Deformation behaviour of styrene/butadiene star block copolymer/hPS blends: influence of morphology

Rameshwar Adhikari*, Goerg H. Michler, Reinhold Godehardt, Elena M. Ivan'kova

Institute of Materials Science, Martin Luther University Halle-Wittenberg, D-06099 Halle/Saale, Germany

Abstract

The influence of morphology on micromechanical deformation behaviour of blends consisting of a lamellar forming styrene/butadiene star block copolymer and polystyrene homopolymer (hPS) was studied by transmission electron microscopy (TEM). The pure star block copolymer and the microphase separated blends revealing lamellar structure with polystyrene (PS) lamella thickness in the range of about 20 nm showed homogeneous plastic deformation of the PS lamellae. The macrophase separated blends with PS particles in lamellar matrix exhibited debonding at the particle–matrix interface associated with extensive plastic deformation of the surrounding matrix. The blends containing PS matrix deformed via crazing.
© 2003 Elsevier Ltd. All rights reserved.

Keywords: Styrene/butadiene block copolymer; Morphology; Micromechanical mechanism

1. Introduction

Styrene/diene block copolymers are generally used in combination with other polymers or additives [1–5]. Blending with homopolymers, similar or dissimilar to the components of the block copolymer, represents an important way of morphology control in these materials. A two component block copolymer may be blended with homopolymers, which are identical with or different from the copolymer's constituent blocks. Of particular industrial interests are the binary blends of styrene/butadiene block copolymers with polystyrene [1,3].

The length of the homopolymer chains compared to that of the block copolymer primarily governs the phase behaviour of a binary block copolymer/homopolymer blend. There is an interplay between microphase and macrophase separation; and which effect predominates depends on the relative molecular weight and the composition of the mixture [6–13]. Hashimoto et al. explored the phase behaviour of binary blends consisting of styrene/diene copolymers and homopolymers by varying the molecular weight of homopolymer, composition of the blends, and by using homopolymers having different interaction with the block copolymer [8–13]. For styrenic block copolymer/homopolystyrene mixtures, three regimes have been identified depending on the molecular weight of the homopolystyrene (M_{hPS}) and that of the same component in the block copolymer ($M_{PS\text{-block}}$) (discussed in detail by Hamley in Ref. [6])

The Effect of copolymer architecture (star and triblock) on miscibility and mechanical properties of styrene/butadiene block copolymer/hPS blends was recently studied by Feng et al. [14]. These authors proposed that there is an hPS molecular weight range for which the mechanical properties of the mixtures are enhanced. Depending on the M_{hPS}, added hPS was found to exist both in polystyrene (PS) and polybutadiene (PB) phases. The role of block copolymer architecture on the miscibility of the blends was, however, not found.

Low molecular weight hPS, though most soluble in the corresponding block domain of the block copolymers, is generally not desirable for technical applications. This, of course, may reduce the cost but also deteriorates the mechanical properties. Due to lack of stable entanglements, the products do not possess optimum strength level. Therefore, hPS with quite a higher molecular weights (~ 100 kg/mol) is used. The molecular weight of hPS and PS block of the copolymer should be optimised because the

* Corresponding author. Tel.: +49-3461-46-2790; fax: +49-3461-46-2535.

E-mail address: rameshwar.adhikari@iw.uni-halle.de (R. Adhikari).

hPS tends to macrophase segregate when M_{hPS} approaches $M_{PS\text{-}block}$. This is again undesirable because it may lead to a loss of transparency.

Hashimoto et al. and Kotaka et al. explored morphology and strain induced structural changes in blends consisting of SBS triblock copolymers and polystyrene [15,16]. Particularly, the healing of deformed domain structures on annealing was investigated. Determining the strain induced structural changes in SBS triblock copolymer/homopolymer blends, they demonstrated the hindrance of healing process by the added homopolymer. Furthermore, the micromechanical behaviour of blends of styrene/butadiene block copolymer with polystyrene was discussed by Argon and co-workers [17] and Aggarwal [2]. In both the cases role of block copolymer as impact modifier was analysed. Block copolymer particles dispersed in the PS matrix were able to both initiate and terminate the crazes. Aggarwal has even argued the superior mechanical properties of block copolymer modified PS than the conventional rubber modified one [2]. Though a great deal of works have been devoted to the deformation behaviour of ternary blends containing two homopolymers and a block copolymer as compatibiliser, only limited investigations are made on binary block copolymer/homopolymer blends and binary block copolymer blends.

The aim of this paper is to study the influence of morphology on the micromechanical behaviour of blends consisting of an asymmetric styrene/butadiene star block copolymer and polystyrene homopolymer.

2. Experimental section

2.1. Materials studied

The block copolymer sample used in this study was an asymmetric styrene/butadiene star block copolymer (named as ST2 in this work) prepared by sequential anionic polymerisation and has a number average molecular weight of 109,000 g/mol and a polydispersity of 1.69. It contains a total polystyrene volume fraction of 0.74. The sample was kindly supplied by the BASF. The star block copolymer was solution blended with polystyrene homopolymer (hPS) of varying molecular weights (see Table 1). Details about

Table 1
Characteristics of polystyrene homopolymers (hPS) used to prepare binary blends with the star block copolymer (ST2) by solution casting

Sample code	$^a M_n$ (g/mol)	$^a M_w$ (g/mol)	M_w/M_n
PS012	11,800	15,200	1.29
PS018	18,300	33,100	1.81
PS082	82,600	190,000	2.30

[a] Number average (M_n) and weight average (M_w) molecular weights determined by gel permeation chromatography (GPC).

synthesis and structure of the star block copolymer may be found elsewhere [18–20].

2.2. Sample preparation

Each sample was dissolved in toluene, and approximately 0.5 mm thick films were prepared in a petri-dish by evaporating the solvent over several days in order to allow the formation of well ordered structures. The films were dried at room temperature for few days and annealed for 48 h at a temperature of 120 °C (above the glass transition temperature of polystyrene) in a vacuum oven.

2.3. Tensile testing

About 50 mm long tensile bars were cut from the cast films. Tensile tests were performed at a cross head speed of 50 mm/min using a universal tensile machine (Zwick 1425) at room temperature (23 °C).

2.4. Morphological characterisation

The morphology of the samples before and after deformation was imaged by transmission electron microscope (200 kV TEM, Joel). Ultrathin sections of the samples (ca. 50–70 nm) prepared by ultramicrotomy were selectively stained by osmium tetroxide (OsO_4).

