MICROMECHANICAL STUDIES OF STYRENE/BUTADIENE BLOCK COPOLYMER BLENDS

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ABSTRACT

The microhardness behavior of binary blends comprising a star block and a triblock copolymer, both consisting of polystyrene (PB) and polybutadiene (PB), was investigated over a wide composition range. In particular, a correlation between the microhardness H , the yield stress σ_y and the Young's modulus E was examined. The hardness was found to correlate with the mechanical parameters obtained by uniaxial tensile testing as follows: $H/\sigma_y \sim 2$ and $E/H \sim 30$. In agreement with the studies performed in case of the pure microphase separated block copolymers, the microhardness behavior was found to be strongly dependent on the morphology of the blends. The glass transition temperature of the hard phase (T_{g-PS}) is shown to remain nearly constant in the blends with lower LN4 content. The glass transition temperature of the soft phase (T_{g-PB}), which varies with blend composition, is not related to the microhardness variation in the blends.

Keywords: Styrene/butadiene block copolymer blends, amorphous polymers, morphology, micromechanical properties, microhardness, electron microscopy

INTRODUCTION

For many practical applications of polymers, toughness is a relevant property. In brittle polymers, toughness can be enhanced by incorporation of a small amount of rubber, which forms the dispersed phase embedded into the brittle polymer matrix [1,2]. Due to the intrinsic incompatibility between several polymer pairs, there is a possibility of deterioration of the mechanical properties resulting from poor adhesion. One can overcome such a problem by the introduction of phase compatibilizers or graft polymerization. However, the resulting polymer may be opaque due to the relatively large size of dispersed particles.

For the application of plastics as packaging films for fresh meats and vegetables, making toys and cups for beverages, a combination of, both, toughness and transparency is desirable. Hence, classical impact modified thermoplastics, which are opaque due to large particles' size, do not fulfill some of the demands of the polymer market. Blending of the microphase separated block copolymers, one being a thermoplastic and the other one an elastomer, may open a new way of toughness modification based on nanostructured heterogeneous polymers [3].

Lamellar styrene/butadiene block copolymers are one example of heterophase polymers that show a tough behavior under slow tensile loading conditions [4]. These polymers are found, however, to be brittle under impact loading. One prefers to have polymers that behave as tough materials under tensile as well as impact loading conditions. As shown in a previous study, binary block copolymer blends may provide a new route to develop tough nanostructured polymeric materials [3].

Polymer blends have been the subject of preceding microhardness studies [5,6]. It is known that the microhardness of the miscible polymer blends is correlated to the glass transition temperature of the mixture. In semicrystalline polymers with rubber phase inclusion, the hardness is influenced by the degree of crystallinity and crystal thickness. In general, the microhardness of incompatible polymer blends may be tuned by changing the

composition. So far, a systematic study of structure-microhardness correlation in the nanostructured block copolymers and in particular their blends, is not available.

In a preceding study [7], we explored the influence of molecular architecture on the microhardness behavior of styrene/butadiene block copolymers. It was found that morphology of the block copolymers is the most important factor with respect to the microhardness behavior. The aim of the present study is to report on the microhardness-morphology correlation in binary block copolymer blends. In particular, the correlation between the microhardness H , the yield stress σ_y and the Young's modulus E will be discussed. As far as we know, this is the first study concerning the structure-microhardness correlations in styrene/butadiene block copolymer blends.

EXPERIMENTAL

Materials

The architecture of the block copolymer, both based on styrene and butadiene, used to prepare the binary blends studied in the present investigation is schematically illustrated in fig. 1. The samples were kindly supplied by the BASF, Ludwigshafen. The total styrene volume content values for the linear (LN4-S65) and for the star block copolymer (ST2-S74) are 0.65 and 0.74, respectively (table 1). The linear block copolymer comprises styrene-co-butadiene random (PS/PB) copolymer as the soft phase. Styrene as a hard outer block is in 32-vol % while the middle statistical block contains about 50% styrene, the total content being 65%. The star block copolymer has four asymmetric arms in average. A pure polybutadiene block having a tapered composition profile to the center styrene block forms the soft rubbery phase in the star block copolymer.

Details on the morphology, phase behavior and macroscopic mechanical properties can be found in other preceding publications [8,9]. The synthesis of these block copolymers has been discussed by Knoll and Nießner [10]. After mixing the materials in an extruder, the

tensile bars were prepared by injection molding (mass temperature 250°C and mold temperature 45°C). The blends contain 20, 40, 60 and 80 wt.-% of LN4-S65.

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 according to ISO 527. At least 10 samples were tested in each case. The Young's modulus (E) and yield stress (σ_y) were derived from the evaluation of the initial slope and from the first maximum of the corresponding stress-strain curves.

Dynamic mechanical analysis (DMA) was carried out using the DMTA Mark 3E (Rheometric Scientific) in the torsion and temperature-sweep mode in order to characterize the glass transition temperature of the blends. The measurements were performed at a frequency of 1 Hz within a temperature range from -120°C to 120°C and at a heating rate of 1°C/min. Test specimens of the dimension of 30 mm×10 mm×2 mm were prepared from compression molded samples.

