morphology and the mechanical properties of nanostructured blends, comprising an asymmetric styrene/butadiene star block copolymer, exhibiting cocontinuous-like morphology and low molar mass homopolymers, was studied by electron microscopy, microindentation hardness, and tensile testing methods. Results show that the deformation behavior of these systems is significantly modified by the presence of unentangled homopolymer chains, leading partly to a decrease in mechanical properties. In contrast to common polymer blends, in which usually, the hardness values do not mark-

edly deviate from the additivity law, the *H*-values in the system investigated show large deviations from the linear additivity behavior. The observed anomalous behavior is discussed in terms of the enhanced local flow processes induced by the phase-separated morphology at a nanometer scale. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 998–1006, 2006

Key words: block copolymer; electron microscopy; microhardness; deformation behavior

INTRODUCTION

Block copolymers are nanostructured systems in which microscopic heterogeneities from ordered structures arise from intramolecular phase separation. The nature, the dimensions, and the orientation of these nanostructures can be adjusted by controlling composition, molecular architecture, and processing conditions.^{1–3} There are still a number of structural modifications that can be achieved through new processing routes of block copolymer-based nanostructures, aiming at new, not yet exploited, properties of block copolymers.⁴

Block copolymers are model materials not only for the study of self-assembly phenomena, but also they may have potential applications in nanotechnology.

They are, as well, known for their excellent mechanical properties.³ The deformation micromechanisms occurring in block copolymers are different from those found in physical blends having identical composition, which are attributed to the nanosize effect of the former. Owing to the growing interest in block copolymers, a deeper insight into the structure–property correlations is desirable. Direct information on the micromechanical processes of deformation and fracture, which furnish a bridge between the morphology and mechanical properties, can be gained using electron and scanning force microscopy techniques, including *in situ* microscopy. These techniques permit a direct visualization of the morphology and influence the micromechanical deformation processes under the action of an applied load in heterogeneous polymers, including block copolymers.^{5–9}

Additional information on the nanostructure can be gained from microindentation hardness measurements. The microhardness technique has found in recent years widespread application in polymer research.¹⁰ The technique has been increasingly used in the characterization of the homopolymers, polymer blends, and copolymers. In addition, microhardness may be successfully used to gain information on the morphology–mechanical property correlations in heterophase systems. Since the microindentation method

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is, on one hand, relatively simple and, on the other hand, very sensitive to the phase behavior of the heterogeneous systems, it may serve as an important tool to gain a straightforward and deeper insight into the microstructure–morphology correlation.^{10,11} In the past, semicrystalline aliphatic polymers, such as polypropylene (PP),¹² polyethylene (PE),¹³ and condensation polymers,^{10,11} have been extensively investigated by means of microindentation hardness. In particular, this technique was used to assess strain-induced polymorphic transitions in semicrystalline polymers.¹⁴

The microhardness behavior of triblock and star block copolymers, binary block copolymer blends, and blends containing homopolystyrene has been the object of recent studies.^{15–17} The relevant finding here was that microhardness is not determined by the phase constitution of the block copolymers, but mainly by the nanostructural arrangement of the components, i.e., by the morphology. In contrast to polymer blends and random copolymers, in which the microhardness generally follows the additivity rule, the behavior of the investigated block copolymers was found to significantly deviate depending on their molecular architecture.

The aim of the present article is to extend the aforementioned studies to the blends of a styrene/butadiene star block copolymer with low molar mass homopolymers so as to further explore the influence of nanophase-separated morphology on mechanical properties and microhardness behavior.

EXPERIMENTAL

Materials and sample preparation

Styrene/butadiene star block copolymer (named as ST3) that was used to prepare the binary blends was kindly supplied by the BASF AG, Ludwigshafen. The total styrene volume content value for the star block copolymer is 0.74. The block copolymer has a number average molecular weight (M_n) and polydispersity index (M_w/M_n) of 85,700 g/mol and 2.1, respectively. Details on the characterization of the copolymer have been reported elsewhere.^{18,19}

The polystyrene homopolymer (PS010; courtesy of Dr. Marc Langela, Max Planck Institute for Polymer Research, Mainz), prepared by anionic polymerization, has a number average molecular weight (M_n) of 9800 g/mol and a polydispersity index (M_w/M_n) of 1.06. The polybutadiene homopolymer (PS004) used has a number average molecular weight (M_n) of about 4000 g/mol.