To investigate the strain induced structural changes of some of the samples, semithin sections approximately 500 nm in thickness specimen were cut at a cryo-temperature. These sections were strained in a special tensile device. The butadiene phase was allowed to selectively stain with OsO_4 vapour for overnight in the strained state and investigated by means of a high voltage electron microscope (1000 kV HVEM, Joel).

3. Results and discussion

3.1. Morphology of star block copolymer/hPS blends

The microphase separated morphology of the star block copolymer used in this study was described in detail in previous studies [19,20]. In particular, a 'two-component three-phase' morphology was observed in this star block copolymer, Fig. 1. The presence of thin polystyrene domains (white) scattered in the polybutadiene phase (dark) was attributed to the separation of the PS core of the star molecules and shorter PS blocks from rest of the longer polystyrene blocks [18,19].

The longest polystyrene block of the asymmetric star block copolymer has a molecular weight in the range of about 70,000 g/mol, and the ratio of molecular weight of the longest block to that of the shortest one is greater than 10. We discuss the morphology formation in the blends taking
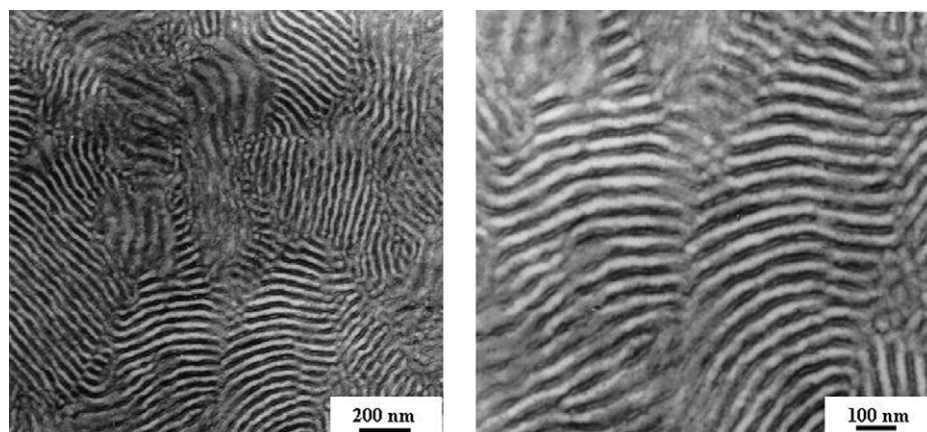
Fig. 1. Lower (left) and higher (right) magnification of TEM images showing morphology of solution cast star block copolymer (ST2) showing a peculiar 'two-component three-phase' lamellar morphology.

the longest block of the block copolymer as a reference (see below).

The influence of homopolystyrene molecular weight (M_{hPS}) on phase behaviour of block copolymer/hPS blends is demonstrated by the TEM micrographs presented in Fig. 2 (data about the internal details of blend morphology in Table 2). The molecular weight of hPS lies in the following range (see Table 1): $M_{hPS} \ll M_{PS-block}$, $M_{hPS} < M_{PS-block}$ and $M_{hPS} > M_{PS-block}$. The composition of the blends is fixed at 20 wt% hPS in each case. The morphology of the blends observed by TEM can be explained on the basis of molecular weight of the homopolymer relative to that of corresponding block of the block copolymer ($M_{hPS}/M_{PS-block}$).

An interplay between microphase and macrophase separation is found in these blends. The molecular weight of added PS012 ($M_n = 11,800$ g/mol) is much smaller than that of the longest PS block of the star block copolymer ($M_n \sim 70,000$ g/mol) but it is slightly higher than that of the smaller blocks ($M_n \sim 7,000$ g/mol). Hence, according to the situation discussed in literature [11–13,21,22], most of the hPS chains may penetrate into the PS domains of the block copolymer leading to the microphase separated structures given in Fig. 2(a).

Due to the solubilisation of homopolymer in corresponding copolymer block, respective domain size may expand both laterally and normal to the interface. The expansion of PS lamellae normal to the interface is indicated by an increase in the thickness of the PS lamellae (Table 2).

The mixing entropy of hPS increases with the ratio $M_{PS-block}/M_{hPS}$. Since this ratio is quite high in ST2/PS012 blend, the hPS molecules are able to penetrate deeply into the PS domains close to the chemical junction points [13]. As a result, the junction points are shifted apart. To compensate this shift and to make up entropy loss, butadiene phase has to contract, which causes a decrease in lamellar long period. The decrease in the PB lamellae thickness should be more than compensated for by an addition of a small amount of low molecular fraction of PS012 in the butadiene phase as indicated by an increase in $T_{g\text{-}PB}$ [23,24].

As M_{hPS} approaches $M_{PS-block}$, mixing entropy of the homopolymer chains is decreased, and these chains become less successful to wet the copolymer brush effectively. The hPS and PS block become, hence, less miscible. As a result the copolymer shrinks, and the hPS chains tend to be segregated in the middle of the PS domains or even completely expelled from the microdomains to form the macrophase separated PS particles (chapter 2 in Ref. [6]). Nearly this situation is present in ST2/PS018 blend. Since a large part of PS018 molecules tend to segregate to the centre of the PS lamellae, the thickness of PS lamellae increases (Table 2) while the junction points are not displaced. Hence, the PB lamellae thickness is again maintained. This causes a small increase in lamellar long period in sample ST2/PS018. However, a part of hPS is expelled out of the PS lamellae which forms hPS particles a few hundred nanometers in diameter (Fig. 2(b)).

Molecular weight of PS082 is much higher than that of

Table 2
Average lamellar long period ($\bar{L}$) and PS lamella thickness ($\bar{D}_{PS}$) measured in TEM images of solution cast ST2/20% hPS blends (variation of hPS molecular weight). The values correspond to the peak of corresponding Gaussian fitting of the data

