



# Relating microhardness to morphology in styrene/butadiene block copolymer/polystyrene blends

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Received 18 December 2002; received in revised form 28 February 2003; accepted 28 October 2003

## Abstract

The microhardness behaviour of binary blends comprising a styrene/butadiene star block copolymer and polystyrene homopolymer (hPS) over a wide composition range is investigated. In particular, the interrelation between the morphology, tensile properties (such as yield stress  $\sigma_Y$  and the Young's modulus,  $E$ ) and the microhardness  $H$  is explored. As in the case of microphase separated block copolymers and binary block copolymer blends, as reported in preceding publications, a clear deviation in the microhardness behaviour from the additivity law is observed. The lamellar block copolymer system is compared with the nanostructure of semicrystalline polymers having a lamellar morphology. A dependence of  $H$  upon PS lamellar thickness is found. For the samples with lamellar morphology the hardness value was found to correlate with the mechanical parameters obtained by uni-axial tensile testing according to:  $H/\sigma_Y \sim 2.2$  and  $E/H \sim 22$ .

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*Keywords:* Styrene/butadiene block copolymer/polystyrene blends; Microhardness; Electron microscopy

## 1. Introduction

Polystyrene (PS) is a thermoplastic polymer that has many advantages. It can be easily synthesized, conveniently processed and recycled; it is relatively resistant to thermal degradation and shows high stiffness and toughness values. Its optical transparency makes it attractive for many applications such as packaging, insulation, automotive, etc. However, disadvantage of this material is its brittleness at room temperature. Nevertheless, it is known that the polymers break macroscopically in a brittle manner (e.g. poly(methyl methacrylate) PMMA, polystyrene, PS). On the other hand they show highly ductile deformation zones (e.g. crazes, shear yielding, etc.) with a maximum natural draw ratio ( $\lambda_{\max}$ ), for polystyrene of about 4 and for PMMA of about 3. This means that these polymers are intrinsically tough (elongation at break of several hundred percent) [1–3]. Hence the main goal for the toughness modification of the brittle plastics like polystyrene is to transfer their intrinsic toughness to the macroscopic scale.

In brittle polymers, toughening is achieved by incorporation

of a small amount of rubber, which forms the dispersed phase embedded in the brittle polymer matrix [1,2,4]. However, due to intrinsic incompatibility and poor adhesion between several polymer pairs, there is a danger of deterioration of the mechanical properties. One can avoid this problem by the introduction of phase compatibilisers or graft polymerisation. However, the resulting polymer may be opaque due to the relatively large size of the dispersed particles.

It is well known that linking the polystyrene (PS) chains with the polybutadiene (PB) chains by means of covalent bonds in block copolymers leads to the formation of highly ordered structures called microphase separated systems whose dimension lie in the range of the radius of gyration of the molecules [5]. Through the variation of molecular weight, composition, chain architecture and processing conditions, the dimension, nature and orientation of these structures can be considerably controlled [5–10]. This allows producing transparent nano-structured materials having a tailored mechanical property profile.

Because of their higher production costs, the block copolymers are seldom used as pure materials. Styrene/butadiene block copolymers are, for example, often used in combination with polystyrene homopolymer (e.g. general purpose polystyrene, GPPS) [10,11]. The compatibility of

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the added polystyrene with the block copolymer is limited by the molecular weight and amount of the homopolystyrene (hPS) chains, relative to the corresponding PS blocks within the block copolymer [5,9]. The molecular weight of the polystyrene blocks is, however, restricted by the requirement of the rheological properties.

The changes in the styrene/butadiene block copolymers' architecture do not only modify their phase diagram but also influence their miscibility, as well as the mechanical and micromechanical behaviour of their blends with polystyrene [12]. In other words, the architectural modification of the block copolymers may open a new way of controlling mechanical performance of their blends, most especially with polystyrene. As an example to this respect we can cite the case of block copolymers having an asymmetric star architecture. In contrast to linear block copolymers having analogous chemical composition and morphology, star block copolymers are found to possess more attractive mechanical and rheological properties [10–14]. Thus, it is of special interest to gain a deeper insight into the structure–property correlations in star block copolymer/hPS blends.

