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# Extrusion Induced Morphologies and Properties of Layered Block Copolymer/Polystyrene Mixtures

*R. Adhikari,*[*1] *M. Buschnakowski,*[2] *W. Lebek,*[2] *R. Godehardt,*[2] *G. H. Michler,*[2]
*K. Knoll*[3]

**Summary:** Using transmission electron microscopy (TEM) and tensile testing, we investigated the morphology and the micro-deformation processes in a new kind of highly asymmetric polystyrene/polybutadiene based triblock copolymer and its blends with general purpose polystyrene (GPPS). The emphasis has been put on the analysis of blends morphology evolved under extrusion conditions and the impact of the later on the micromechanical behaviour of the blends. It was found that the phase separated structures were strongly oriented along the extrusion direction leading to the anisotropic mechanical behaviour. The blends showed more ductile performance and lesser strength on loading the sample perpendicular to the extrusion direction. The ductile to brittle transition was observed when the morphology of the blends was dominated by the glassy phase for 60 wt.-% GPPS.

**Keywords:** block copolymers; electron microscopy; extrusion; polymer blends

## Introduction

The optimisation of mechanical properties is one of the primary concerns of contemporary physical polymer science. For most of the applications of heterogeneous polymers, one is interested to increase their toughness without sacrificing strength and stiffness.[1] Usually, this is achieved by incorporating a small amount of rubber into the glassy polymer matrix. In these modifications, which involve the initiation of various local energy absorbing processes in the material, an increase in toughness is usually accomplished by compromise of transparency of polymeric materials. An alternate way is to assemble the chains of otherwise brittle polymers with rubbers in a variety of block copolymer architectures.[1–3]

Living anionic polymerization allows the synthesis of styrene/butadiene block copolymers (SBCs) having well-defined molecular parameters. One can precisely control not only the hard/soft block ratio in the molecular chains but also the microstructure, constitution, conformation and topology of the polymer chains.[3,4] Especially interesting in this respect are the possibilities of proper control of the interfacial structures (e.g. via introduction of tapered or statistical sequences[3]) and molecular symmetry (e.g. by designing ABA copolymers having unequal A outer blocks[5,6]). It has been known for some time that such architectural modifications of the block copolymer systems have a pronounced impact on the microphase separation phenomena [5–8], rheological properties[9] and hence on the resulting mechanical and micromechanical properties.[10–12]

Styrene-butadiene block copolymers (SBCs) possessing polystyrene chains as terminal blocks and possessing lamellar or co-continuous morphologies[13–16] are special toughened plastics owing to the pronounced plastic deformation of the glassy polystyrene phase. Due to high production costs,

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[1] Central Department of Chemistry, Tribhuvan University, Kirtipur, Post Box No: 24411, Kathmandu, Nepal
E-mail: nepalpolymer@yahoo.com
[2] Institute of Physics, Martin Luther University Halle-Wittenberg, D - 06099 Halle/Saale, Germany
[3] BASF SE, Polymer Research, GKT/I - B 1, D - 67056 Ludwigshafen, Germany

however, the block copolymers are seldom used in pure state. For industrial applications, they are rather often blended with general purpose polystyrene (GPPS) to reduce cost and tailor optimum stiffness/toughness ratio. One critical aspect to be taken into account is the molar mass of the added PS relative to that of PS block of the SBC.[17] In order to adjust the favourable morphology and resulting mechanical properties, rheological parameters should also be optimized.

From the thermodynamics point of view, the phase behaviour of block copolymer/homopolymer blends is primarily determined by the molar mass of the homopolymer chains relative to that of the corresponding block of the block copolymer.[1,17] The toughening efficiency of the SBCs in their blends with general purpose polystyrene (GPPS) can be improved by designing strongly unsymmetrical copolymer architecture having a long styrene outer block, which has the molar mass similar to that of the polystyrene. Keeping this aspect in mind, this paper deals with the correlation among solid state morphology and mechanical behaviour of the blends of a highly asymmetric styrene/butadiene triblock copolymer and general purpose polystyrene (GPPS).