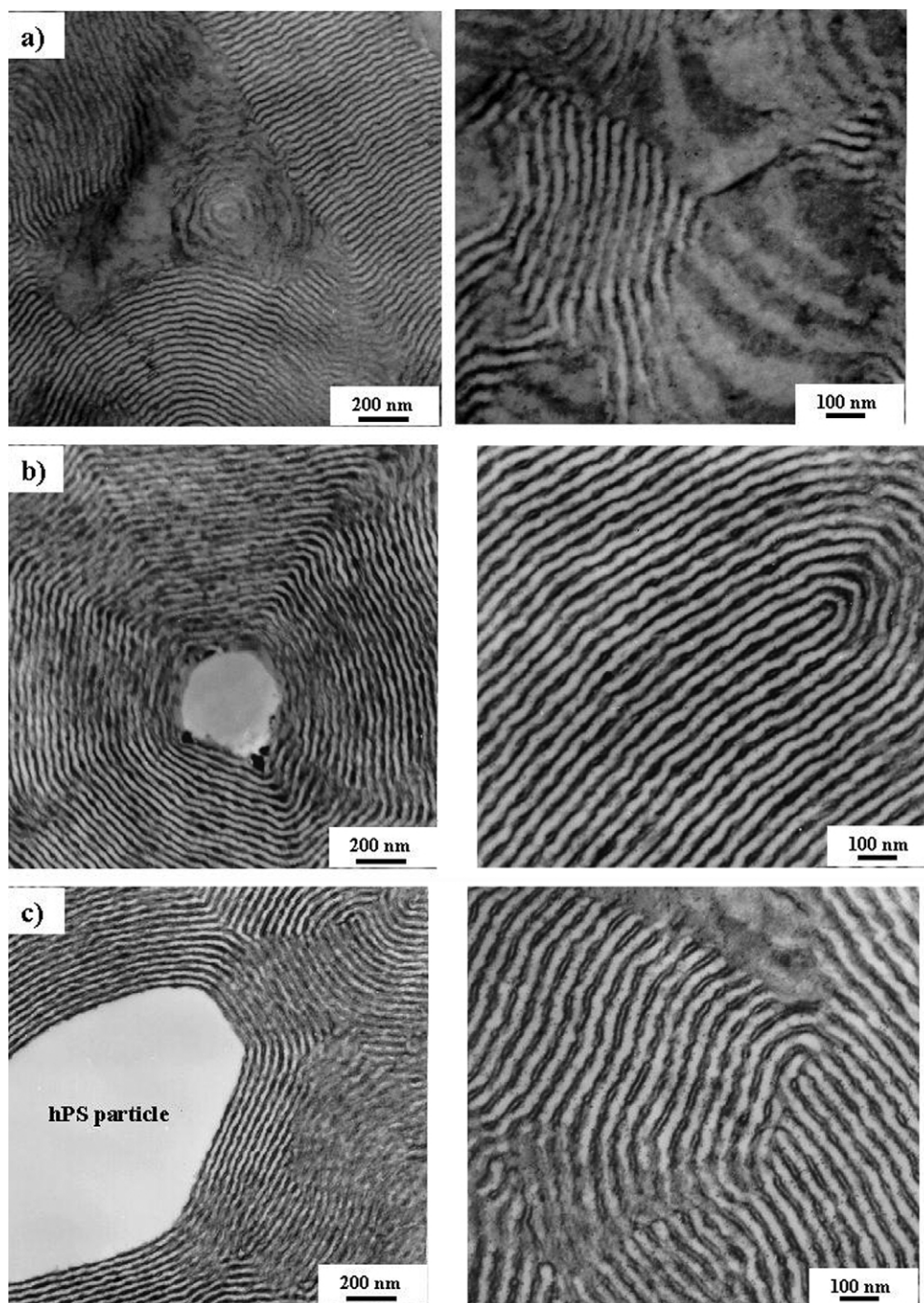| Blends	$\bar{L}$ (nm)	$\bar{D}_{PS}$ (nm)	Remarks
Pure ST2	39–54	20.2	–
ST2/PS012	37–43	22.2	hPS Completely solubilised in PS block of ST2
ST2/PS018	42–58	22.1	hPS Only partly solubilised, hPS particles about 0.3–1.0 μm in diameter
ST2/PS082	49–54	21.2	hPS Almost completely macrophase separated, hPS particles about 1–4 μm in diameter

Fig. 2. Lower (left) and higher (right) magnification of TEM images showing morphology of solution cast ST2/hPS blends as a function of hPS molecular weight (M_{hPS}); (a) ST2/PS012, (b) ST2/PS018 and (c) ST2/PS082; hPS content in each case is $\Phi_{hPS} = 20\%$.

any PS blocks of ST2 (i.e. $M_{hPS} > M_{PS\text{-block}}$). Hence, the hPS molecules tend to phase-separate forming hPS particles in block copolymer matrix (Fig. 2(c)). The three-phase morphology of the matrix is again maintained, and PS082 particles, a few microns in diameter, are formed. Nevertheless, owing to a broad molecular weight distribution of polystyrene, a part of lower molecular weight fraction of PS082 might be solubilised by the PS domains.

It may be, in general, assumed that criteria for solubilisation of homopolymers in the corresponding block of copolymers discussed in the literature is valid for investigated asymmetric star block copolymer/hPS blends. So, an increase in concentration of PS082 would lead to further macrophase separation, and finally, block copolymer particles in PS082 matrix are formed at higher PS082 concentration, Fig. 3 [23].
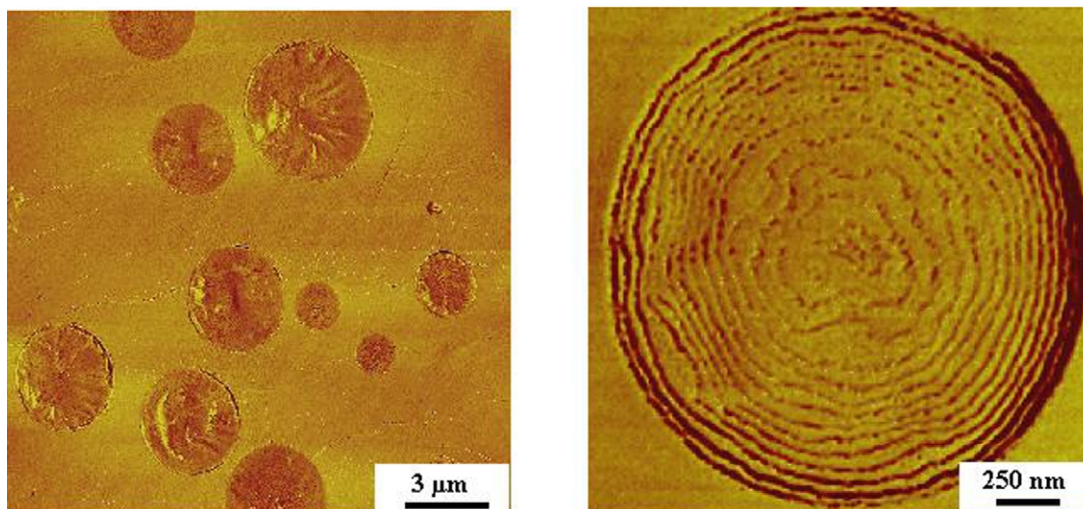
Fig. 3. Lower (left) and higher (right) magnification of scanning force microscopy (SFM) phase images showing morphology of solution cast ST2/PS082 blend, the blend composition is $\Phi_{hPS} = 80\%$ (from p. 91 of Ref. [23]).

