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Morphology and Micromechanical Behaviour of Styrene/Butadiene Block Copolymers and Their Blends with Polystyrene

Rameshwar Adhikari,[1] *Goerg H. Michler,* *[1] *Konrad Knoll*[2]

[1] Institute of Materials Science, Martin-Luther University Halle-Wittenberg,
D-06099 Halle/Saale, Germany
[2] BASF Aktiengesellschaft, Polymers Laboratory ZKT/I-B1,
D-67056 Ludwigshafen, Germany

Summary: The correlation between the morphology and the deformation mechanism in styrene/butadiene block copolymers having modified architecture and in blends with homopolymer polystyrene (hPS) was studied. It was demonstrated that the morphology formation in the block copolymers is highly coupled with their molecular architecture. In particular, the micromechanical behaviour of a star block copolymer and its blends with polystyrene was investigated by using electron microscopy and tensile testing. A homogeneous plastic flow of polystyrene lamellae (*thin layer yielding*) was observed if the lamella thickness was in the range of 20 nm. The deformation micromechanism switched to the formation of craze-like deformation zones when the average PS lamella thickness changed to about 30 nm and more.

Keywords: blends, electron microscopy, micromechanism, styrene/butadiene block copolymers, thin layer yielding

Introduction

The use of polymeric materials in everyday life is increasing day by day, where often a balance of mechanical and optical properties is desired. From the economical point of view, one may be interested to produce the plastics as cheap as possible. In order to be successfully competent in the market, these products should possess attractive price and interesting property profile. On the other hand, the concern of the recyclability of the plastics is also being a very important aspect from both ecological and economical points of view.

For the applications like food packaging films, beverage drinking cups etc., an excellent optical property is desired in addition to the optimum level of the mechanical parameters such as toughness, stiffness and strength.[1] These demands should be fulfilled by the plastics which are

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easy to synthesise, and are processable by easy means. The goal may be achieved by the heterogenisation of commodity plastics like polystyrene. The heterogenisation of polystyrene, a brittle polymer in the bulk state, by the incorporation of a small amount of rubber (e.g., polybutadiene PB) may lead to a drastic increase in the toughness but the product is opaque.[2,3] A common example of toughened polystyrene is the high impact polystyrene (HIPS). Hence, one of the challenges in academia and industries in the field of polymer research is the development of tough and transparent heterogeneous polymers, e.g., toughened polystyrene.

It has been demonstrated that the polymers which break macroscopically in a brittle manner (e.g., poly(methyl methacrylate) PMMA, polystyrene PS) are intrinsically ductile.[2,4] The theoretical maximum natural draw ratio (λ_{max}) of polystyrene is about 4 and that of PMMA is about 3.[2] This means that these polymers can show an elongation to break of several hundred percent. Hence the main goal of the toughness modification of the brittle plastics like polystyrene is to transfer their intrinsic ductility to the macroscopic scale.

It is well known that joining the polystyrene chains with the polybutadiene chains with covalent bonds leads to the intramolecular phase separation of these chains and result in the formation of highly ordered structures called microphase separated structures (MSS) whose dimension lies in the range of gyration-radius of the molecules.[5] Through the variation of molecular weight, composition, chain architecture and the processing conditions, the dimension, nature and orientation of these structures can be adjusted.[5-10] This allows to produce the transparent nanostructured heterogeneous polymeric materials and enables a precise control over their mechanical properties.

Because of their higher production costs, the block copolymers are seldom used as pure materials. Styrene/butadiene block copolymers, for example, are often used in combination with homopolystyrene (e.g., general purpose polystyrene GPPS).[1,10] The compatibility of the added polystyrene with the block copolymer is limited by concentration and molecular weight amount of the homopolystyrene (hPS) chains relative to the corresponding block of the block copolymer.[5,9] The molecular weight of the polystyrene blocks is, however, practically restricted by the requirement of the rheological properties.

In our pervious studies, we reported about the toughening mechanism in the asymmetric styrene/butadiene star block copolymers and the influence of molecular architecture on their microphase morphology and micromechanical behaviour.[11,12] The aim of this study is to investigate the influence of the modified molecular architecture of styrene/butadiene block copolymers in a narrow composition range (ca. 70 volume % polystyrene) on their morphology and to analyse, in particular, the micromechanical behaviour of the blends consisting of a star block copolymer and general purpose polystyrene (GPPS).

Experimental Section

Materials and Sample Preparation

The important characteristics of the block copolymers and homopolystyrene studied are listed in Table 1. The details of the morphology of the block copolymer may be found in the references mentioned in the parentheses. In particular, the morphology formation in the linear triblock copolymers and their correlation with the tensile properties was studied by tapping mode scanning force microscopy.[13] In this work, we report the equilibrium morphology of the bulk materials investigated by means of transmission electron microscopy (TEM).

The block copolymers have nearly identical chemical composition (about 70 volume % of styrene). Except the sample LN1-S74, which is a linear symmetric SBS triblock copolymers, the remaining block copolymers possess non-classical molecular architecture (asymmetric structure, tapered transition, etc.). The samples were provided by the BASF Aktiengesellschaft, Ludwigshafen.