It is well known that the microhardness of polymer systems is sensitive to different molecular parameters (molecular weight, branching, etc.), microscopic morphology, degree of crystallinity in the semi-crystalline systems, etc. [15]. In a preceding study we found that the microhardness of the glassy/rubbery block copolymer systems is strongly dependent on the molecular architecture and the microphase separated morphology [16].

For crystalline polymers and copolymers, the microhardness depends primarily on crystal characteristics such as size and perfection of crystals, chain conformation within the crystals, etc. [17,18]. In the co-reactive blends of polyethylene terephthalate (PET) and polycarbonate (PC), the microhardness behaviour is dictated by the change in glass transition temperature resulting from the chemical reaction leading to the copolymer formation [17]. In general, the glass transition temperature may be regarded as the main parameter that is sensitive to the microhardness of amorphous polymers [19].

In preceding papers, we discussed the microhardness behaviour of styrene/butadiene block copolymers [16] and of binary block copolymer blends [20] with respect to their molecular architecture. The aim of the present study is to examine the correlation between the morphology and microhardness behaviour of blends consisting of a star block copolymer and general-purpose polystyrene (GPPS). A detailed account of the morphology and micromechanical behaviour of these blends may be found elsewhere [12].

## 2. Experimental

### 2.1. Materials studied

The architecture and morphology of the star block

Table 1  
Characteristics of the blend components

Blend component	$M_n$ (g/mol) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>	$\Phi_{\text{styrene}}$ <sup>b</sup>	Morphology (TEM)
ST2-S74	109,200	1.69	0.74	Lamellar
hPS	82,600	2.30	1.0	–

<sup>a</sup> Number average ( $M_n$ ) and weight average ( $M_w$ ) molecular weights determined by the gel permeation chromatography (GPC).

<sup>b</sup> Total styrene volume content determined by Wijs double bond titration.

copolymer used to prepare binary blends with general-purpose polystyrene homopolymer (hPS) is shown in Fig. 1 (details are given in Ref. [21]). The main features of the samples are collected in Table 1.

After mixing the materials in an extruder, tensile bars were prepared by injection moulding (mass temperature 250 °C and mould temperature 45 °C). The blends contain 20, 40, 60 and 80 wt% of hPS. The samples were kindly supplied by the BASF Aktiengesellschaft.

### 2.2. Techniques

*Tensile testing* was performed using a universal tensile machine (Zwick 1425) at room temperature (23 °C) at a crosshead speed of 50 mm/min using injection moulded samples according to ISO 527. At least 10 samples were tested in each case. The Young's modulus ( $E$ ) and yield stress ( $\sigma_Y$ ) were derived from the initial slope of the stress–strain curve and from the first maximum of the corresponding stress–strain curves, respectively.

*Transmission electron microscopy* (200 kV TEM, Joel) was used to image the microphase separated morphology of the blends. Ultrathin sections (ca. 50 nm thick) were ultramicrotomed from a bulk specimen. Polybutadiene phase was selectively stained by osmium tetroxide ( $\text{OsO}_4$ ) vapour. The structures were quantified by the use of a special image-processing program.

*Microhardness measurements* were performed using a Leitz tester. A Vickers square-based diamond indenter was employed. To minimize the creep of the sample holder under the indenter, indentation times of 6 s were used. Details on the procedure for the microhardness measurements may be found elsewhere [15]. Microhardness is based on the measurement of the residual impression made by a

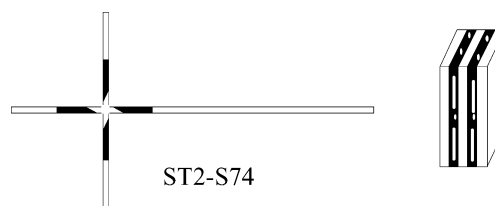


Fig. 1. Scheme showing the architecture and morphology of the star block copolymer used to prepare binary blends with polystyrene homopolymer (hPS). The white and dark areas correspond to the hard and soft phases, respectively.