## Experimental Part

### Materials and Sample Preparation

The characteristics of the block copolymer used (named as LN3 hereafter; see Figure 1) in this work is a highly asymmetrical triblock copolymer comprising polystyrene (PS) as outer blocks and polystyrene/polybutadiene random copolymer (PS-co-PB) as middle block. The total polystyrene volume content of the copolymer is 0.74. More details on the synthesis of these kinds of polymers can be found elsewhere.[18–20]

The polymer is asymmetric with respect to both composition (PS volume content = 0.74) and molecular architecture (i.e., the length ratio of PS1/PS2 is much higher than unity). Number average molecular weight and polydispersity index determined by gel permeation chromatography (GPC) using polystyrene (PS) as standard is 127 KDa and 1.10 respectively. Details on the morphology of the copolymer have been described in our previous paper.[13]

The polystyrene homopolymer (named as PS158k) used to prepare the binary blends with LN3 is a commercial product of the BASF has a number average molar mass and polydispersity index of 190 kDa and 2.3, respectively. The blends contained 20, 40 and 60 wt.-% of PS158k.

The granular polymeric materials were mixed with the aid of a mini drum-mixer before the extrusion process. Extruded strands were prepared at 200 °C using a single - screw extruder (Thermo-Haake) at apparent shear rates of about 9 $s^{-1}$. The extrudates coming out of the rectangular slit-die were cooled by an aluminium plate, which is supplied with continuous flow of cold water in order to freeze the shear oriented nanostructures. Information on the extrusion process can be found elsewhere.[21,22] The extruded sheets had a typical thickness and width of 1 mm and width of 10 cm, respectively.

### Tensile Testing

Dog bone shaped tensile specimens, 50 mm long and 4 mm wide, were punched out of the extruded sheets. The mechanical properties were evaluated parallel and perpendicular to the extrusion direction with the aid of a universal tensile machine (Zwick 1425, Ulm, Germany) at 23 °C and cross-head speed of 50 mm/min. The mechanical parameters obtained were an average of 6 tests.

**Figure 1.**
Simplified scheme of molecular architecture of the block copolymer used.

### Transmission Electron Microscopy (TEM)

The morphology was investigated using a transmission electron microscope (120 kV Leo and 100 kV, JEOL, Japan). Ultra-thin sections, approximately 70 nm thick, were prepared from each sample by means of an Ultramicrotome (Leica Ultracut UCT, Leica Mikrosysteme GmbH, Austria) operated at cryo conditions. Prior to the TEM examination, the sections were treated with osmium tetroxide ($OsO_4$) vapour to selectively stain the double bond containing polybutadiene phase. For the study of deformation micromechanisms, the specimens were prepared from deformed tensile bars close to the fracture surface. The TEM images presented in this paper represent the view of morphology of the corresponding extruded sheets along the shear-gradient direction.

## Results and Discussion

### Morphological Orientation vs. Block Copolymer Properties

The effect of morphological orientation on the block copolymer deformation has been the object of several previous studies. It has been demonstrated that the orientation of the BCP nanostructures affects critically their mechanical performance.[14–16,23,24] Here we present the typical examples of how the extrusion process influences the morphological development and mechanical properties in block copolymers. Figure 2 compares the tensile stress-strain diagrams of extrusion moulded LN3 with that of LN4, the latter being a linear triblock copolymer thermoplastic elastomer (Styroflex BX6105 of BASG SE [20]).

It should be kept in mind that under equilibrium conditions, LN3 possesses lamellar morphology while LN4 possesses polystyrene domains dispersed in rubbery matrix.[13] Due to the extrusion process, the basic morphologies of the block copolymers remained unaltered, i. e. the morphology did not change compared to the equilibrium state.[25]

In is interesting to note that, unlike the orientation of the triblock copolymers discussed in the literature,[25] the lamellar block copolymer studied in this work depicts the lamellar orientation similar to that of the diblock copolymers. Independent of the loading direction relative to the extrusion direction, the block copolymer possessing originally the dispersed morphology (i.e., polystyrene domains embedded in the rubbery matrix) show identical stress-strain curves (see Figure 2). This behaviour is consistent with isotropic morphology of the sample LN4, which shows no preferential orientation of the microphase-separated structures in the extruded sheets.[25] However, the lamellar block copolymer LN3 showed a clear loading direction dependent tensile behaviour. On loading the sample, parallel to the extrusion direction, the sample exhibited higher yield stress (approximately 15 MPa) than for the perpendicular loading (approximately 10 MPa). During tensile deformation up to several hundred percent, the level of the stress at a given strain is higher for the parallel deformation than for perpendicular deformation. In contrast, the samples show significantly larger elongation at break during perpendicular deformation. The larger stress level achieved by the samples during tensile deformation parallel to the extrusion direc-