The block copolymer chosen to prepare blends with polystyrene was an asymmetric star block copolymer (ST2-S74, volume fraction of PS, $\Phi_{ST} = 0.74$; see Table 1). It has 4 asymmetric SBS arms in average, one of which is much longer than the others. The longest arm is styrene-rich while the shorter ones are butadiene-rich.[1,12]

Two different types of polystyrene homopolymer (hPS) samples were used: one of them has a lower molecular weight $M_w = 15,000$ g/mol and $M_w/M_n = 1.29$ (named as PS015) and the other one has a higher molecular weight $M_w = 190,000$ g/mol and $M_w/M_n = 2.3$ (named as PS190). The latter was a general purpose polystyrene (GPPS).

The samples were prepared by two different methods: solution casting and injection moulding (mass temperature 250°C and mould temperature 45°C). The mixtures were prepared in various weight ratios: 20, 40, 60 and 80 wt-% hPS. Solution casting was performed using a neutral solvent toluene allowing the solvent to evaporate from the sample solution (3 % weight/volume) over a period of about two weeks. The films, about 0.5 mm thick, were dried and annealed for 48 hours in a vacuum oven under reduced pressure.

Table 1. The characteristics of the block copolymers investigated, LN and ST stand for linear and star architectures, respectively.

samples	§M_w (g/mol)	§M_W/M_n	*Φ_{ST}	remarks
LN1-S74	87,700	1.07	0.74	symmetric SBS triblock, neat transition with the pure PB mid-block, linear architecture [13]
LN2-S74	105,100	1.13	0.74	asymmetric S_1BS_2 triblock copolymer, ($S_1 \neq S_2$), tapered transition [13]
LN4-S65	139,200	1.20	0.65	random PS-co-PB copolymer as rubbery mid-block, symmetric outer PS blocks, linear architecture [1,13]
ST2-S74	184,000	1.69	0.74	highly asymmetric star architecture, each arm with S_1BS_2 structure ($S_1 \neq S_2$), tapered transition [1,11,12]
PS015	15,200	1.29	100	polystyrene homopolymer
PS190	190,000	2.30	100	polystyrene homopolymer

* total styrene volume fraction determined by Wijs titration and procedures

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

Tensile Testing

Macroscopic tensile tests using the injection moulded bars were carried out using universal tensile machine (Zwick 1425) at a cross head speed of 50 mm/min at room temperature (23°C) according to ISO 527.

Transmission Electron Microscopy (TEM)

Morphological details of undeformed as well as deformed samples were examined using transmission electron microscopy (TEM, Joel 200 kV). For the TEM investigations, a small block of specimen taken from the middle of a tensile bar approximately 0.10 mm below the surface was trimmed to a pyramidal shape and immersed in an osmium tetroxide (OsO_4) solution for several days at room temperature (23°C) to selectively stain the butadiene phase. Ultra-thin sections of the samples were cut from each block using a Leica Ultracut-C Ultramicrotome operated at room temperature (23°C). Sections from strained samples were taken from the location close to the fracture surface. Lamellar long period and lamellar thickness were quantified from the transmission electron micrographs using a special image processing program and Fourier transformation.

Results and Discussion

Influence of Block Copolymer Architecture on Their Morphology

Classically the nature and the dimension of the diblock copolymer morphologies are adjusted by the variation of composition and molecular weight. In the strong segregation limit, with increasing polystyrene (PS) content, body centred cubic spheres, hexagonal arranged cylinders or 3D 'gyroid' network of polystyrene (PS) domains dispersed in the matrix of polyisoprene were observed in poly(styrene-block-isoprene) SI diblock copolymers.[5,8] With further increase in the PS content, the alternating layers of PS and PB lamellae and the structures mentioned above in the reversed order were found (Figure 1, top). As demonstrated by our works, one may notice that the microphase separated morphology of the styrene/butadiene based block copolymers can be considerably changed also by the variation of the molecular architectures (Figure 1, bottom).

In consideration of the classical diblock copolymer phase diagram, hexagonal PB cylinders in the matrix of PS phase would be expected in the SBS triblock copolymers with 74% volume fraction of polystyrene without any modification of the molecular architecture (Figure 1a, bottom). The results of our investigations showed that the relative volume fraction of the hard and the soft components may be altered significantly by the modification of the molecular structure of the styrene/butadiene block copolymers: a 'two-component three-phase' morphology consisting of alternating layers of polystyrene and polybutadiene (where the PB lamellae contain scattered PS domains) appeared in the tapered asymmetric star block copolymer (Figure 1b, bottom). This characteristic ‘two-component three-phase’ morphology was observed in the copolymer having polystyrene chains in the molecule core.