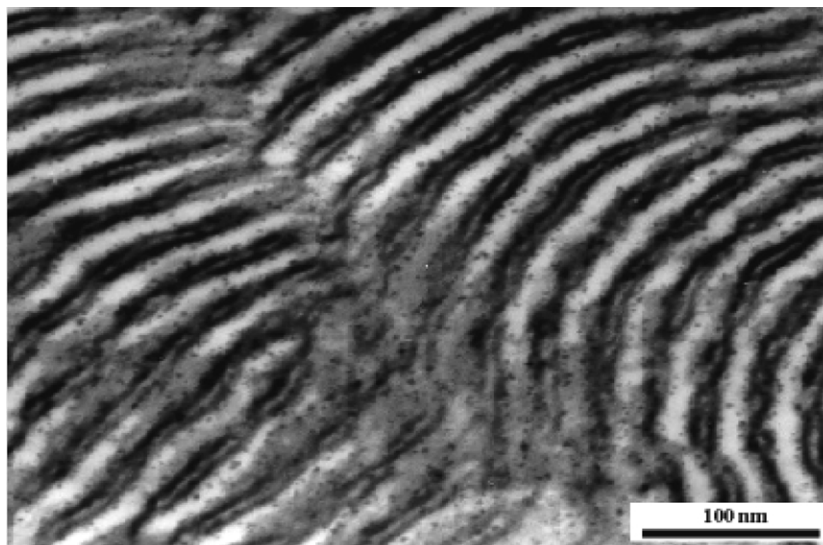


Fig. 2. A TEM micrograph showing the microphase separated morphology of the star block copolymer used (ST2-S74). Solution cast film, OsO<sub>4</sub> staining.

sharp indenter upon the application of a given load. The hardness value is defined as

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

where  $P$  is the applied load in  $N$ ,  $d$  the diagonal of the impression in  $m$ , and  $k$  the geometric factor equal to 1.854. A load of 50  $N$  was used. The measured penetration depth of the indenter (10–20  $\mu\text{m}$ ) involves the plastic deformation of very many domains; i.e. each hardness measurement represents an averaging value over the domains. The  $H$  values were derived from an average of at least 10 indentations.

### 3. Results and discussion

#### 3.1. Morphology of injection moulded block copolymer/hPS blends

The morphology of the pure star block copolymer used in this study has been characterized in recent studies [11,12,21]. The structure of the samples was determined at several places and analysed using image processing techniques. The star block copolymer shows (see the TEM micrograph of a solution cast sample in Fig. 2) a peculiar lamellae-like morphology with alternating layers of polystyrene (PS) and polybutadiene (PB). Such a well ordered lamellar arrangement shows a periodicity of about 42 nm. After injection moulding of the star block copolymer and the blends with hPS, the microphase-separated structures are oriented in the injection direction.

By adding the hPS to the star block copolymer the thickness of the PS lamellae are continuously increased while the thickness of the butadiene layers remained almost

unchanged. Therefore it is possible to systematically alter the thickness of the PS layers and quantify the morphological details.

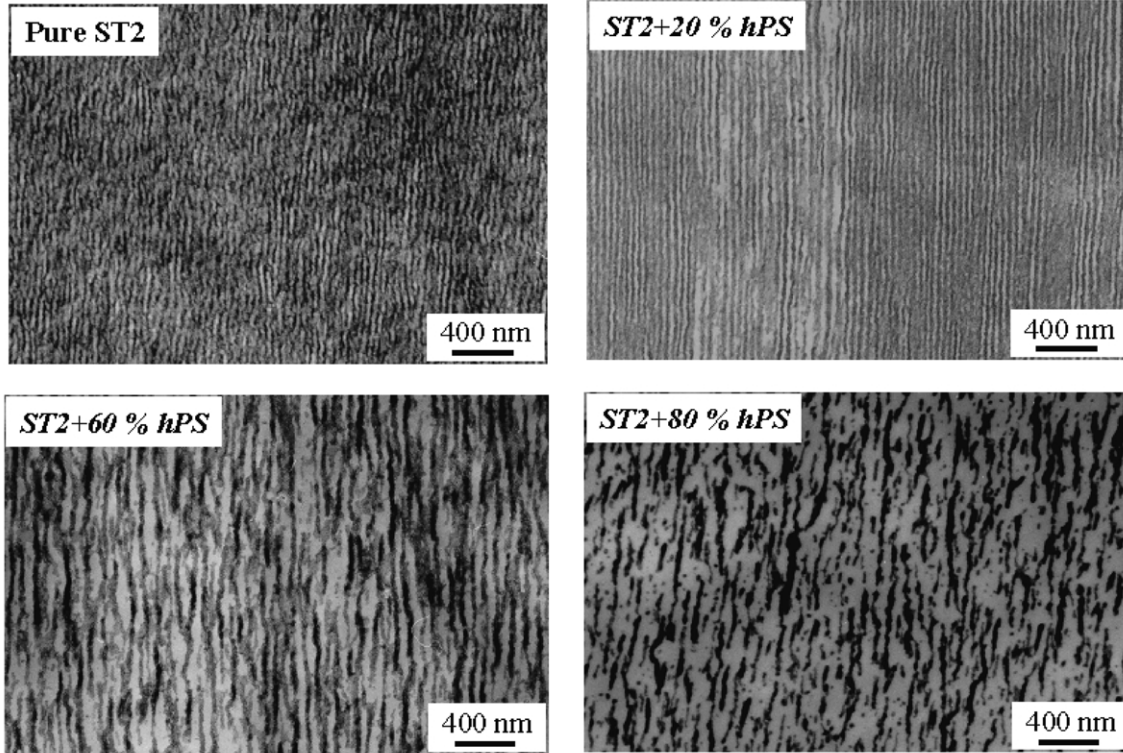
It is worth mentioning that the morphology of the injection-moulded samples may change along the length of the bar and across the thickness of the sample. Hence the morphology formation in the injection-moulded bars is a rather complex phenomenon. In order to compare the different samples systematically, sections from the middle of the injection-moulded bar parallel to the injection direction at about 50  $\mu\text{m}$  beneath the surface were prepared. Fig. 3 illustrates some representative TEM micrographs (Fig. 3a) and the frequency distributions of the PS lamellae thicknesses (Fig. 3b) in the star block copolymer and of some of the blends with the hPS.