Both polymers were mixed with the star block copolymer to different weight ratios and dissolved in toluene to prepare a 3% (weight/volume) solution. Each solution was poured into a petri-disc, and the

solvent was allowed to evaporate for a period of about 2 weeks. The obtained films, of ~0.5 mm thickness, were dried for several days at room temperature and finally annealed at 130°C for 24 h to allow the formation of well-ordered structures.

Techniques

Uniaxial tensile testing was employed to determine the mechanical properties of the materials, using a universal tensile machine (Zwick 1425). 80-mm-Long dog-bone shaped tensile bars were punched out of the solution cast films. The distance between the cross-heads was 50 mm, and the tensile test was conducted at a speed of 50 mm/min. At least six specimens were tested to obtain a good statistics of the measured values.

Electron microscopy

The morphology of the samples was investigated by transmission electron microscope (TEM, 120 kV, Leo 912). Ultrathin sections of the samples (*ca.* 70 nm) were microtomed from a bulk specimen, which was immersed in an aqueous solution of osmium tetroxide for several days to selectively stain the butadiene phase. The fracture surface morphology of the samples broken in tensile tests was imaged by a scanning electron microscope (SEM; JSM 6300, Jeol). Prior to the SEM imaging, the fracture surfaces were sputtered with about 5-nm-thick gold film.

Microindentation hardness experiments were performed using a Leitz microhardness tester in combination with a square-based diamond indenter. To minimize the creep of the sample under the indenter, an indentation time of 6 s was used. The imaging technique is based on the measurement of the residual impression made by a sharp indenter upon application of a given load. The microhardness is defined as follows:¹⁰

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

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 six indentations, using loads of 100 and 150 Nm.

RESULTS AND DISCUSSION

Morphology of block copolymer/homopolymer blends

Figure 1 illustrates the morphology of the star block copolymer and selected blends using PB004 and