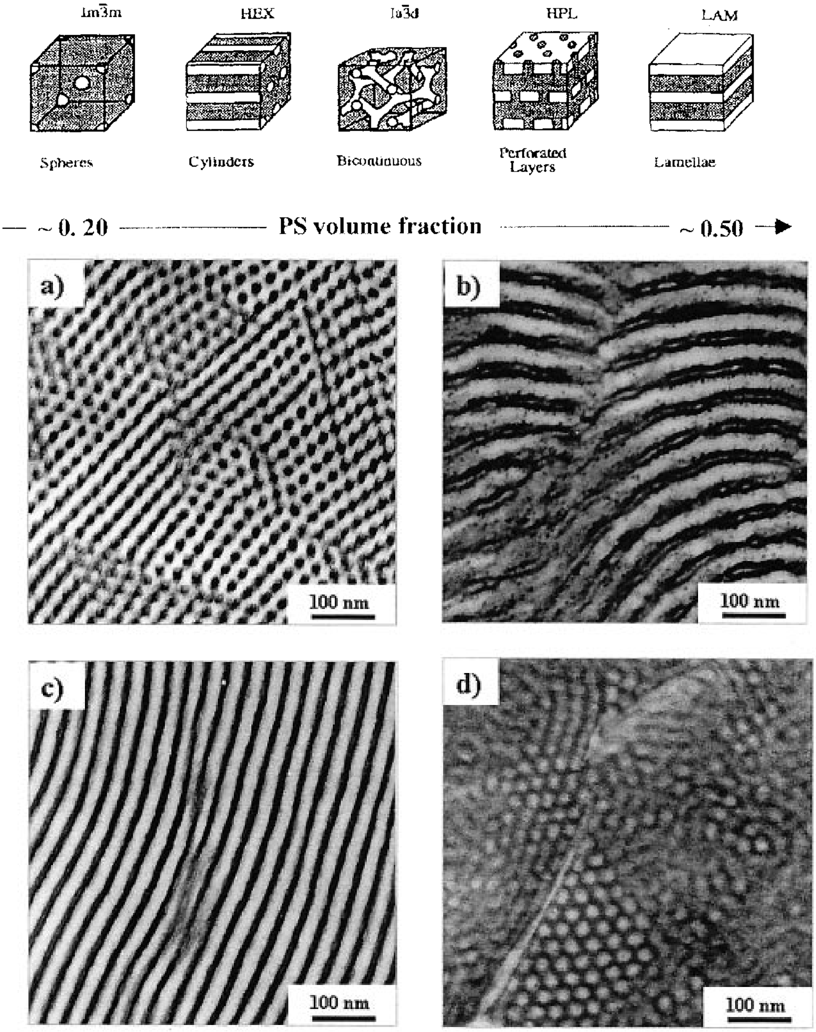

Fig. 1. Top: Scheme representing the morphology of styrene/butadiene diblock copolymer as a function of polystyrene content (the picture from ref. 5, p. 27); bottom: TEM micrographs showing the morphology of the investigated block copolymers – a) LN1-S74, b) ST2-S74, c) LN2-S74 and d) LN4-S65.

The PS core with a total molecular weight of about 20,000 g/mol, which is enough for the formation of the phase separated domains, makes it possible that the scattered cylinder-like domains are formed inside the PB lamellae in this star block copolymer. Such a morphology was reported in an ABC triblock copolymer by Shibayama et al.[14]

Keeping the overall chemical composition constant (Φ_{PS} = 0.74) and introducing quite a long tapered transition between the polybutadiene (PB) and the polystyrene (PS) blocks in an asymmetric SBS triblock copolymer (LN2-S74, see Figure 1c, bottom) further modifies the block copolymer morphology. In LN2-S74, an unambiguous lamellar morphology was observed. The formation of lamellae-like (as in ST2-S74) or clear lamellar (as in LN2-S74) morphology in the asymmetric block copolymers is also associated with a large shift in the glass transition temperature of polybutadiene phase ($T_{g\text{-}PB}$). The formation of lamellar morphology in ST2-S74 and LN2-S74 instead of the hexagonal PB cylinders (one similar to that of LN1-S74 presented in Figure 1a, bottom) is the result of following factors: i) asymmetric architecture (shift of phase diagram) and ii) presence of a part of polystyrene in the butadiene phase (increase in volume fraction of the soft phase).

Table 2. Glass transition temperature of the soft and the hard phases in the investigated block copolymers (data obtained by differential scanning calorimetry, DSC, heating rate 10°C/min).

Polymer	**$T_{g\text{-}PB}$ (soft phase)/°C**	**$T_{g\text{-}PS}$ (hard phase)/°C**
LN1-S74	-98	101
LN2-S74	-53	101
LN4-S65	-34	70
ST2-S74	-79	104

The presence of a fraction of PS chain segments in the PB phase is suggested by a significant increase in the $T_{g\text{-}PB}$ (see Table 2). Additionally, the presence of tapered interface might favour an increase in volume fraction of the soft phase.[1] In the literature, it was discussed that the tapered transition has a strong influence on the interface width; and it may even lead to a separate phase, which has its own glass transition temperature.[15] However, we observed only a strong shift of $T_{g\text{-}PB}$ towards higher temperature in the tapered SBS block copolymers relative to the neat ones.[16]