3.2. Micromechanical deformation behaviour

In the system investigated, three different types of morphologies were observed depending on hPS molecular weight and blend composition: microphase separated morphology (e.g. pure ST2, ST2 + 20% PS012); macrophase separated morphology having ST2 matrix (e.g. ST2 + 20% PS018 and ST2 + 20% PS082) and macrophase separated blends having PS082 matrix (e.g. ST2 + 80% PS082). Accordingly, the micromechanical mechanisms may be discussed under three headings.

3.2.1. Microphase separated samples (e.g. pure ST2 and ST2 + 20% PS012)

The micromechanical behaviour of the star block copolymer used in this study has been discussed in our recent publication preparing samples by different methods [20]. The lamellar star block copolymer was found to deform by the mechanism of 'thin layer yielding' without formation of any localised deformation zones. The PS lamella thickness and the lamellar long period was reduced by more than 50% resulting in a local plastic deformation of over 300%. This homogeneous plastic yielding of PS layers (necking and drawing of PS lamellae) was found to be responsible for the observed high ductility of the star block copolymer.

The homogeneous plastic deformation of PS lamellae and the formation of so called 'fish-bone' morphology may be clearly noticed in the deformed star block copolymer film, Fig. 4. Locally confined deformation zones such as crazes are not noticeable. Small bulges along the PS lamellar axis indicate the necking and drawing of the PS lamellae as observed previously with TEM investigations [20]. One of these regions is shown by a white circle in Fig. 4. The plastic deformation of the lamellae leading to the

yielding of PS lamellae is consistent with earlier results by Kawai et al. [15,16]

Formation of the fish-bone or 'chevron' morphology seems to be universal in lamellar block copolymer samples subjected to uniaxial tensile deformation. Recently, Thomas and co-workers reported similar observation ('chevron-fold' morphology) in an oriented lamellar block copolymer sample loaded perpendicular to the lamellar orientation direction [25,26]. They demonstrated that a macroscopic strain of a few hundred percent can be achieved in these samples simply through the lamellar folding without noticeable stretching of the lamellae. In our samples, since the lamellae are randomly oriented, macroscopic elongation can be regarded as being a result of the combined effect of folding, twisting and stretching of the lamellae along the deformation direction (Fig. 4).

The deformation structures found in sample ST2 + 20% PS012 are shown in Fig. 5. One can see that the lamellae in the deformed sample are predominantly aligned towards the deformation direction. Both lamellar stretching and the formation of fish-bone structure, similar to that observed in the pure block copolymer (Fig. 4) may be clearly noticed. A remarkable difference is in the mode of deformation of the PS lamellae. Alternating thicker and thinner regions (small bulges along a PS lamella) are pronounced. Hence, the plastic deformation process of the glassy PS lamellae in this blend is less homogeneous compared to the pure block copolymer. The restriction in the plastic flow might have been borne by the presence of dissolved low molecular weight hPS molecules, which act as molecular defects (due to presence of larger number of chain ends) and cause an early failure of the tensile specimens. One consequence of this behaviour would be the reduced ductility compared to the pure star block copolymer. As a result, in spite of analogous morphology and similar deformation structures, the elongation at break for this blend was much smaller than
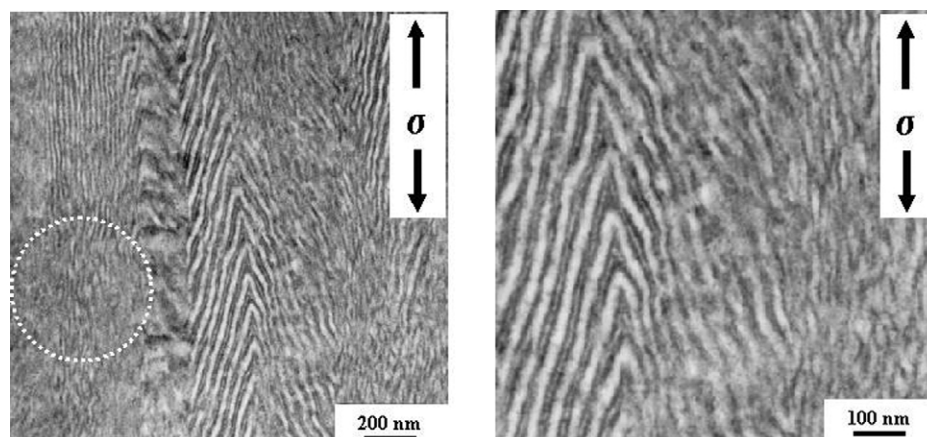
Fig. 4. Lower (left) and higher (right) magnification of TEM images showing morphology of solution cast ST2; deformation direction is shown by an arrow.

the pure ST2 (discussed later, see Fig. 8). The worsening in the ductility may be explained by the plasticisation of PS lamellae by PS012, whose molecular weight ($M_{PS012} \sim$ 12,000 g/mol) lies well below two times the entanglement molecular M_e weight of polystyrene (M_e for PS 19,100 [27]). These hPS chains might partly be mixed even to the butadiene phase due to its low molecular weight. In any case, these chains may act as defects sites.

3.2.2. Macrophase separated sample having ST2 matrix (e.g. ST2 + 20% PS082)

Fig. 6 presents a series of high voltage electron microscopy (HVEM) images showing the details of deformation structures in macrophase separated ST2 + 20% PS082 blend which possesses hPS particles in ST2 matrix. Especially, morphological changes around the PS particles during deformation are very helpful to understand the micromechanical processes.

Growth of microvoids at the poles (i.e. in the direction of applied stress) of the particles is well known from particle filled polymers [27]. In the present case, the PS082 inclusions act as stiff particles embedded in the soft ST2

matrix. At the pole regions of the hPS particles microvoids appear due to stress concentration.

If the elastic modulus of the inclusions is much larger than that of surrounding matrix, the stress is reduced at the equator, and a compressive stress component acts at the equator of these spherical PS082 particles yielding a good contact with the matrix. The maximum stress concentration exists at the poles of the particles, which is the reason for void formation as shown in Fig. 6(a).

The contrast in the electron micrographs given in Fig. 6 arises from two facts: staining of the rubber phase (namely PB phase) by osmium tetroxide and the variation in local sample thickness induced by the straining. Due to high deformation of the lamellar matrix, it looks brighter than the dispersed PS082 particles (see low magnification image in Fig. 6(a)). The extremely high deformation of the lamellar matrix is also confirmed by the extended elliptical shape of the microvoid at the poles of the dark polystyrene particles (Fig. 6(a)).