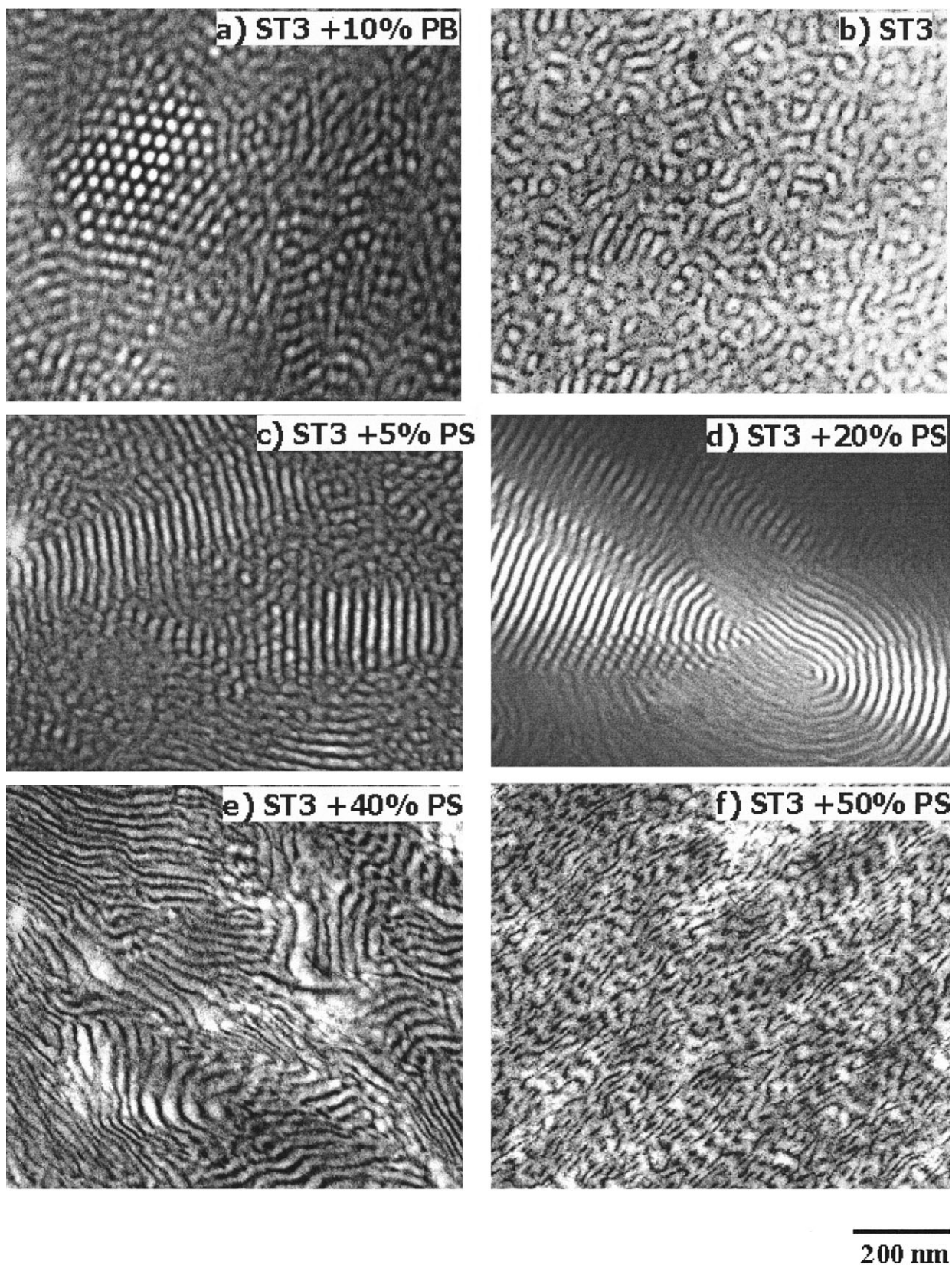


Figure 1 TEM image of the star block copolymer and its blends with PB004 and PS010 homopolymers.

PS010. In the TEM micrographs, the rubbery phase (i.e., the one containing polybutadiene chains) appears dark because of selective staining by osmium tetroxide, while the unstained polystyrene phase appears white.

The microphase-separated structure of the pure block copolymer [see Fig. 1(b)] consists of bright polystyrene domains dispersed in a matrix of gray random styrene-*co*-butadiene copolymer (PS-*co*-PB).

The morphology of the blends appears to be made up of a cocontinuous interpenetrating network of the hard (i.e., polystyrene) and soft (i.e., PS-*co*-PB copolymer) phases. This special morphology is a consequence of its special molecular architecture.^{19,20}

It is known that the low molar mass homopolymer can swell the corresponding block domains, leading to a transition in morphologies.¹ Assuming the structure of the star block copolymer to be intermediate between the PS cylinders and alternating lamellae, one may expect that cylinders and spheres of PS will be formed by adding different amounts of low molar mass PS004, as the latter practically increases the effective soft phase volume fraction. Similarly, addition of low molar mass PS leads to the formation of alternating lamellae and finally the PS matrix. In agreement with the aforementioned expectation, we have noticed that an addition of low molar mass PB004 leads to the formation of PS domains dispersed in the rubbery matrix, a morphology corresponding to the samples having lower overall PS content [see Fig. 1(a)]. In some regions, the PS domains are arranged in a hexagonal packing, suggesting the formation of a cylindrical morphology.

On the other hand, the addition of low molar mass PS leads to the formation of microphase morphologies, corresponding to the structures of a pure block copolymer having a higher PS content. For a homopolystyrene content of 20 wt % and more, a well-defined lamellar morphology develops [see Figs. 1(d) and 1(e)]. The transformation of a cocontinuous-like morphology to the lamellar one begins already at a PS content of 5 wt % [see Fig. 1(c)], in which isolated regions of lamellar microdomains are observed. By increasing the homopolystyrene content up to 50 wt %, a morphology predominantly comprising the PS matrix appears [Fig. 1(f)]. In this way, one can modify the morphology of the system by adding the corresponding homopolymer.

The discussion of the different morphologies arising by addition of the PB and PS homopolymers establishes the basis of the forthcoming microhardness study (see Microhardness behavior).

From the literature, it is well known that a stable gyroid morphology arises in monodisperse block copolymers within a narrow composition range between lamellae and cylinders.¹ In the present system, the change in the nature of microphase-separated mor-

phology by addition of low molecular weight homopolymers indicates that the added homopolymer chains are solubilized by the corresponding block domains (so-called wet-brush regime¹). Since the addition of low molar mass PB and low molar mass PS results in cylindrical and lamellar morphologies, respectively, it is reasonable to consider the equilibrium morphology of the block copolymer being close to the gyroid morphology. An important aspect from the viewpoint of the block copolymers' application is that gyroid-like morphology with apparently dispersed PS phase can be achieved by modifying their molecular architecture even at very high PS content (74 vol % polystyrene).