Randomising the rubbery block (e.g., by the incorporation of a styrene/butadiene random copolymer as the rubbery block) may shift the soft phase volume fraction to even higher magnitude enabling the formation of 'gyroid'-like morphology, the latter being expected in a neat diblock copolymer at a composition range of $\Phi_{PS} \sim 0.32$. In a star block copolymer whose structure is analogous to that of ST2-S74 (see Table 1 and ref. [11,12]), 'gyroid'-like morphology was observed.[17]

The shift of morphology scheme, discussed so far, is valid for the block copolymers independent of their molecular topology. As shown by our TEM investigations of a linear styrene/butadiene triblock copolymer having a random styrene-co-butadiene centre block and total 65 vol.-% styrene (Figure 1d, bottom), the morphology consists of the dispersed polystyrene domains. Dispersed PS domains in the matrix of styrene-co-butadiene is expected since the volume fraction of the PS blocks in this copolymer is about 0.32.

It should be mentioned that a modification in molecular architecture, which leads to an increase in the effective volume fraction of the soft component, must be associated with the intervention of the stiff polystyrene segments in the butadiene phase which comprises the flexible chains at room temperature. This hinders the mobility of the soft phase (here the PB phase) and hence causes an increase in the glass transition temperature ($T_{g\text{-}PB}$). In all the block copolymers with modified architectures an increase in the $T_{g\text{-}PB}$ was found (see Table 2).

In fact, besides the volume fraction of the phases, the thermodynamics at the interface is the key factor that plays a decisive role in determining the interfacial curvature, i.e., via the interaction parameter of the two species in contact.[5] Thus a change in the chemical nature of the blocks at the interfacial region (neat versus tapered or random) should affect the thermodynamic equilibrium and the resulting morphology.

The equilibrium morphologies of the block copolymers outlined above are stable ones. These were observed independent of preparation conditions. The processing history influences mainly the orientation and order of the microdomains and not their nature and dimension.[16] The results discussed present an excellent evidence of possibility of modifying the block copolymer phase diagram via a change in molecular architecture. Thus, the architectural modification of block copolymers may open an important way of controlling their morphology and mechanical properties.

Morphology Formation in Block Copolymer/PS Blends

It is well known that the length of the homopolymer chains relative to that of the corresponding block of the block copolymer plays a vital role in the phase behaviour of the block copolymer/homopolymer blends.[5,9] The molecular weight of the longest PS block in the star block copolymer ST2-S74 is in the range of 70,000 g/mol.

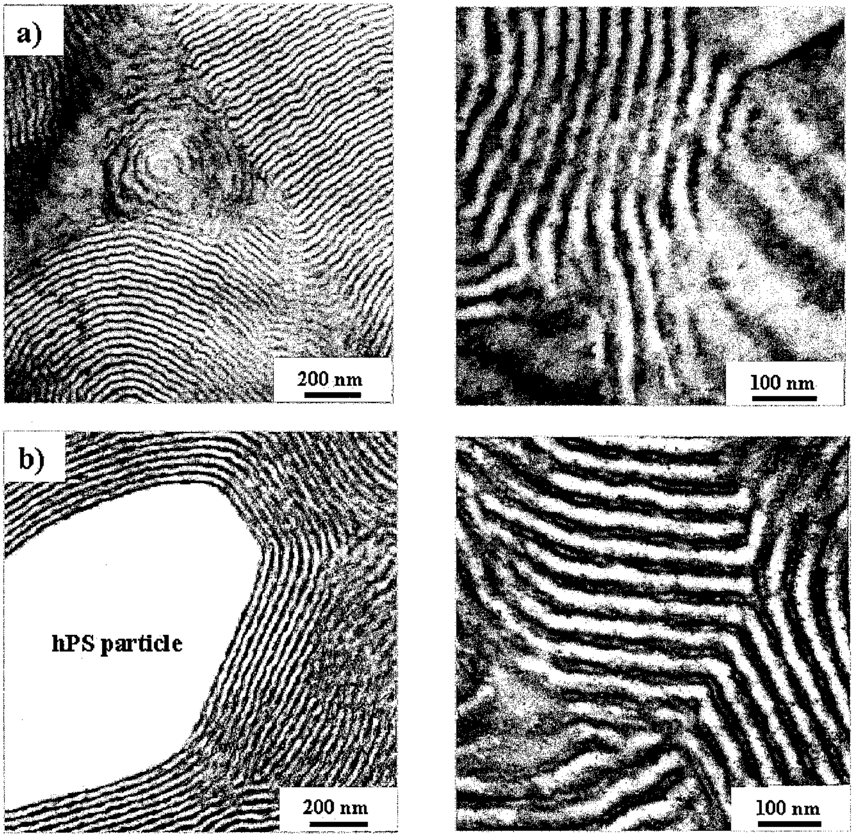

Fig. 2. Lower (left) and higher (right) magnifications of TEM micrographs of the star block copolymer/hPS blends as a function of hPS molecular weight M_{hPS}: a) M_{hPS} = 15,200 g/mol and b) M_{hPS} = 190,000 g/mol; hPS content 20 wt.-% in each case; solution cast films.