The micrographs show the lamellar morphology of the injection moulded star block copolymer and the blends with polystyrene homopolymer (hPS). The shear stress during injection moulding process makes the microphase-separated structures to align along the injection direction (Fig. 3a). It is to be noted that, both, peak value and the width of the thickness distribution of the PS lamellar shift continuously towards higher values with increasing hPS content (Fig. 3b), demonstrating that a major part of the added hPS is accommodated by the corresponding PS lamellae of the star block copolymer.

#### 3.2. Structure–microhardness correlation

Addition of hPS to the star block copolymer results in the increase of total hard phase content that causes an increase in the  $H$  values. Fig. 4 illustrates the microhardness variation of the ST2-PS blends as a function of the added homo-polystyrene ( $\Phi_{\text{hPS}}$ ) content in the block copolymer/hPS investigated. The increase of  $H$  with  $\Phi_{\text{hPS}}$  is first relatively slow until 60 wt% hPS and then rises more

a)



b)

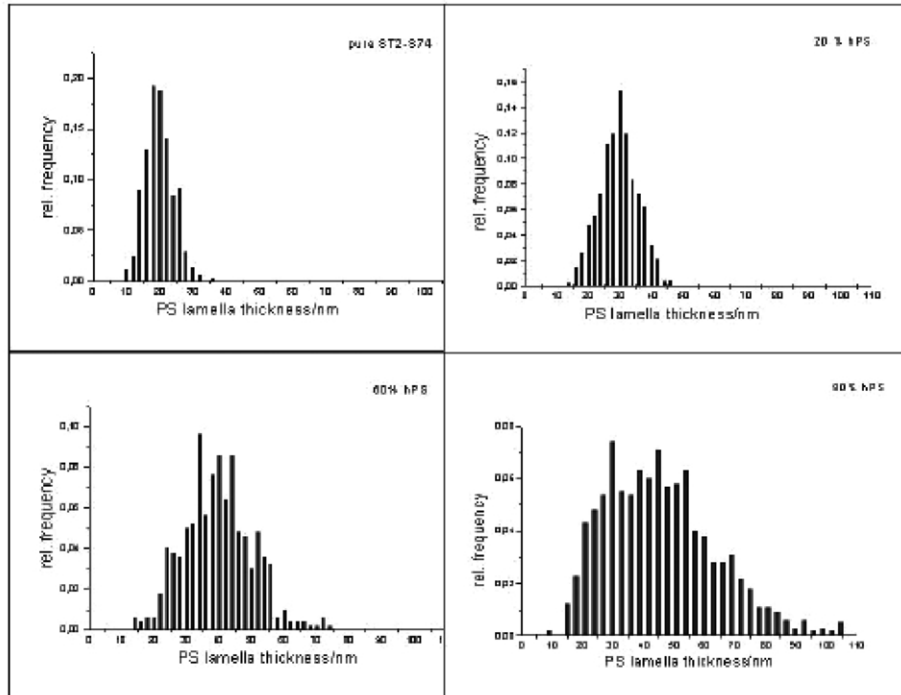


Fig. 3. (a) TEM images of the injection moulded star block copolymer and some blends with hPS, OsO<sub>4</sub> staining (injection direction: vertical) and (b) distribution of PS lamellae thicknesses measured in the corresponding TEM micrographs.