It is interesting to note what happens at the pole regions of the particles right before the formation of microvoids. The higher magnifications of the HVEM micrographs presented in Fig. 6 indicate that the enormous stress
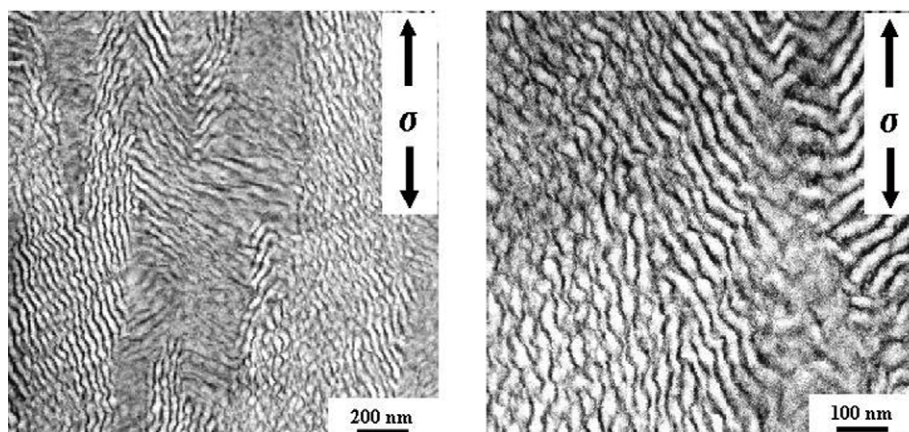

Fig. 5. Lower (left) and higher (right) magnification of TEM micrographs revealing strain induced structural changes in microphase separated ST2/20% PS012 blend; deformation direction is shown by an arrow.
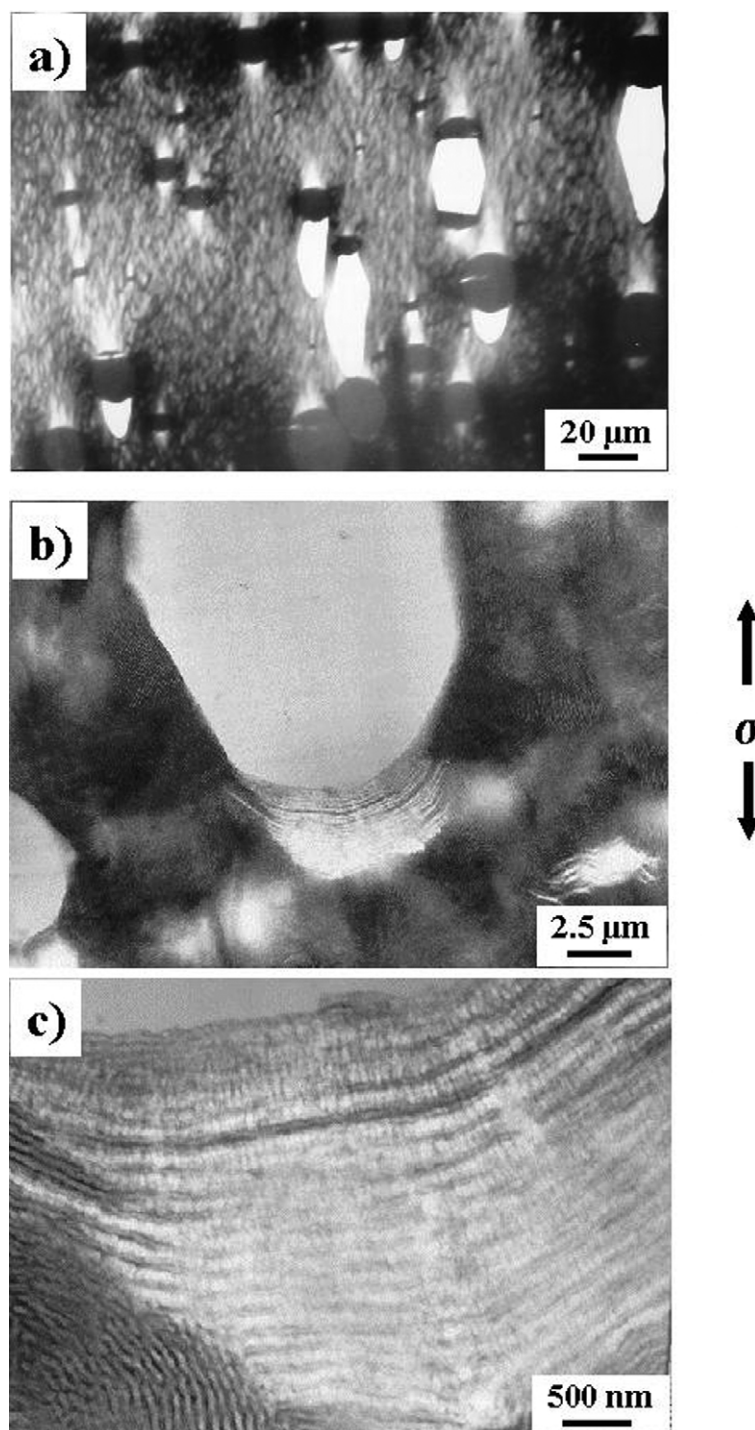
Fig. 6. Series of HVEM images showing the deformation structures around the poles of hPS particles in macrophase separated blend ST2 + 20% PS082, strain direction shown by an arrow.

concentration at the particle poles makes both PS and PB lamellae turn to fibrillar structures. Every lamellae appears to be formed by a parallel array of 'fibrils' normal to the lamellar axis. Both PS and PB lamellae seem to take part in the formation of these fibrillar microstructures (Fig. 6(c)).

Formation of microvoids results in the relieve of stress concentration at the particles' poles. This is followed by a large homogeneous plastic deformation of lamellar matrix.

The contour length of lamellae around a microvoid is more than three times of original length at PS particle surface (Fig. 6(a)), indicating a local deformation with an extension ratio of $\lambda > 3$ (i.e. strain, $\varepsilon > 200\%$). This is similar to the experimentally measured strain at break of the star block copolymer (see Fig. 8).

The growth of microvoids formed at the poles of hPS particles and subsequent large plastic deformation of

surrounding lamellar matrix, result in a high elongation at break (discussed later). The growth of these microvoids into cracks and propagation of the cracks cause the specimen-failure.