Tensile mechanical properties

The tensile properties of the star block copolymer have been reported in our recent article.¹⁹ The tensile stress-strain curves of the star block copolymer and its blends with PB004 and PS010 are shown in Figure 2. Owing to its morphology, comprising the cocontinuous network of PS and PS-*co*-PB, the star block copolymer behaves in a ductile manner (curve 3 in Fig. 2). The yield strength of the block copolymer is about 8 MPa, showing an elongation at break (ϵ_{br}) of several hundred percent. Since an addition of 10% PB004 results in a morphology comprising PS domains dispersed in random PS-*co*-PB copolymer [e.g., see Fig. 1(a)], one may expect a similar behavior to that of a SBS thermoplastic elastomer; i.e., the absence of pronounced yield point and a homogeneous deformation, leading to a high strain at break.³ The latter is confirmed by the stress-strain curves of the blends containing 5 and 10 wt % of PB004 homopolymer (curves 1 and 2 in Fig. 2).

The increase in overall PS content in the blends of star block copolymer by adding PS010 results in an increase in yield stress (σ_y) (compare the curves 4–7 with curve 3 in Fig. 2). During tensile testing, the deformation of the blends is characterized by necking and drawing of the specimens. Until 40 wt % PS010, necking and drawing of tensile specimens prevails, as the morphology of the blends is lamellar up to this composition. Macroscopic necking and subsequent drawing of the tensile specimens accompanied by rotation, twisting, and micro-yielding of lamellar nanostructures are known in lamellar forming heterogeneous polymers.²¹ In spite of lamellar morphology, which should be responsible for ductile behavior of monodisperse SBS triblock copolymers, the blends at high PS010 content show a strong reduction in strain at break (ϵ_{br}) (see curve 7 in Fig. 2). For a PS010 concentration of 50 wt %, as the morphology of the blend changes to that having a PS matrix, a dramatic decrease in ϵ_{br} occurs. Beyond this composition, the