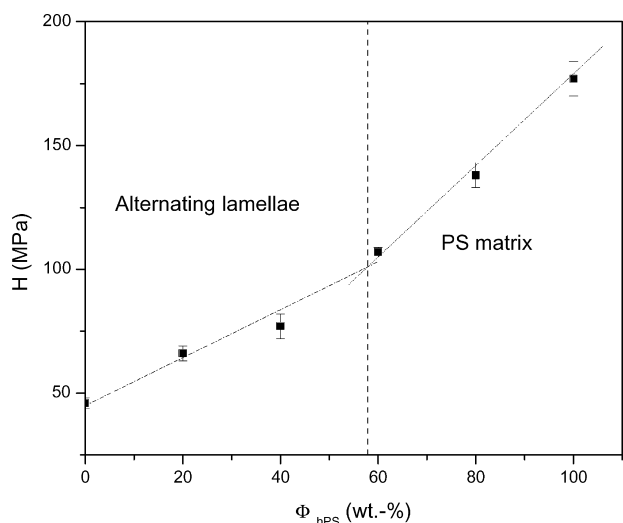


Fig. 4. Microhardness plotted as a function of  $\Phi_{\text{hPS}}$  for the star block copolymer/hPS blends.

rapidly. In the present case, the glass transition temperature  $T_g$  of the components does not change significantly [16]. With increasing hPS content, the lamellar morphology does not change either up to a certain composition. The components of the blends, i.e. polybutadiene and polystyrene, are present as pure phases. Hence, the change in slope of the microhardness suggests that there should be some other property determining parameters other than  $T_g$  and overall composition of the blends.

In consonance with previous studies on styrene/butadiene block copolymer systems [16], the present results show that microhardness of the block copolymer/hPS blends significantly deviates from the additivity law (dotted line in Fig. 5). The reasons for this deviation may have different origins: the molecular architecture which modifies the effective phase volume ratio, the presence of microphase separated morphology and some specific effects such as yielding of thin layers, etc. (see below).

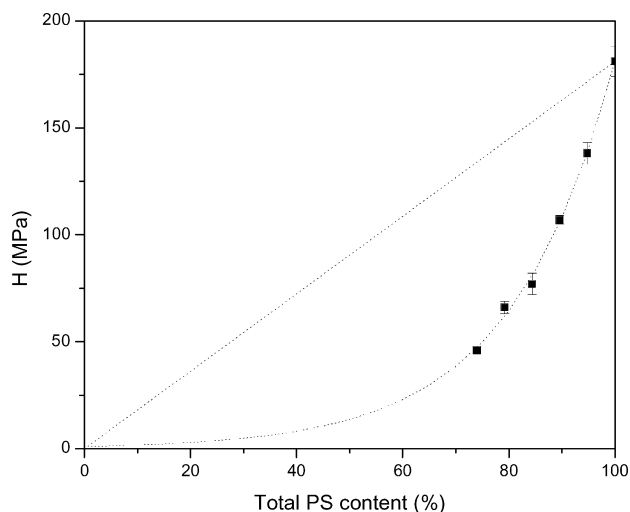


Fig. 5. Hardness of the star block copolymer/hPS blends as a function of total PS content. Dotted line: hardness additivity law.

It should be stressed at this point that the morphology of the blends containing hPS < 60 wt% was found to consist of separate PS and PB layers (see Fig. 3a). Beyond this composition, the definition of the PB layers decreases, and the PS phase practically forms the matrix where the PB lamellae appear as elongated worms embedded in the PS matrix (see Fig. 3a, details discussed in [12]). Thus, the predominant lamellar morphology showing a small increase of PS layer thicknesses is the dominating parameter for the lower increase of  $H$  values observed (see Fig. 4). Fig. 6 illustrates the microhardness variation of the lamellar samples (hPS content  $\leq 60$  wt%) as a function of thickness of the PS lamellae ( $D_{\text{PS}}$ ). From the above results one can conclude that the microhardness values in the region  $\Phi_{\text{hPS}} < 60$  wt% hPS are determined by two parameters: a) added PS content, b) thickness of the PS lamellae.