Figure 2 shows representative TEM micrographs of the two blends of ST2-S74 with 20 wt.-% hPS. The samples were prepared by solution casting. The polystyrene samples differ in the molecular weight. PS015 and PS190 have the weight average molecular weight (M_w) of 15,200 g/mol and 190,000 g/mol, respectively (Table 1). Details about the morphology and micromechanical behaviour of the blends may be found in another publication.[18]

The molecules of the sample PS015 are shorter than the longest polystyrene block of the parent star block copolymer. Hence these chains may diffuse into the PS blocks of the block copolymer and swell the PS lamellae (Figure 2a). This leads to the formation of a microphase separated morphology (absence of PS particles). The PS lamellae in this blend thicker (about 22 nm) than in the pure star block copolymer (about 20 nm).

Increasing the molecular weight of the added polystyrene (hPS) decreases the entropy of these chains and the hPS chains cannot diffuse deeply into the PS block of the block copolymer. These hPS chains 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 in the matrix of microphase separated block copolymer matrix at low hPS concentration. 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 (Figure 2b). The lamellar thickness (20 nm) and the spacing (about 42 nm) in the macrophase separated blend is the same as in the pure block copolymer.

It should be mentioned that the polystyrene samples used in this work have a wide molecular weight distribution. Hence, a low molecular weight part of PS190 might still be added to the PS block of the block copolymer. Moreover, a part of PS015 may even be added to the butadiene phase of the pure block copolymer as suggested by recent works of Feng et al.[19]

The situation changes when the blends are mixed in extruder and processed by injection moulding. Due to the high speed processing and rapid cooling conditions during the moulding process, there is not enough time for the components to form the structures that may be expected under equilibrium conditions.

Figure 3 presents the TEM micrographs of the pure block copolymer and two blends prepared by injection moulding. Details on the morphology and micromechanical behaviour of these blends may be found in.[17] Since the thickness of the structures doesn't exceed 100 nm, the blends may be regarded as being microphase separated. This is the reason why the blends were nearly as transparent as the pure block copolymer itself. The microphase separated structures are oriented in the direction of shear force (i.e., along the injection direction) in the pure block copolymer as well as in the blends.

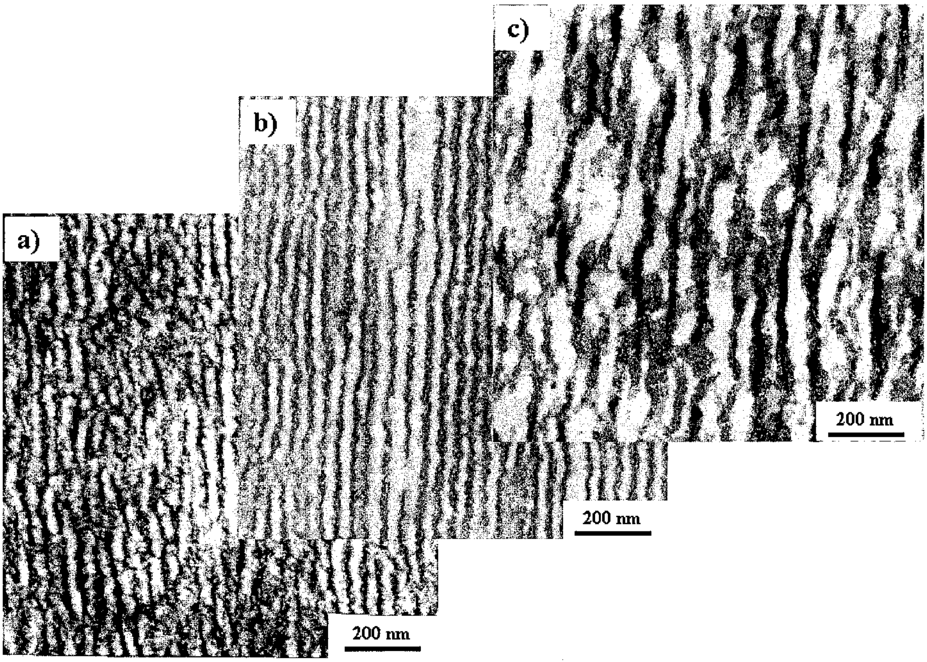

Fig. 3. Representative TEM images showing the morphology of injection moulded samples: a) pure ST2-S74, b) blend with 20 wt.-% PS190 and c) blend with 60 wt.-% PS190, injection direction vertical.

The thickness of the PS lamellae (or PS strands) increases continuously with increasing PS190 content in the blends. At the same time, the thickness of the PB lamellae doesn't change significantly. This suggests that the homopolystyrene chains are accommodated at the PS block lamellae of the pure copolymer. At higher PS content, the PB lamellae appear as elongated worms dispersed in the PS matrix Figure 3c.