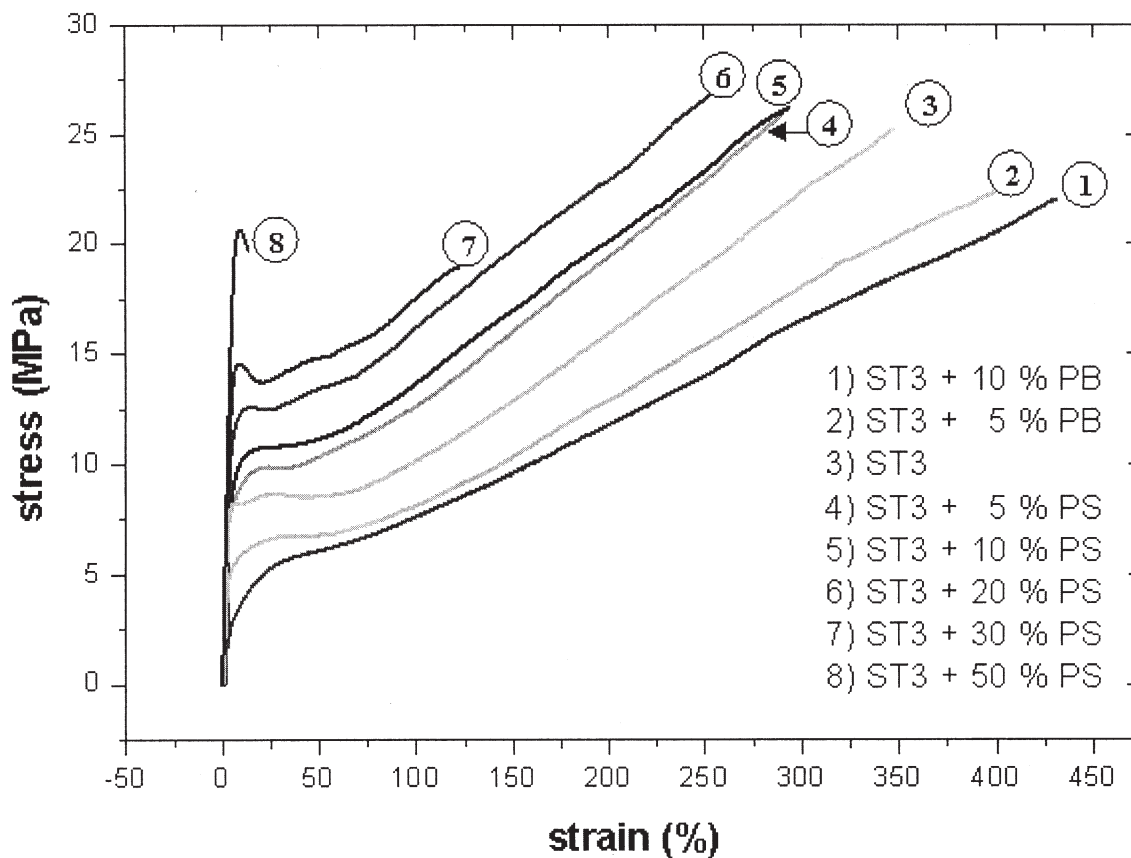


Figure 2 Tensile stress-strain curves of the samples studied; tensile testing at 23°C.

properties of the blends are obviously controlled by the PS matrix.

The discussion outlined earlier reveals that, in general, the mechanical properties of the microphase-separated systems are governed by their microscopic morphology (i.e., the nature of the nanostructures formed). However, a closer analysis of the curves for the blends with PB004 suggests that the decrease in stress level, as compared to the pure star block copolymer, is much higher than the gain in strain at break (ϵ_{br}). In these blends, the value of ϵ_{br} is significantly lower than that of a SBS triblock copolymer with a similar morphology (i.e., PS domains dispersed in rubber matrix³), such as a Kraton SBS triblock copolymer having about 30% polystyrene. Similarly, the value of ϵ_{br} for the lamellar sample (e.g., curve 7 in Fig. 2) is quite low as compared to the pure lamellar SBS block copolymer.

The addition of low molar mass homopolymer, as shown in Figure 1, swells the corresponding block domains and leads to a change in the nature of morphology. This additionally increases the amount of uncoupled chains, which may act as molecular defects during mechanical loading and initiate microcrack propagation, leading to early failure of the samples. As the molar mass of both homopolymers added to

the block copolymer lies well below their entanglement molecular weights, their chains weaken significantly the molecular knots that are necessary for the overall strength of the material. As a consequence, deterioration in the mechanical properties takes place. In conclusion, the mechanical behavior of the microphase-separated systems is not governed by the nature of morphology alone; the presence of unentangled chains may significantly alter their deformation behavior.

Analysis of fracture surface morphology

SEM micrographs showing the representative fracture surface morphology of some of the samples studied are collected in Figure 3. The surfaces were obtained by tensile testing at room temperature (23°C).

The study of the fracture surface of incompatible polymer blends and composites (where the size scale of the dispersed phase lies within the range of several microns), by means of SEM allows the estimation of domain size distribution as well as the analysis of adhesion with the matrix and possible interaction between the phases. In nanostructured polymer mixtures, however, no such structural information can be gained by the inspection of fracture surfaces morphol-