In principle, it is not possible to quantitatively separate the contribution of the increasing PS lamellae thickness and of the increasing PS content in the blends containing  $\Phi_{\text{hPS}} \leq 60$  wt% hPS. As compared to the influence of PS content alone, the  $H$  values contributed by the PS layer thickness should be smaller than the  $H$  values predicted by the additivity law. For the samples with the PS lamellae thickness  $D_{\text{PS}} \leq 30$  nm a lower  $H$  value is indeed observed (see Table 2). This could be due to the lower value of the local yield stress of the material. In other words, the local yield stress of the lamellar samples (i.e. with  $D_{\text{PS}} \leq 30$  nm) appears to be smaller when compared with that of the bulk PS sample and the blends with PS matrix (i.e. with  $D_{\text{PS}} > 30$  nm). Such a yield stress decrease could provide additional evidence to the mechanism of ‘thin layer yielding’ (homogeneous plastic deformation of glassy polymer layers if their thickness is below a critical thickness, leading to a highly ductile behaviour compared with the bulk polymer) proposed for lamellar block copolymer systems [21]. This result is in consonance to the occurrence of a lower glass transition temperature for thin PS films, as recently reported by Kramer et al. [22] and

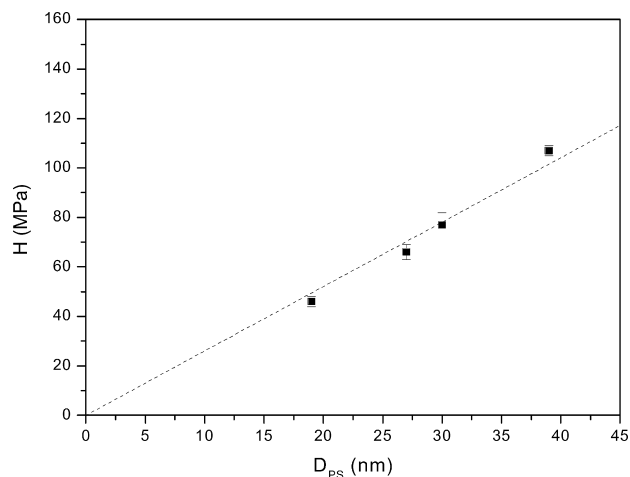


Fig. 6. Plot of microhardness for the lamellar samples as a function of thickness of the PS lamellae ( $D_{\text{PS}}$ ).



Table 2

PS content, thickness of PS lamellae  $D_{PS}$ , experimental,  $H_{exp}$  microhardness, yield stress  $\sigma_Y$  and Young's modulus  $E$  of the investigated blends

hPS content (wt%)	$D_{PS}$ (nm) <sup>a</sup>	Total PS (wt%)	$H_{exp}$ (MPa)	$\sigma_Y$ (MPa)	$E$ (MPa)	$E/\sigma_Y$
0	19	74	44	24	1205	50
20	27	79	64	30	1596	54
40	30	84	75	37	2072	56
60	39	90	100	45	2522	56
80	43	95	138	51	2926	57
100	–	100	180	55	3300	60

<sup>a</sup> Maximum in the PS lamella distribution curves (e.g. from Fig. 3b).

Wang et al. [23]. However, in our materials we do not detect such a  $T_g$  decrease [16].