To demonstrate the result of the added hPS to the PS block lamellae of the star block copolymer, the thickness distribution of the PS lamellae in pure ST2-S74 and the blend with 20 wt.-% PS190 is represented in Figure 4. One can see that the average thickness of the PS lamellae changes from ca. 20 nm (pure block copolymer) to about 30 nm (blend with 20 wt.-% PS). The average value of the PS lamella thickness continuously increases with increasing PS190 content in the blends.

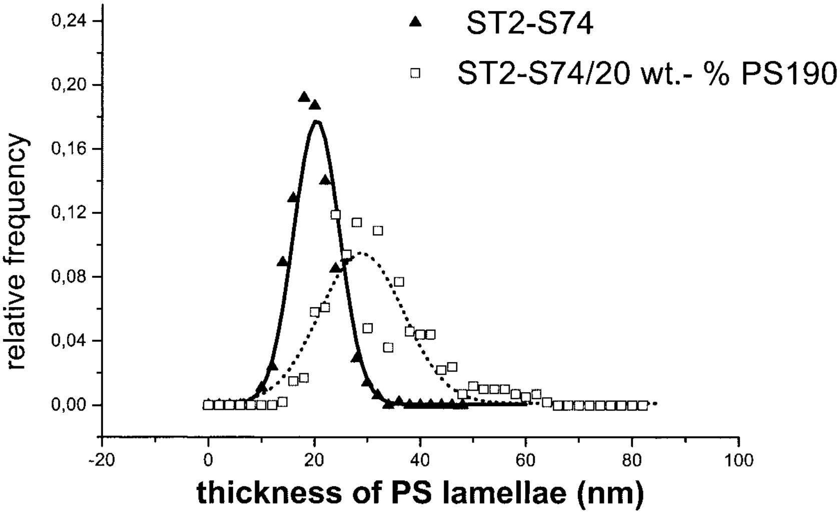

Fig. 4. Distribution of PS lamella thickness in ST2-S74 and a blend with 20 wt.-% PS190.

Micromechanical and Mechanical Behaviour

Micromechanical and mechanical behaviour of the phase separated block copolymer systems are generally controlled by two variables: molecular parameters and phase morphology. The molecular parameters include the molecular construction (diblock, triblock, star block, graft block structure, and the location of the rubbery block in the molecule etc.), molecular weight, chain topology (star block, graft block structure etc.).

Our previous works showed that the molecular structure of the block copolymers affects also the phase volume ratio (soft/hard volume ratio) and hence enables the formation of morphologies which would be expected in another composition range in a neat diblock copolymer.[13] The resulting morphology has the decisive impact on the micromechanical and mechanical behaviour of these block copolymer systems. Obviously, the block copolymers

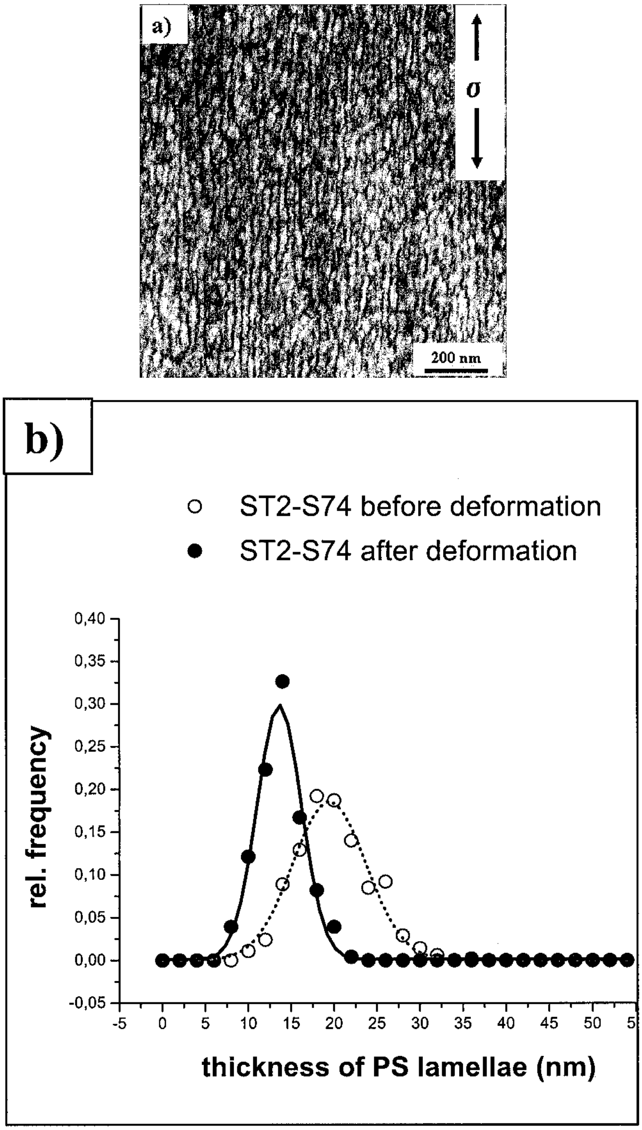

Fig. 5. a) TEM micrograph showing the morphology of the injection moulded ST2-S74 after deformation up to fracture, sample location close to the fracture surface (compare with Figure 3a), and b) the distribution of PS lamella thickness in ST2-S74 before and after deformation.

presented in Figure 1, due to the presence of different morphologies, are characterised by different micromechanical behaviour and result in entirely different kinds of macroscopic mechanical properties.