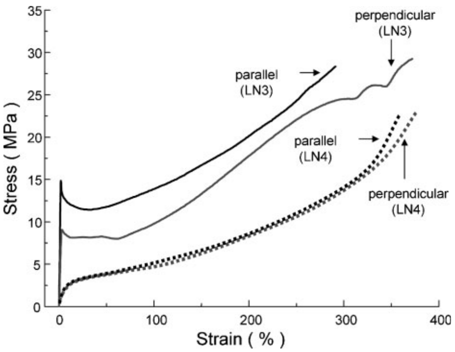

***Figure 2.***
Stress-strain curves of two different triblock copolymers (LN3 and LN4) having entirely different microphase-separated morphologies.

tion implies that the microphase-separated structures, in particular the glassy lamellae of LN3, are aligned towards the extrusion direction, which is confirmed by TEM studies (see the discussion below). The anisotropic tensile deformation behaviour of the lamellar block copolymer LN3 relative to extrusion direction can be correlated with the extrusion induced evolution of anisotropic morphology.

Figure 3 shows TEM micrographs of the block copolymer LN3 prepared by subjecting the block copolymer melt to low strain rate extrusion (i.e. ca. 9 $s^{-1}$), the extrusion direction is being indicated by an arrow. The specimen for the TEM investigations were taken from the centre of the extruded bar, which was ultramicrotomed along the extrusion direction. The images reflect the morphology of the sample perpendicular to the normal axis of the extrusion. Figure 3a was taken from a location approximately 1 μm beneath the surface while Figure 3b from the location approximately 500 μm inside the surface. In the TEM images, one can see clearly the lamellar morphology of the block copolymer: the lamellae are oriented towards the extrusion direction towards the skin (Figure 3a) while they are randomly arranged towards the middle (Figure 3b) of the sample. The PS lamellae are approximately 16 nm and the typical periodicity lies in the range of 26 nm.

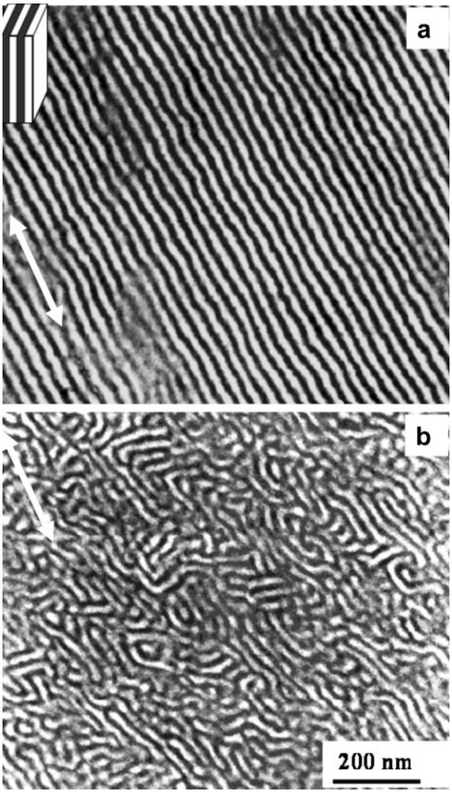

*Figure 3.*
TEM micrographs of extrusion moulded LN3: a) aligned lamellae towards the skin and b) lamellae without preferential alignment towards the middle of the mould; the arrow shows the extrusion direction.

Going towards the centre of the extruded strand, the shear stress goes on decreasing and reaches a minimum at the centre of the sheet. Thus the lamellae have no preferential alignment in this region. The decreased long range order of the lamellae compared to the solution cast sample[13] is due to the insufficient time which the melt has to form the structures close to the equilibrium.