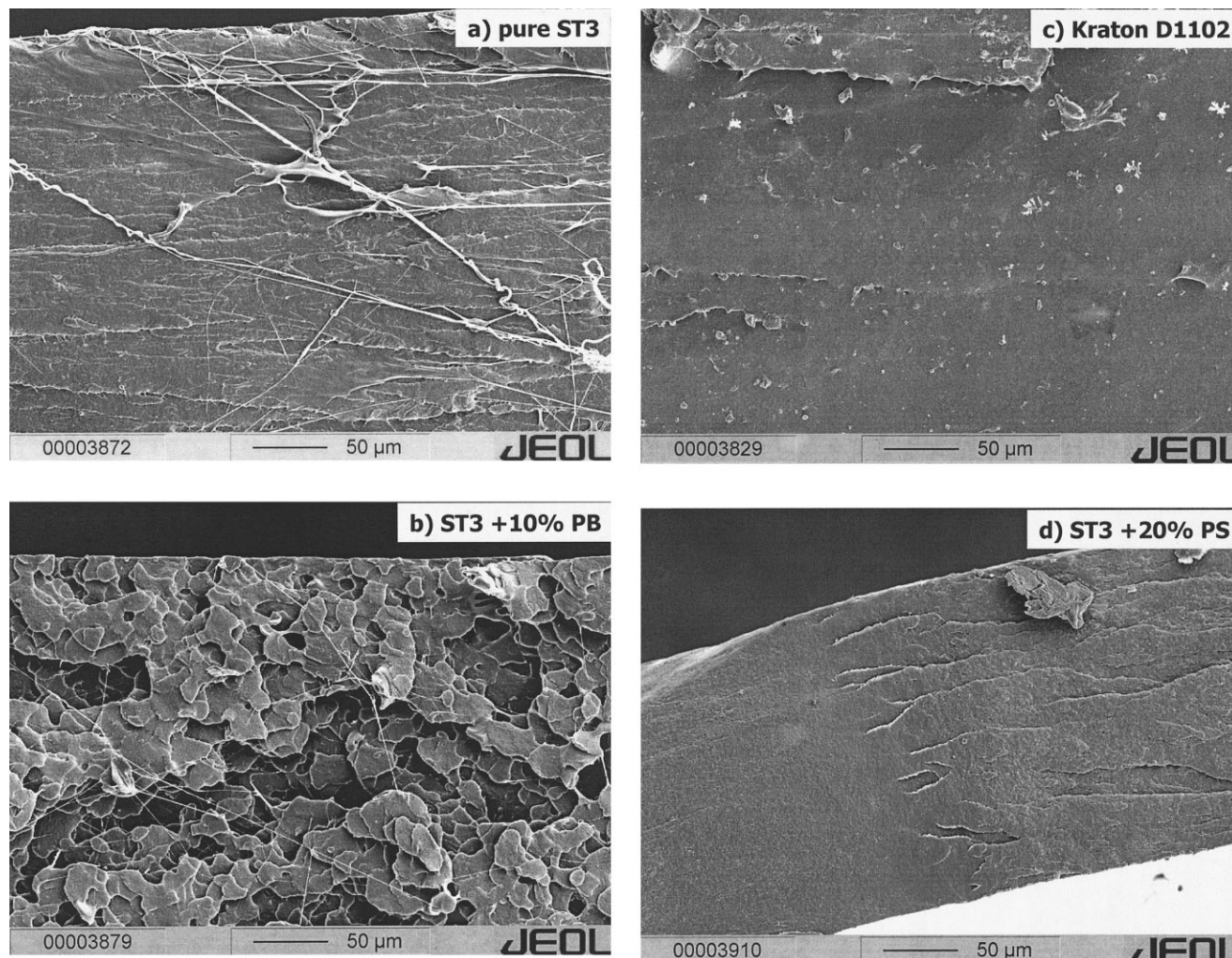


Figure 3 Representative SEM micrographs showing the fracture surface morphology of some of the samples studied.

ogy because of the very small length scale of phase-separated structures. Nevertheless, some basic phenomena occurring at a stage prior to the specimen-fracture may be traced by inspecting the fracture surface morphology of the samples broken during the tensile test.

Figure 3(a) shows a typical SEM micrograph of the fracture surface morphology of the pure block copolymer. The presence of highly stretched fibrils on the fracture surface agrees well with the ductile tensile behavior of the copolymer (see Fig. 2, curve 3). However, it should be distinguished from the fracture surface of semicrystalline polymers exhibiting a similar tensile behavior, such as high density polymer. In the latter, a dense mass of fibrils pointing to a fracture surface is observed.²²

The appearance of the fracture surface changes dramatically by adding a small amount of low molar mass polybutadiene. Actually, a blend containing 10 wt % of PB004 changes the morphology from cocontinuous to one having glassy domains dispersed in a

rubbery matrix, i.e., the added PB004 chains are accommodated by the copolymer matrix. Thus, one would expect that the fracture surface morphology is similar to that of an SBS block copolymer having similar morphology [like Fig. 1(a)] and mechanical properties (like curve 1 in Fig. 2), e.g., commercial Kraton D-1102; polystyrene content ~30%. Figure 3(b) shows that, besides isolated "spider net"-like fibers on the fracture surface, a large population of flat "platelets" originating from different depths covers the fracture surface.