Figure 5a shows the morphology of the injection moulded star block copolymer ST2-S74 after tensile deformation (compare with Figure 3a). The sample was taken from the locations close to the fracture surface after tensile testing. Quantification of the PS lamella thickness in this block copolymer before and after deformation is presented in Figure 5b. It can be easily noticed that the average thickness of the PS lamellae has been reduced by from about 20 nm to about 12 nm, i.e., a reduction by about 50 %. Assuming the same degree of reduction in the lateral direction of the lamellae during deformation, a stretching ratio of $\lambda \sim 4$ (a local strain of about 300%) may be calculated. It is interesting to note that this calculated strain of the lamellae is in the same range as the macroscopically measured value of the strain at break of the bulk injection moulded specimens (Figure 6a). This value corresponds also to the maximum draw ratio of craze fibrils in bulk polystyrene samples.[3]

The fact, that the local strain of the PS lamellae approximately corresponds to the macroscopic strain at break of the compact star block copolymer, suggests that the ductility of the star block copolymer is a consequence of the homogeneous plastic deformation of the PS lamellae. Of course, the deformation of the rubbery phase (which may be regarded as being in the liquid state with the T_g of about -76°C) combined with the slipping of the glassy layers have contributed partly to the high elongation achieved by the compact star block copolymer (see Figure 6).

Since the PS lamellae in the investigated block copolymers are about 20 nm thick, it can be easily noticed that the drawing of the PS lamellae is quite similar to that of the craze fibrils in the polystyrene homopolymer. Both craze fibrils and PS lamellae have similar dimensions (thickness) and also show a similar extension ratio. Due to a very low glass transition temperature of the butadiene phase in the block copolymers, it may be regarded as a liquid and has analogous function as the microvoids in the PS craze. This means that the intrinsic ductility of the PS can be achieved by reducing the dimension of the PS layers down to a critical value (in the range of 20 nm in styrene/butadiene triblock copolymers). Based on the results obtained from a number of lamellar block copolymers, we formulate the mechanism of '*thin layer yielding*'. As the name already suggests, the PS layers are capable of undergoing a homogeneous plastic deformation

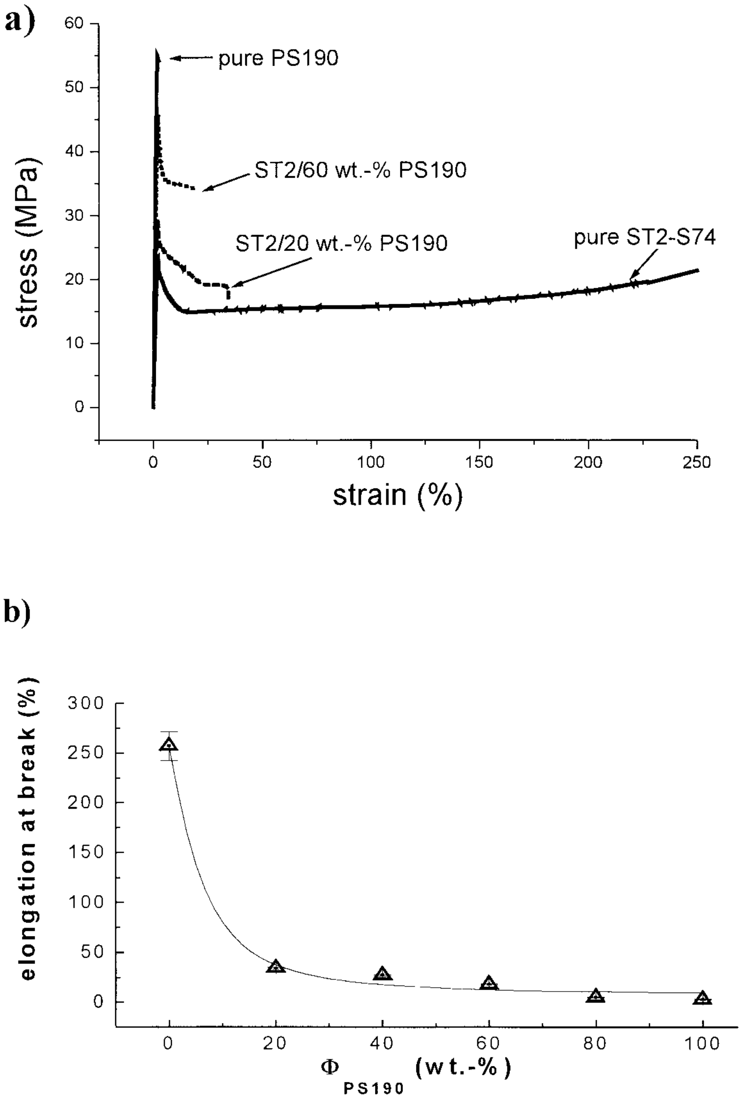

Fig. 6. a) Stress-strain curve of the star block copolymer ST2-S74 compared with that of pure polystyrene PS190 and blends containing 20 and 60 wt.-% PS190; b) elongation at break plotted against the PS190 content in the ST2-S74/PS190 blends.