There is a clearly defined consequence of the extrusion induced orientation of the microphase-separated structures of the block copolymer on the tensile mechanical properties. Figure 2 makes it evident that the yield stress of the block copolymer is higher when subjected to tensile deformation along the extrusion direction (ca. 15 MPa vs. ca. 10 MPa) than for the perpendicular deformation. Similar behaviour was reported previously by Cohen et al.[14] For the whole strain range the stress level for the perpendicular deformation is lower than for the parallel deformation. Finally, the breaking strain for perpendicular deformation is approximately 100% higher than for the parallel deformation. The higher strength of the material at every strain for parallel deformation results from the arrangement of continuous glassy phase along the tensile deformation direction. During tension, the load is preferentially received by the glassy PS lamellae phase. During perpendicular deformation both PS and rubbery lamellae are subjected to tensile deformation. As a

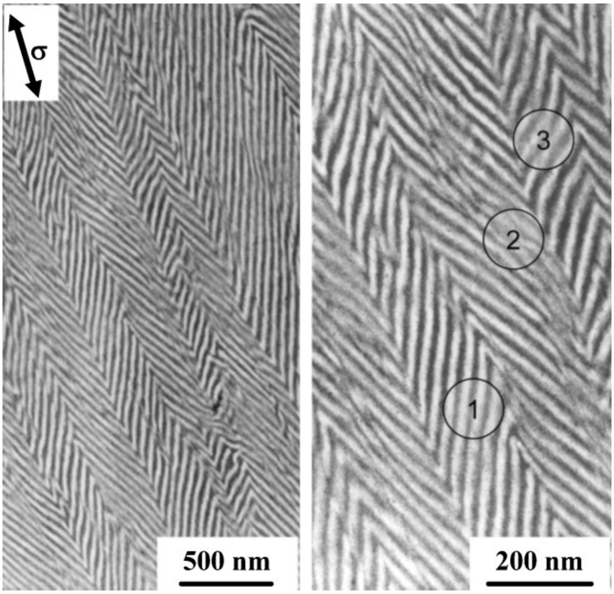

***Figure 4.***
Different magnifications of TEM micrographs showing tensile deformation induced *fish-bone* pattern in the block copolymer formed by perpendicular deformation of the lamellae; the arrow shows the deformation direction.

consequence, the resistance towards plastic flow decreases.

This correlation can be more conveniently characterized by the analysis of strain induced structural changes in the block copolymer during tensile deformation. Figures 4 and 5 illustrate the deformation structures of the lamellar block copolymer. The specimens were taken from the deformed tensile bar from an area close to the fracture surface. Thus the deformation structures discussed correspond to the high strain deformation of the lamellae.

On deforming the sample parallel to the extrusion direction (i.e. along the lamellar alignment), the thickness of both PS and PS-co-PB lamellae was found to decrease significantly. The lamellae deformed plastically to several hundred percents contributing to the ductile behaviour of the block copolymer. The mechanism is similar to that of the polygranular sample of LN3[13] as well as that of other oriented lamellar samples subjected to parallel tensile deformation.[10,14] The mechanism of plastic flow of the polystyrene layers, which are thinner than the critical value, has been termed as *thin layer yielding*.[10] In this paper, we focus on the deformation of the sample perpendicular to the extrusion direction.

Figure 5 collects the TEM micrographs of the deformation zone from the skin layer, i.e. only a few microns away from the sample surface. As observed previously by Cohen and co-workers,[14] the lamellae deform by the formation of *chevron* morphology or *fish bone* pattern. In the studies by Cohen et al., it was concluded that the long spacing remains nearly constant in the straight limbs of the chevron folds, but in the hinge regions the soft rubbery layers are more dilated than the glassy ones. In consistence with the observation in a pervious study on a similar system,[14] in which the constancy of the long spacing relative to the undeformed state was reported, the lamellar long period in the deformed sample does not change significantly. However, there are regions of different periodicities in the deformed