3.2.3. Macrophase separated samples having PS082 matrix (e.g. ST2 + 80% PS082)

The morphology of ST2 + 80% PS082 blend (see Fig. 3) is comparable to that of rubber toughened thermoplastics. By analogy, the deformation mechanisms observed in this blend (Fig. 7) can be compared to the deformation of rubber modified thermoplastics (with soft inclusions dispersed in the hard matrix). The effectiveness of rubber toughening depends on the size, distribution and microstructures of the rubber particles [27–29]. Toughening glassy thermoplastics by block copolymers have been studied by Aggarwal and

shown that block copolymer particles can act as good toughening agents if these are able to undergo plastic deformation [2]. The toughening mechanism involves the initiation and/or termination of fibrillated crazes in the thermoplast matrix by the soft block copolymer particles.

In the macrophase separated blend with hPS matrix, crazes were observed perpendicular to the principal stress direction (Fig. 7). Since the block copolymer particles are softer than the polystyrene matrix, the stress concentration should occur at equator of the particles [27,30]. The concentric arrangement of PS and PB lamellae in the block copolymer particles (see e.g. Fig. 3), however, seems to cause a more uniform distribution of stress around the block copolymer particle. This results in the rupture of a contact between the particle and the matrix somewhere at the interface. Hence, the stress is not necessarily concentrated at
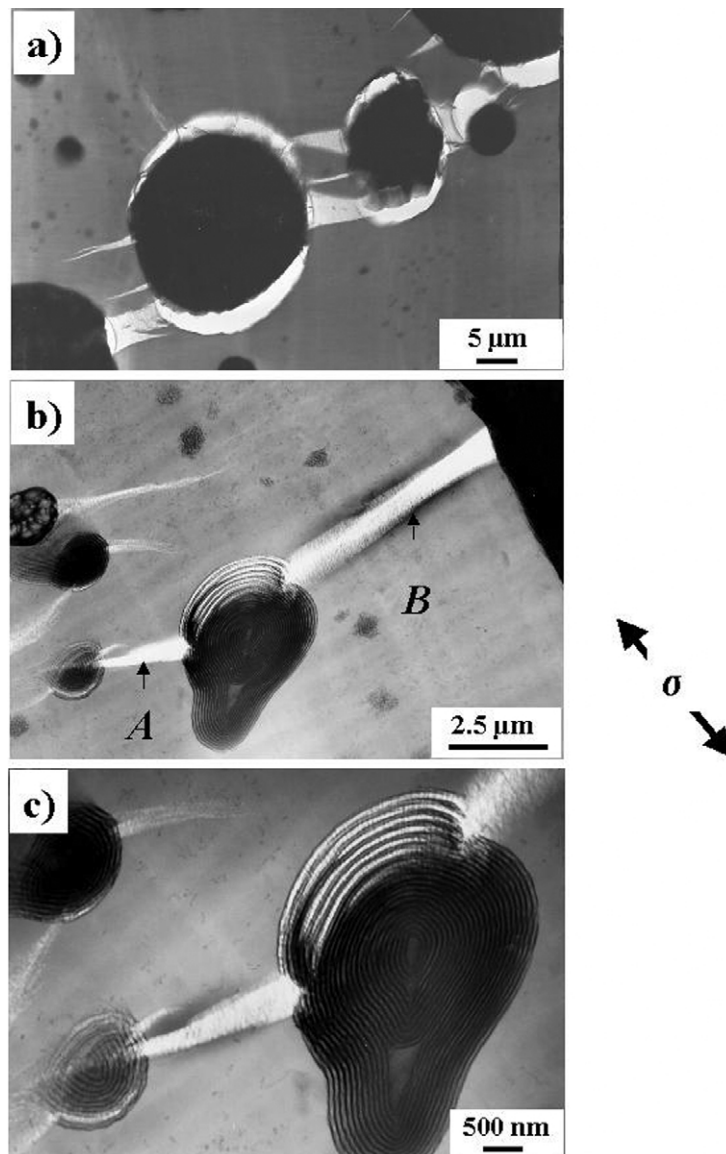

Fig. 7. HVEM images showing deformation of the macrophase separated blend having PS matrix: (a) debonding at the block copolymer particles, (b–c) deformation of lamellar particles, deformation direction indicated by an arrow.

the equatorial region. The Young's moduli of PS matrix and star block copolymer are 3300 and 1205 MPa, respectively [23]. This mismatch in Young's modulus is large enough for the nucleation of crazes. The stress concentration at the particle surface may lead to disentanglement of polystyrene chains between the PS matrix and the PS lamellae of the copolymer particle resulting in particle debonding.

The effectiveness of block copolymer particles as toughening agent depends on the internal morphology and size of the particles. The molecular parameters (like molecular weight and architecture, i.e. AB or ABA type copolymer, with A as matrix component) may play an important role in the toughening mechanism. It is desirable that the molecular weight of the end blocks is greater than $2 \times M_e$, so that a strong matrix/particle coupling is possible.

The longest PS block of the copolymer has the molecular weight of ca. 70,000 g/mol, which is much greater than M_e. This should provide the block copolymer and the blends with polystyrene a good strength. However, a debonding between the particles and the matrix was observed (Fig. 7(a)), which would be expected only for the polymers having a poor interfacial adhesion.

The sample was prepared via solution casting using a 'neutral' solvent toluene followed by subsequent vacuum drying and annealing above the glass transition temperature of both the components. However, due to difference in solubility parameter and the thermal expansion coefficient of the polybutadiene and the polystyrene phases, there may exist an internal stress in the sample. Especially, the excess internal stress inside the copolymer particles and that between the matrix and particles would favour the propagation of micro-crack along the boundary of copolymer particles (Fig. 7(a)) or along a PS lamella.

Like the blends with hPS particles (Fig. 6), an extensive plastic deformation of the block copolymer lamellae leading to the formation of 'fibrillar' structure was observed (Fig. 7). The HVEM micrographs in Fig. 7(b) and (c) shows the deformation process prior to the debonding between the particles and the matrix. In addition to the initiation and termination of the crazes running across the PS matrix, the block copolymer lamellae have undergone a remarkable structural changes.

A closer inspection of the micrographs in Fig. 7(b) reveals a region of lamellar block copolymer particle between a propagating and a terminating craze (indicated by letters A and B, respectively in Fig. 7(b)). The lamellae in this region have transformed into an array of fibrils. These fibrils appear to be elongated along the stress direction and arranged in bundles perpendicular to the lamellar axis.