under tension if the thickness of these layers lies below a critical value. As a result, the elongation to break which is a measure of ductility, drastically increases. Above this critical thickness the material behave brittle (see Figure 6b).[11]

The plastic deformation of glassy PS lamellae in the block copolymer studied is in line with earlier studies of Kawai et el. on unoriented films. Using TEM and SAXS, they showed that, during plastic deformation, shearing and kinking processes occurs prior to the disruption of glassy PS lamellae.[20,21] At higher strains, formation of 'fish-bone structure' (chevron-morphology) characterized by a four-point SAXS pattern was observed.

Recently, Thomas and co-workers explored the deformation behavior of oriented lamellar SBS triblock.[22] During parallel and perpendicular loading, destruction of lamellar morphology and formation of chevron morphology, respectively were observed. The homogeneous plastic flow of glassy lamellae is a cause of destruction of lamellar morphology leading to a reduction in lamellar spacing during parallel deformation as reported by Thomas and co-workers.[22]

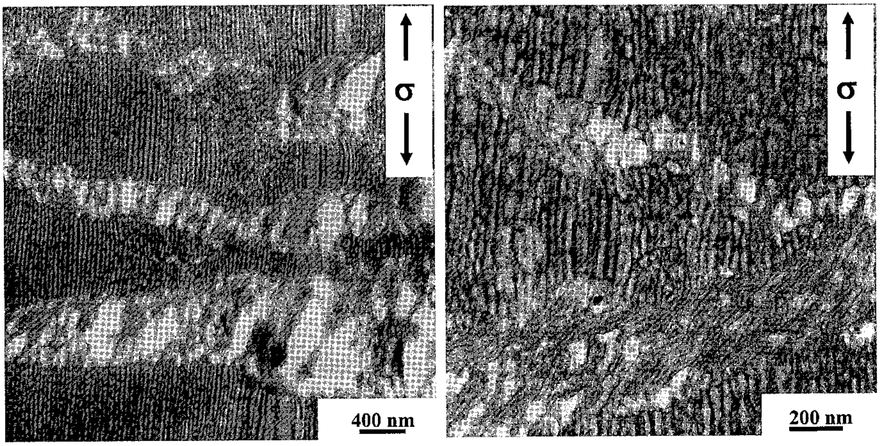

Fig. 7. Lower (left) and higher (right) magnification of TEM micrographs showing the morphology of injection moulded ST2-S74/20 wt.-% PS190 blend and crazes after deformation, deformation direction is shown by an arrow; samples stained by OsO_4.

To examine the influence of the PS layer thickness, we studied the deformation behaviour of blends of the star block copolymer ST2-S74 with polystyrene homopolymer PS190 prepared by injection moulding. With increasing homopolymer content, the PS lamellae thickness increases (see Figure 4). With increasing PS content, the Young's modulus and yield stress was found to increase linearly[18] while the elongation at break decreased from over 200% to about 34% (Figure 6b). This transition from ductile to brittle behaviour is associated with a transition in the deformation mechanism from homogeneous plastic flow to the formation of craze-like zones. The localization of deformation in these craze-like zones is shown by the TEM micrograph of the ST2-S74/20 wt.-% PS190 blend (Figure 7). The transition in deformation mechanism from ductile plastic yielding of PS lamellae to crazing takes place when the thickness of the PS lamellae reaches a value of ca. 30 nm.

The craze-like deformation zones in the blend with 20 wt.-% PS190 are characterised by a high degree of stretching of the lamellae accompanied by void formation. Locally, an elongation ratio of $\lambda > 4$ may be estimated. However, the macroscopically achievable elongation of this sample is relatively low (only about 34 %) due to the extreme localisation of the deformation zones. Hence, one can correlate the transition in the deformation mode from the homogeneous plastic yielding to the formation of local craze-like zones with the thickness of the polystyrene layers. These results are strong evidence of the proposed 'thin layer yielding' mechanism.

Conclusions and Future Works

The results may be summarised as follows:

a. Modified block copolymer architecture leads to a change in the nature of microphase separated morphologies to be formed in the solid state.

b. The lamellar systems having glassy/rubbery alternating layers deform via '*thin layer yielding*' mechanism, where the glassy layers act as craze-fibrils separated by rubbery layers instead of microvoids. This mechanism may be used as an alternative toughening mechanism in the brittle polymers.

In spite of the strong evidence in support of the '*thin layer yielding*' mechanism, the exact magnitude of the critical thickness and its dependence on temperature and loading rate is still unknown. The role of the interface between the polymer layers in this connection is also of interest. The investigation of these aspects are underway.

Acknowledgements

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