For the sake of comparison with the blend containing PB004, the fracture surface morphology of Kraton polymer is presented in Figure 3(c). Here, only a few isolated regions of rougher islands can be distinguished. The observed flat surface extending over a large area results from reversible deformation of the thermoplastic elastomer. A closer look on the micrographs reveals that the surface morphology of each platelet in Figure 3(b) is analogous to that of Kraton polymer in Figure 3(c). Hence, the formation of a

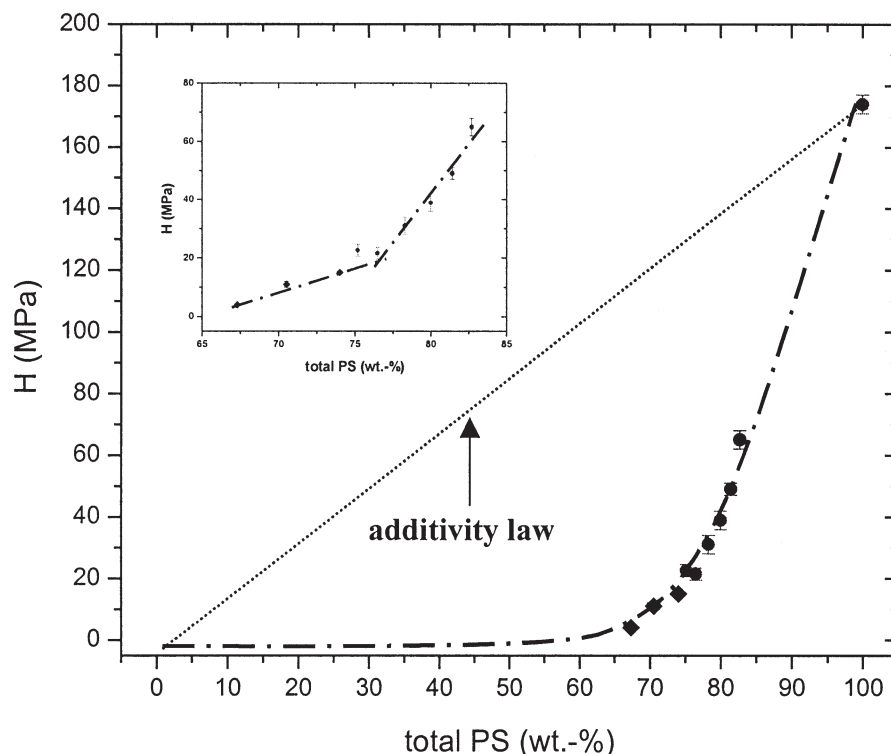


Figure 4 Microhardness as a function of total PS content in the blends of star block copolymer with homopolymers; volume fraction and weight fraction of the components were assumed to be equal.

surface consisting of a large number of small platelets can be envisioned as a result of the breaking of a large flat surface into smaller fragments, indicating that the microcracks are initiated at several locations. The weak points for this process are provided by the presence of unentangled PB004 chains present in the PS-co-PB matrix. These microcracks act as precursors for the premature failure of the sample, finally leading to lower values of tensile stress and elongation at break.

The addition of low molar mass PS leads to an increasing total PS volume fraction and formation of morphologies, corresponding to overall PS content, as PS chains are accommodated by the PS block domains. As discussed in the foregoing section, the blends having 10–40 wt % PS010 exhibit a lamellar morphology (see Fig. 1). Similar to the case of blends with low molar mass PB004, the lamellar blends do not show a deformation behavior characteristic of a pure lamellar block copolymer. In contrast to the expected ductile deformation (e.g., the presence of drawn fibrils on the fracture surface), a large area of flat fracture surface produced by rapid propagation of unstable cracks can be seen already at 20 wt % PS010 [see Fig. 3(d)]. This leads to a decrease in strain at break by about 100% relative to the pure star block copolymer. This implies that the lamellar blends containing low molar mass PS chains tend toward a brittle behavior, such as that of pure polystyrene. It should be stated that the addition of PS010 also leads to a higher yield stress, but the

decrease in strain at break (a measure of ductility) at higher PS010 content is quite significant (see Fig. 2). The latter can be regarded as a result of premature failure related to the weakening of entanglements by the presence of low molar mass homopolymer. In this case, the unstable microcracks are quite likely to originate in the PS lamellae or PS matrix.

In summary, the deformation behavior (mechanical properties and the underlying microdeformation mechanisms) of styrene/butadiene block copolymers at room temperature are controlled by the nature of the nanostructured morphology, only if the glassy outer chains are sufficiently entangled. The presence of homopolymer having molecular weights far below their entanglement molecular weights may act as precursors for unstable microcracks, leading to the early failure of the material.