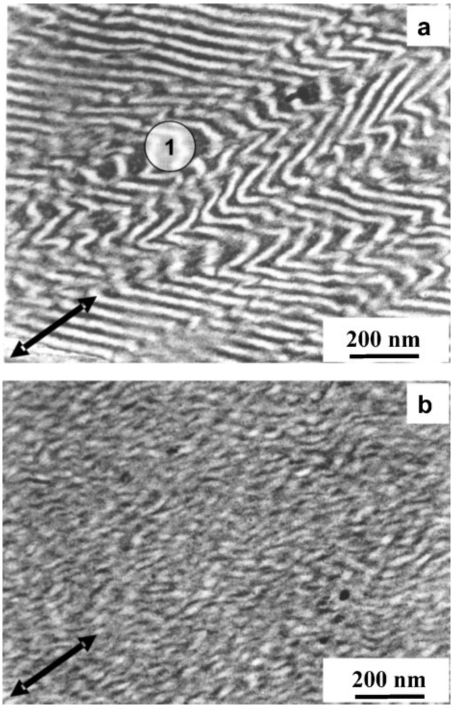

*Figure 5.*
TEM micrographs showing deformation structures in the block copolymer depending on the distance from the sample surface; a) 200 μm beneath the surface and b) 500 μm beneath the surface; the arrow shows the deformation direction.

sample (see, for instance, locations 1, 2 and 3 Figure 4b). This observation indicates that the stress applied to the oriented lamellae is not perfectly perpendicular relative to the lamellae orientation direction. Particularly, the highly dilated rubbery regions (dark areas) indicate the presence of diagonal stretching forces, on one hand while the presence of much thinner lamellae (8 nm or less) demonstrates the plastic yielding on the other.

There are evidences of much intense permanent deformation of the rubbery phase compared to the glassy phase of the block copolymer, see Figure 5a). This region was characterized, in the undeformed state, by the presence of rather long but non-uniformly aligned lamellae (Figure 5a). As a result many of the lamellae experience diagonal forces during deformation of the sample perpendicular to the extrusion direction. As a consequence, the rubbery PS-co-PB lamellae deform up to much higher strain level than the glassy lamellae. Hence, in some locations, the long period almost doubles from the value of undeformed sample (see location 1 in Figure 5a). Still the integrity of the layers remains unaltered due to the connectivity of the glassy domains by the rubbery chain. At still higher local deformation (for example, when driven by local stress concentrators), the rubbery phase might undergo fibrillation and even rupture.[10]

The situation was found completely different at the middle of the extruded plate, where the lamellae were originally short and had no preferential alignment (see Figure 3b). The presence of morphology comprising the destructed lamellae and presence of bulges along the polystyrene struts in the deformed sample (middle of the extruded sheet) suggests the occurrence of the following deformation mechanism.

Initially, the rubbery PS-co-PB phase experiences the tensile force due to the presence of PS lamellae in the form of short fragments leading to the stretching of the rubbery phase. At higher macroscopic deformation, the rubbery chains are further stretched initiating the yielding of PS layers. The PS lamellae fragments appear as the glassy struts in the TEM micrograph (see Figure 5b). This mechanism is consistent with one suggested on the basis of FTIR investigations.[13,24]

## Structure and Properties of Block Copolymer/GPPS Mixtures

Polymer blends based on polystyrene-*block*-polybutadiene-*block*-polystyrene (SBS) block copolymer and polystyrene (PS) homopolymer have been the object of our recent studies.[22,23,26,27] It was demonstrated that, by modifying molecular and processing variables, the morphology and mechanical properties of such blends can be significantly controlled. Under the influence of strong shear-force (such as during injection moulding or extrusion processing), the mixing behaviour of the blends can be drastically changed leading to the morphologies which are far from equilibrium but are more interesting for practical applications.

Under equilibrium condition (i. e. in the solution cast films), the investigated blends showed macrophase-separation.[27] At low homopolystyrene concentration, the LN3/GPPS blends depict the morphology comprising lamellar matrix (LN3) with polystyrene particles (added GPPS) embedded in it. At higher GPPS concentration, the morphology of the blends was found to reverse. During compression moulding, the equilibrium morphology did not change significantly; for instance, only the size of PS inclusions reduced at low homopolystyrene content. During extrusion process, more dramatic change was observed in the block copolymer/polystyrene blends. Under similar conditions, in the corresponding star block copolymer/GPPS blends, typical *droplet-morphology* was observed.[27]