### 3.3. Correlation of microhardness with macroscopic mechanical properties

Fig. 7 shows the plots of  $H$  vs  $\sigma_Y$  and  $H$  vs  $E$  for the star block copolymer/hPS blends. In agreement with the results observed in other semicrystalline and amorphous materials, it is seen that the  $H$  values of the ST2/hPS blends show a general tendency to increase with, both,  $E$  and  $\sigma_Y$ . The  $H$ -data for the blends with a lamellar structure fit into a straight line passing through the origin, which yields the slopes  $H/\sigma_Y = 2.2$  (Fig. 7a) and  $E/H \sim 22$  (Fig. 7b), respectively. It is noteworthy that the  $H/\sigma_Y$  and  $E/H$  values for the pure PS are notably larger and smaller, respectively, ( $H/\sigma_Y = 3.2$  and  $E/H = 18.3$ ), owing to the bulk PS amorphous morphology, and hence to the absence of 'thin layer yielding' mechanism. Evidently, the sample for  $\Phi_{hPS} = 80$  wt% exhibits an intermediate morphology between the lamellar one and the pure PS matrix, as pointed before. Therefore, the  $H/\sigma_Y$  and  $E/H$  values for this sample lie in between those of both morphologies. The linear relationship between  $H$  and  $E$  for the region of lamellar structure is similar to experimental results for PE [24] and Struik's prediction for other polymers [25]. However, the experimental value of  $E/H \sim 22$  measured in the block copolymer/hPS blends is significantly larger than that obtained by Struik [25] and Flores et al. [24].

The value of  $H/\sigma_Y = 2.2$  significantly deviates from that predicted by the Tabor's relation ( $H/\sigma_Y = 3$ ) [26]. Tabor's relation was found to be in good agreement with the results obtained in semicrystalline polymers, provided that the rate of tensile and indentation experiments were identical [27]. The relation is strictly valid for perfectly plastic materials. Thus, deviations may be expected to occur when the contribution of elastic and viscoelastic deformation is increased. The discrepancy in the values of  $H/\sigma_Y$  and  $E/H$  observed in this study may be attributed to the higher strain rate used in the tensile testing.

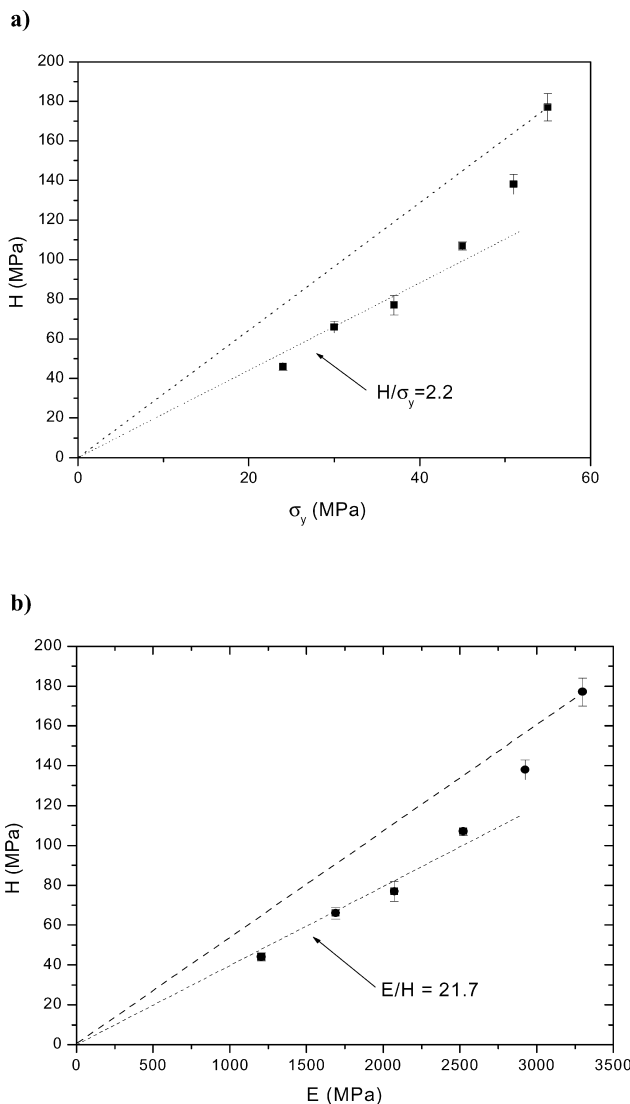


Fig. 7. Plot of microhardness of ST2/PS blends as a function of: (a) yield stress  $\sigma_Y$  and (b) Young's modulus  $E$ .

### 3.4. Analogy with semicrystalline polymers

It is convenient to recall that styrene/butadiene block copolymers are amorphous polymeric systems, i.e. there is no structural order at the molecular scale. However, the self-assembly of these systems leads to microphase separated structures, which resemble to a crystalline-like order at the mesoscopic scale (e.g. in Fig. 2). Hence, there is an analogy of the microphase-separated structures in the block copolymers with the semicrystalline polymers in which the stacks of crystalline lamellae are separated by amorphous layers [15].