Microhardness behavior

Figure 4 illustrates the microhardness variation of the investigated samples as a function of total PS content, assuming polybutadiene to be in the liquid-like state; i.e., having no contribution to the hardness ($H = 0$). The measured hardness of pure polystyrene used to prepare the blends (i.e., one having a molecular weight of 9800 g/mol) is about 172 MPa. The dotted straight line in Figure 4 illustrates

the hardness as a function of composition according to the additivity law:

$$H = H_{\text{PS}}\Phi_{\text{PS}} + H_{\text{PB}}(1 - \Phi_{\text{PS}}) \quad (2)$$

where H_{PS} and Φ_{PS} represent the microhardness and the weight fraction of polystyrene, respectively.

The star block copolymer has a hardness of about 16 MPa, which decreases monotonically with addition of PS004. At 10 wt % PB004, the microhardness reaches a value of 4 MPa. Similarly, addition of low molar mass PS results in a dramatic increase in hardness, as expected. For 50 wt % PS010, a value of ~60 MPa was determined. Most striking is the large deviation of experimentally determined data from the additivity law.

Deviations of the hardness values from the additivity law have been shown to occur before in other polymers, e.g., in rubber-modified semicrystalline polymers, in which the hardness of the crystals in the blends is lower than in the homopolymer.²³ The deviation from the additivity law in polymer blends is correlated to structural changes, such as decrease in crystallinity, variation in crystal thickness, surface free energy of the crystals, etc.¹⁰ However, the deviation in the H -values observed in the present study is significantly larger than that reported in other polymer materials. The larger deviations detected here indicate that the total styrene content present in the block copolymers and in the blends with homopolymers bears no correspondence with the measured data. Irrespective of the nature of the microphase separated morphology, the H -values are far less than those predicted by the additivity law (Fig. 4). A closer look at Figure 4 reveals that the H -values increase almost exponentially with increasing total PS content. The exponential dependence of H with composition seems to be a characteristic feature of nanophase-separated block copolymer systems, consisting of glassy/rubbery components.¹⁵⁻¹⁷ The validity of this tendency should be further tested in other glassy/glassy systems.

One may think that the lower H -values found are caused by the low molar mass of the added homopolymer. We cannot exclude the effect of molecular weight of homopolymer, based on the results obtained so far. However, it can be stated that the lower molar mass effect of the added homopolymers has a negligible consequence. A similar finding was also observed in the blend of standard polystyrene and a star block copolymer.¹⁵ Neither any influence of the glass transition temperature (T_g) is detected. The T_g of either of the components does not change with composition.

A part of the H versus composition curve of Figure 4 is magnified in the inset. It can be seen that the slope of the curve slightly changes at a total PS content of

~80 wt %. At this composition, the formation of lamellar structures begins and below this the morphology comprises the rubbery matrix (see also Fig. 1). In other words, a transition in morphology from rubbery matrix to lamellar structure takes place at this composition. Thus, microhardness measurements can provide evidences on morphological transition in block copolymer systems.

The existence of a phase-separated morphology on the nanometer scale for the block copolymers can be envisioned as a cause behind a strong deviation in the microhardness behavior. As compared to the macrophase-separated morphology of classical polymer blends, the heterogeneity in nanometer range facilitates overall local plastic deformation processes in block copolymers. The intensified local plastic processes, such as shearing in the liquid-like phase, yielding of glassy phase, as well as rotation and alignment of grains, should be regarded as the reason for the observed anomalous micromechanical behavior of the block copolymer systems.¹⁵

CONCLUSION

1. By addition of low molar mass homopolymers, compatible to either of the two blocks of an asymmetric styrene/butadiene star block copolymer, the nanostructure and the mechanical properties can be significantly altered.
2. The deformation behavior of these styrene/butadiene block copolymer blends does not correspond exactly to that of the corresponding SBS block copolymers having similar morphologies, which is attributable to the presence of unentangled homopolymer chains.
3. In contrast to common polymer blends, which show relatively smaller deviations from the hardness additivity law, the measured H -values of the microphase-separated block copolymer systems are found to be significantly smaller than are the predicted ones.
4. It is suggested that the observed large deviation from the hardness additivity behavior may be correlated with the enhanced local flow processes induced by the microphase morphology.

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