Figure 6 shows the TEM micrographs of the extruded mixtures comprising the block copolymer and variable weight fraction of general purpose polystyrene (GPPS). The specimens for the TEM investigations were cut from the extruded sheet in such a way that the ultramicrotomed sections reveal the morphology of the centre of the extruded bar. At the first glance, one can notice that the added polystyrene has a tendency to segregate as separate domains. These domains appear as bright spots and continuous layers in the TEM micrographs (Figure 6). The tendency of the added polystyrene to segregate in the form of glassy domains and layers results from the large molecular weight disparity between the PS block of the copolymer (longer chain having a molar mass of approximately 60 kDa) and the added homopolymer (number average molar mass of 190 kDa). The presence of matrix-particle morphology, typical of a polymer blend is missing, however, indicating a forced mixing. The latter can be attributed to the entrapment of the shear induced non-equilibrium structures of the blends due to rapid cooling from the melt. Thus the structures are exclusively non-equilibrium structure. These results are consistent with our previous results on injection moulded block copolymer homopolymer blends.[26,28]

Independent of the compositions, the polymer blends reveal the lamellar structures of parent block copolymer as well. Continuous layers of polystyrene evolve at higher polystyrene concentrations in addition. Those layers are several hundred

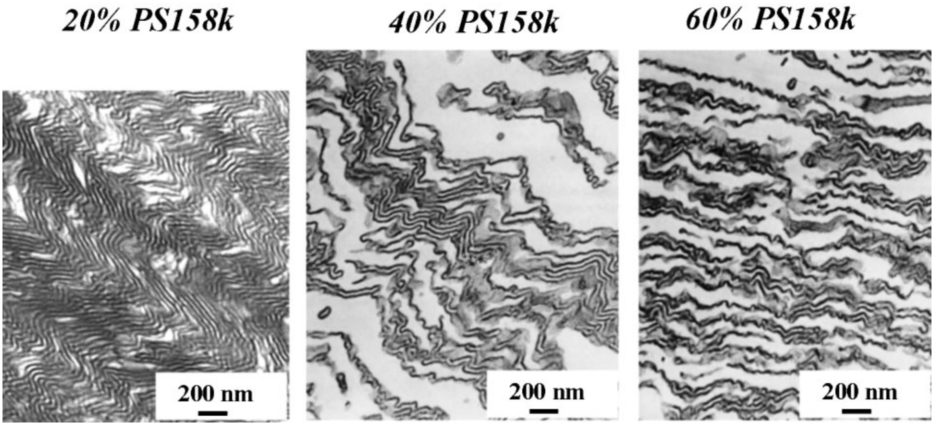

***Figure 6.***
TEM micrographs showing morphology of LN3/GPPS blends with various PS weight fractions; the specimens for the TEM were taken from the middle of the extruded sheet; the structures are aligned towards the extrusion direction.

nanometres thick, which, along with rest of the block copolymer lamellae, assume wavy structures. Such wavy structures were particularly observed at the middle of the extruded sheet, which might have been evolved due to relaxation of the oriented stands during extrusion process.

It should be noted that the formation of layered structures in the blends with polystyrene homopolymer is basically valid for the lamellar block copolymer exhibiting not too high molecular asymmetry. If the asymmetry of the block copolymer is extremely high, such as in star shaped copolymers, one would encounter interesting morphologies with polystyrene *droplets*.[27] The morphology of the parent block copolymer will be progressively destroyed in the blends with homopolymer in such cases.

To summarize the morphology of LN3/GPPS blends in the extruded sheets, the mixtures show extremely non-uniform morphology. Thus, only a qualitative analysis of deformation micromechanisms can be presented. As the morphology of the blends changes practically to form polystyrene matrix at 60 wt.-% GPPS, it can be expected that the blends will show ductile to brittle transition at this composition.

To investigate the influence of morphology on (micro)-mechanical properties of the blends, first the tensile tests were carried out. We focus our discussion on the influence of GPPS weight fraction on the mechanical properties of the blends.

The tensile stress-strain curves of some of the LN3/GPPS blends are presented in Figure 7. The curves were recorded for deformation of the samples both parallel (Figure 7a) and perpendicular (Figure 7b) to the extrusion direction (i.e. the orientation direction). The deformation of each sample is characterized by a well defined yield point. As expected, with increasing GPPS content in the mixtures, the yield stress ($\sigma_Y$) of the blends increases while the elongation at break ($\varepsilon_B$) decreases.