The hardness equation for polymer crystalline lamellae is given by [28,29]

$$H_c = \frac{H^0}{1 + (bl/l_c)} \quad (2)$$

where  $H^0$  is the hardness of an infinitely thick crystal and  $b$  is a parameter related to the surface free energy of the crystals  $\sigma$  and to the energy required for plastic deformation of the crystals.

An analogous equation for the microhardness of the copolymer-PS blends could be written

$$H = \frac{H^{\text{PS}}}{1 + (K/D_{\text{PS}})} \quad (3)$$

Here  $K$  is now a constant similar to the parameter  $b$  in Eq. (2). By plotting  $H$  vs.  $1/D_{\text{PS}}$  should yield a straight line. A similar relation is found to be valid for several semicrystalline polymer systems [18,30–32]. In Fig. 8, the measured microhardness values for the lamellar samples (i.e. the blends with  $D_{\text{PS}} \leq 30$  nm) are plotted as a function of reciprocal thickness of the PS lamellae ( $1/D_{\text{PS}}$ ). The lamellae with infinite thickness are assumed to be pure polystyrene. Surprisingly, the data points nearly match to a straight line suggesting that the lamellar amorphous block copolymer systems may be regarded, in this respect, as an analogue to the semicrystalline systems. According to Eq. (3) the parameter  $K$  could be related to the energy of plastic deformation of the PS lamellae. Therefore, the increasing tendency of the  $H$  values with added hPS content (Figs. 4 and 6) may be regarded as the result of increasing thickness of the PS layers (organized in ‘crystalline-like’ manner).

#### 4. Conclusions

- The microhardness behaviour of the binary star block copolymer/polystyrene blends deviates significantly from the additivity law.
- The microhardness depends strongly on the phase morphology. A higher hardness rate increase (and hence an increase in the local yield stress) is observed when the morphology changes from stacks of alternating lamellae to that of the polystyrene matrix.

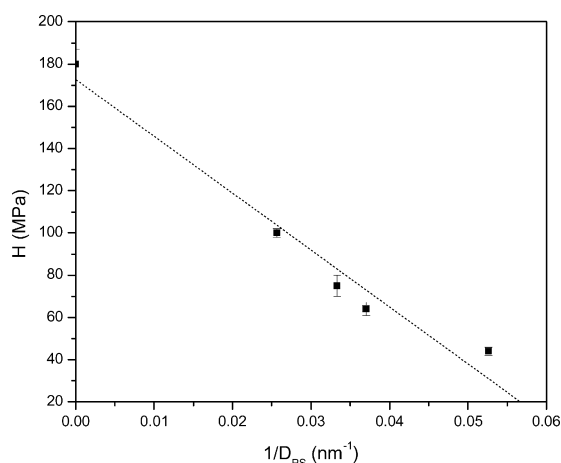


Fig. 8. Plot of  $H$  vs.  $1/D_{\text{PS}}$  for the lamellar block copolymer/hPS blends (samples with  $D_{\text{PS}} \leq 30$  nm).

- In case of lamellar morphologies ( $\Phi_{\text{hPS}} = 0\text{--}60$  wt%), a correlation between the  $H$  values and the thickness of the PS lamellae has been found.
- For the lamellar morphologies, the hardness turns out to correlate to the yield stress and Young's modulus values according to the relations  $H/\sigma_Y = 2.2$  and  $E/H \sim 22$ , respectively.

#### Acknowledgements

The authors gratefully acknowledge the financial support from the Deutscher Akademischer Austauschdienst (DAAD) and the Alexander von Humboldt-Stiftung. This project is partly funded by the Deutsche Forschungsgemeinschaft and the Kultusministerium des Landes Sachsen-Anhalt. We gratefully acknowledge MCYT, Spain (grants BFM 2000-1474 and HA 2000-0070) for the generous support of this work. One of us (G.H.M.) thanks the Dirección General de Universidades, Ministerio de Educación, Spain, for the award of the Humboldt-Mutis Prize. We thank the BASF Aktiengesellschaft for the supply of the samples and Ms. S. Goerlitz for the TEM investigations.

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