It was found that the deformation mechanism in a lamellar block copolymer is predominantly a homogeneous plastic deformation of PS and PB lamellae (Figs. 4 and 5). Recent studies of Wang [31] and Hartmannn [32] show that the glass transition temperature (T_g) of glassy polymers is a strong function of film thickness. The T_g of a polymer decreases as the film thickness

decreases. These findings are in line with our previous results, in which the mechanism of thin layer yielding was proposed [20]. According to this mechanisms, the homogeneous plastic deformation of the glassy layer occurs if the thickness of these layers is in the range of 20 nm. On the basis of present study, however, the deformation mechanisms seems to alter dramatically as the local stress concentrators (e.g. presence of particle–matrix morphology) are present.

If a craze propagates from a surface flaw (e.g. Fig. 7(b); top, right), the stress is concentrated at the tip of the craze. The maximum stress at the craze-tip is, hence, transferred to the block copolymer particle. This high stress may exceed the yield stress of the lamellar block copolymer, which enable the PS lamellae to split into the fibrillar structure.

3.3. Formation of fibrillar structure

The deformation of lamellae-forming styrenic block copolymers and even their blends with hPS have been addressed in a numerous earlier studies [15,16,25,26, 33–35]. However, this is the first time that we report the formation of fibrillar structure parallel to the lamellar normal. This is especially the case if loading direction is perpendicular to the lamellae and appears at the locations close to the particle–matrix boundary. It can be clearly seen that the formation of fibrillar structures is not limited to one of the lamellae type and practically resembles the craze-fibrils (5–20 nm thick). It should be stressed that the alternating bright and dark areas along each fibrillating lamella is not necessarily only the effect of presence of alternating array of microvoids. This may appear due to a local density fluctuation caused by local non-uniform plastic deformation.

The above discussion indicates that the fibrillar structures observed is nothing but an intermediate stage of deformation during perpendicular deformation of lamellae close to a stress concentrator.

The previous studies on block copolymer/hPS blends dealt only with the deformation structures formed at the final stage of deformation. In such studies using TEM, the sections are prepared from strained specimens, in which the strain induced details might significantly heal-up. Post-deformation history (store of deformed specimens, sectioning etc.), generally leads to the relaxation of many of the fine deformation structures. As a result the fibrillar structures were not observed. In our case, semithin sections (ca. 500 nm thick) were strained and stained in OsO_4 vapour keeping the section in the stretched state so that the deformation structures were fixed in position. As a result, it was possible to resolve the detailed fine arrangement of fibrillar structures in lamellae at the vicinity of particles which were not detached from the matrix yet.

3.4. Influence of micromechanical mechanisms on macroscopic mechanical behaviour

It has been already pointed out that the micromechanical mechanisms play the decisive role in determining the mechanical behaviour of the heterophase polymers. Therefore, a direct correlation between the strain induced structural changes and the macroscopic mechanical properties may be established.

Fig. 8 shows the stress–strain curves of the pure block copolymer and some blends with hPS. The samples have a pronounced yield point. The stress level achieved beyond the yield point in the blends with hPS is clearly higher than that in the pure star block copolymer ST2. The higher stress level in the blends is caused by the higher overall polystyrene content.

As the polystyrene forms matrix (e.g. the blend with 80% PS082 in Fig. 3), the yield stress level increases drastically indicating a highest resistance to plastic deformation. The pronounced strain softening in the blend is a consequence of stress-relieve due to localised plastic deformation process (e.g. crazing). The high stretching of the fibrils in the crazes (e.g. in Fig. 7) and subsequent chain orientation might lead to strain hardening effect, which could again increase the stress. However, the blend with 80% PS082 lacks this behaviour. The reason is that the crazes grow to critical size; and the specimen undergoes fracture via crack formation and propagation.

For the rest of the samples, the deformation occurs almost homogeneously, and the stress level rises continuously with strain after the yield point. The absence of sharp yield point may be correlated with the presence of polygranular lamellar matrix. With the initiation of plastic deformation processes, the shearing of the rubbery layers and slipping of the glassy PS lamellae begin [24]. The twisting, rotation and drawing of the lamellae relieve the stress and initiates simultaneously the orientation of rubbery and glassy chains. These processes are responsible for the observed strain hardening in star block copolymer and the blends with low PS content.

The strong plastic stretching of the lamellae in ST2 has a consequence of a drastically increased macroscopic elongation at break. A significant contribution also comes from the rotation and folding of the lamellae in the fish-bone structures. In spite of similar morphology and deformation structures as in ST2, the lower value of strain at break for ST2 + 20% PS012 may be explained by the premature failure of the PS lamellae as discussed in preceding section. In this microphase separated blend, the added PS homopolymer chains act as defect points and hinder the drawability of the PS layers (see alternating thicker and thinner regions formed along the PS lamellae in Fig. 5).

The ductility in ST2 + 20% PS082 blend is higher than that of the blend with 20% PS012. The additional contribution to the higher strain at break arises from the void formation and extensive plastic deformation at the poles of the PS particles in this blend (see Fig. 6). Nevertheless, this blend does not reach the maximum strain and stress level of the pure star block copolymer, which could be attributed to the premature failure of the sample via propagation of crack initiated at the pole of large particles.

4. Conclusions

The results discussed in this paper may be concluded as follows (see also Table 3):

- *Morphology*. In accordance with the results for diblock copolymer/homopolymer blends discussed in the literature, the morphology of ST2/hPS blends is greatly influenced by the hPS molecular weight.
- *Micromechanical behaviour*. The microphase separated blends show analogous behaviour as the parent block
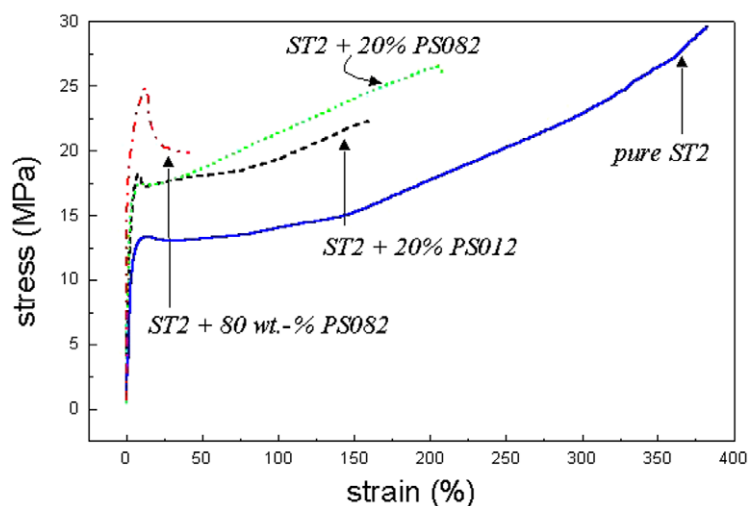

Fig. 8. Stress–strain curves of the investigated solution cast films; total specimen length 50 mm and thickness ca. 0.5 mm, tested at 23 °C at a cross head speed of 50 mm/min.