As already discussed, the block copolymer deformation is characterized by an extremely high ductility in spite of high overall polystyrene content (74 vol.-%). The deformation of each blend parallel and perpendicular to the extrusion direction gives rise to different values of yield stresses (compare Figure 7a and Figure 7b), which is in agreement with the recent results on linear block copolymers oriented by roll casting.[14–16] The values of yield stresses ($\sigma_Y$) of the samples measured for parallel deformation were higher than that for perpendicular deformation irrespective of blend composition. Similar trend was also noticed for Young's modulus as well. A large anisotropy in mechanical properties (such as Young's modulus, yield stress etc.) was observed in block copolymer comprising of alternating glassy/rubbery lamellae and even glassy cylinders,[14] where the glassy phase extended over a macroscopic dimension.

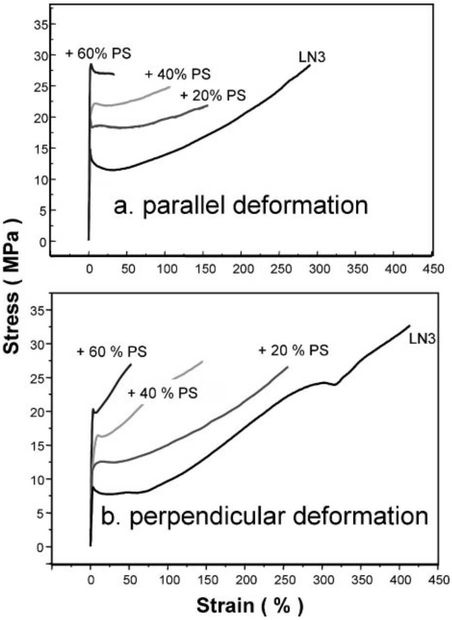

***Figure 7.***
Stress-strain curves of extruded LN3/GPPS blends subjected to tensile deformation parallel (a) and perpendicular (b) to the extrusion direction.

It is interesting to note that the yield stress of each blend is lower for parallel deformation than for the perpendicular deformation. However, the strain hardening effect is stronger for perpendicular deformation for each sample which correlates well with the predominant stretching of the rubbery layers followed by plastic flow of glassy layers. Hence, the elongation at break for perpendicular deformation is higher than for the parallel deformation. Finally the maximum stress level reached during perpendicular deformation is nearly identical with that for parallel deformation.

The investigated blends show a sharp transition in elongation at break ($\varepsilon_B$) between 40 and 60 wt.-% of added GPPS. Note that the value of $\varepsilon_B$ decreases from about 120% (for blend containing 40 wt.-% GPPS) to about 30% (for blend containing 60 wt.-% GPPS), during parallel deformation for instance (see Figure 7a), indicating a change in deformation mechanism. It should be noted that the *ductile-to-brittle* transition occurs when the morphology of the blends changes from predominantly lamellar to the polystyrene matrix. It has been demonstrated that the deformation mechanisms changes from predominantly plastic deformation of the glassy phase to the localization of deformation zones in the form of crazes at the thick polystyrene layers.[22]

## Conclusion

The results reported in this paper can be summarized as follows:

i. The lamellar block copolymer investigated in this work showed a pronounced anisotropic morphology which resulted in anisotropic tensile mechanical properties. The lamellae of the block copolymer were oriented along the extrusion direction towards the film surface. The alignment of the layers was found to vanish gradually on going from surface to the centre of the extruded film.
ii. The block copolymer/GPPS blends also exhibited anisotropy in both morphology and tensile mechanical properties. The yield stress of the samples was higher for the entire samples subjected to parallel deformation than those subjected to perpendicular deformation relative to the extrusion direction (which is also the direction of the orientation of the micro- and nanostructures). The samples showed more ductile behaviour during perpendicular deformation while they exhibited higher yield strength during parallel deformation.
iii. The ductile to brittle transition was observed for the blend containing 60 wt.-% GPPS, when the morphology of the blends was dominated by GPPS phase.

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