Table 3
Summary of the deformation mechanisms observed in star block copolymer/hPS blends having different morphologies

Samples	Morphology	Deformation mechanism
Pure ST2	Lamellae	'Fish-bone' formation, necking and drawing of PS lamellae (*thin layer yielding*)
ST2/PS012 (20% PS)	Lamellae	As in pure ST2, lower drawing of the PS lamellae leading to a premature failure
ST2/PS082 (20% PS)	PS Particles in lamellar matrix	Void formation at poles of PS particles, high deformation of lamellae adjacent to these particles
ST2/PS082 (80% PS)	Block copolymer particles in PS matrix	Crazing in the PS matrix, particle debonding

copolymer as far as the morphology of the parent block copolymer is preserved (the thickness of the PS lamellae ~20 nm). A pronounced localisation of deformation is observed in macrophase separated blends. The fibrillar structures appear in the lamellae if the stress concentrators are present.

- *Mechanical response*. The ductility of the blends of low molar mass hPS (at low PS concentration) and star block copolymer is lower than that of the block copolymer partner, which may be attributed to the weakening of the molecular knots in the PS domains. In contrast, higher molar mass hPS enhances the mechanical stability.

References

[1] Knoll K. In: Gausepohl H, Gellert R, editors. Kunststoff-handbuch: 4. Polystyrol. München: Hanser Verlag; 1996. p. 145. Chapter 3.

[2] Aggarwal SL. In: Folkes MJ, editor. Processing, structure and properties of block copolymers. London: Elsevier Applied Science Publishers; 1986. p. 1. Chapter 2.

[3] Holden G. Understanding thermoplastic elastomers. Munich: Carl Hanser Verlag; 2000. p. 15.

[4] Holden G. In: Holden G, Legge NR, Quirk RP, Schroeder HE, editors. Thermoplastic elastomers, 2nd ed. Munich: Hanser Publishers; 1998. p. 574. Chapter 16.

[5] Arridge RGC, Folkes MJ. In: Folkes MJ, editor. Processing, structure and properties of block copolymers. London: Elsevier Applied Science Publishers; 1986. p. 125. Chapter 4.

[6] Hamley IW. The physics of block copolymers. Oxford: Oxford University Press; 1998.

[7] Matshuhita Y. In: Araki T, Tankong U, Shibayama M, editors. Structure and properties of multiphase polymeric materials. New York: Marcel Dekker Inc; 1998. p. 121. Chapter 5.

[8] Hashimoto H, Fujimara M, Hashimoto T, Kawai H. Macromolecules 1981;14:844.

[9] Hashimoto T, Tanaka T, Hasegawa H. Macromolecules 1990;23:4378.

[10] Koizumi S, Hasegawa H, Hashimoto T. Macromolecules 1994;27:7893.

[11] Koizumi S, Hasegawa H, Hashimoto T. Makromol Chem Macromol Symp 1992;62:75.

[12] Koizumi S, Hasegawa H, Hashimoto T. Macromolecules 1994;27:6532.

[13] Hasegawa H, Hashimoto T. In: Aggarwal SL, Russo S, editors. Comprehensive polymer science: suppl. 2. London: Pergamon; 1996. p. 497.

[14] (a) Feng H, Feng Z, Yuan H, Shen L. Macromolecules 1994;27:7830.
(b) Feng H, Feng Z, Shen L. Macromolecules 1994;27:7835.
(c) Feng H, Feng Z, Shen L. Macromolecules 1994;27:7840.

[15] Hashimoto T, Fujimora M, Saito K, Kawai H, Diamant J, Shen M. In: Cooper SL, Estes GM, editors. Advances in chemistry series-multiphase polymers. Washington, DC: Americal Chemical Society; 1979. p. 257.

[16] Kawai H, Hashimoto T, Miyoshi K, Uno H, Fujimura M. J Macromol Sci-Polym Phys 1980;17:427.

[17] Argon AS, Cohen RE, Gebizlioglau OS, Schwier CE. In: Kausch HH, editor. Advances in polymer science 52/53, crazing in polymers. Berlin: Springer; 1983. p. 275.

[18] Knoll K, Nießner N. Macromol Symp 1998;132:231.

[19] Adhikari R, Michler GH, Huy TA, Ivankova E, Godehardt R, Lebek W, Knoll K. Macromol Chem Phys 2003;204:488.

[20] Michler GH, Adhikari R, Lebek W, Goerlitz S, Weidisch R, Knoll K. J Appl Polym Sci 2002;85:683.

[21] Winey KI, Thomas EL, Fetters LJ. J Chem Phys 1991;95:9367.

[22] Winey KI, Thomas EL, Fetters LJ. Macromolecules 1992;25:2645.

[23] Adhikari R. PhD Thesis, University of Halle-Wittenberg, Germany 2001; http://sundoc.bibliothek.uni-halle.de/diss-online/01/02H046/of_index.htm.

[24] Huy TA, Adhikari R, Michler GH. Polymer 2003;44:1247.

[25] Cohen Y, Albalak RJ, Dair BJ, Capel MS, Thomas EL. Macromolecules 2000;33:6502.

[26] Cohen Y, Brinkmann M, Thomas EL. J Chem Phys 2001;114:984.

[27] Michler GH. Kunststoff-mikromechanik-morphologie, deformations-und bruchmechanismen. München: Carl Hanser; 1992.

[28] Michler GH. J Macromol Sci-Polym Phys 1999;38:787.

[29] Bucknall CB. In: Haward RN, Young RJ, editors. The physics of glassy polymers. London: Chapman and Hall; 1997. p. 363. Chapter 8.

[30] Michler GH, Starke J-U. In: Riew CK, Kinloch AJ, editors. Advances in chemistry series 252: toughened plastics II. Washington, DC: American Chemical Society; 1994. p. 251.

[31] Wang X, Zhou W. Macromolecules 2002;35:6747.

[32] Hartmann L, Gorbatschow W, Houwede J, Kramer F. Eur Phys J-E 2002;8:145.

[33] Sakurai S, Aida S, Okamoto S, Ono T, Imaizumi K, Nomura S. Macromolecules 2001;34:3672.

[34] Sakurai S, Sakamoto J, Shibayama M, Nomura S. Macromolecules 1993;26:3351.

[35] Adhikari R, Henning S, Michler GH. Macromol Rapid Commun 2002;23:622.