Transmission electron microscopy (200 kV TEM, Jeol) was used to examine the morphology of the blends. Ultrathin sections of the samples (ca. 50 nm thin) were ultramicrotomed from a bulk specimen. Polybutadiene phase was selectively stained with osmium tetroxide (OsO_4) vapor.

Microindentation hardness experiments were performed using a Leitz microhardness tester in combination with a square-based diamond indenter. To minimize the creep of the sample under the indenter, an indentation time of 6 seconds was used. The microhardness technique is based on the measurement of the residual impression made by a sharp indenter upon application of a given load. The microhardness, H , is defined as [5]:

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

where P is the applied load in N, d the diagonal of the impression in m, and k a geometric factor equal to 1.854. The H values were calculated from an average of at least 10 indentations.

RESULTS AND DISCUSSION

Phase Behavior and Morphology

TEM images in fig 2 illustrate the representative phase morphology of the binary blends including the pure block copolymers. All the samples are microphase separated and consist of glassy (light) and rubbery (dark) components. The pure star block copolymer ST2-S74 possesses a lamellar morphology with alternating layers of polystyrene (PS) and polybutadiene (PB). The morphology shows a well ordered arrangement of the nanostructure with a lamellar periodicity of about 40 nm (fig 2 top, left). On the other hand, the linear block copolymer LN4-S65 reveals dispersed PS domains in the matrix of the middle block consisting of styrene-co-butadiene (PS/PB) random copolymer (see fig 2 bottom, right).

An addition of 20 wt.-% LN4 leads to a transition from the well ordered lamellar arrangement to a disordered morphology, which seems to comprise the hard PS domains in a matrix of dark rubbery phase. This is an indication of a transition in mechanical and micromechanical behavior. With increasing LN4 content, the nature of the microphase separated morphology remains almost unchanged with PS domains dispersed in a rubber-like matrix. Similar behavior was observed in solution cast samples as well [11].

Fig. 3 shows the nearly linear increase of the glass transition temperature of the soft phase (T_{g-PB}) with increasing LN4 content, (see table 2). In contrast, the glass transition temperature (T_g) of the hard phase in the blends with lower LN4 content does not show any significant change. However, the lower glass transition temperatures of the polystyrene (PS) phase in pure LN4 and the blends with higher LN4 content suggests that the hard phase in these compositions does not constitute polystyrene blocks alone.

If one measures the glass transition temperature of the soft phase in both single components (ST2 and LN4), one may derive the T_g value for the butadiene phase (T_{g-PB}) in the mixtures using the Fox's equation (see table 2):

$$\frac{1}{T_{g-PB}} = \frac{w_{ST2}}{T_{g-PB_ST2}} + \frac{w_{LN4}}{T_{g-PB_LN4}} \quad (2)$$

The T_{g-PB} values calculated from Fox's equation are in good agreement with those determined experimentally by the DMA. This means that the soft phase in the blends is formed by combination of the soft phases of both components. The measured and the calculated T_{g-PB} data are plotted in fig 3 as a function of composition for comparison.

In amorphous polymers, the microhardness behavior was found to be linearly correlated with the glass transition temperature T_g [5,6,12-14]. The T_g value of the soft phase in the present case is always well below the test temperature (i.e., the room temperature, 23°C); i.e. the soft phase may be regarded as being at the liquid-like state. Therefore, it does not affect the measured H values. Therefore, there is no correlation between the soft phase glass transition temperature and the microhardness of the polymer blends discussed in the present study (see table 2).

Structure-Microhardness Correlation

The microhardness values (H) of the pure block copolymers and the studied blends are collected in table 2. In a preceding study [7], we concluded that the microhardness behavior of the microphase separated block copolymers cannot be predicted by their relative composition. The H values measured for the block copolymers with modified architectures were significantly smaller than the values expected from the additivity law.

Fig 4a shows the H values of the binary block copolymer blends as a function of composition (Φ_{LN4}). Since LN4 is a rubber-phase-rich block copolymer, its addition to the lamellar block copolymer ST2 causes a decrease in the microhardness values.

The steep decrease in the microhardness at $\Phi_{\text{LN4}} = 20$ wt.-% correlates well with a transition of the microphase separated morphology from well ordered lamellae to the disordered PS domains dispersed in the rubbery matrix (fig 2). This is in support of the concept that the microhardness behavior of the microphase-separated systems is mainly dictated by the morphology [7]. The steep variation for the H value at $\Phi_{\text{LN4}} = 20$ wt.-% additionally suggests that the effective volume fraction of the hard phase in the blends drastically decreases for this composition.

With increasing amount of LN4, the number of butadiene-rich molecules increases facilitating the mixing of the butadiene-rich stars from the star block copolymer ST2. Such a kind of phase mixing, which is caused by the molecular reorganization, could decrease the effective volume fraction of the PS as hard phase thereby leading to a decrease of the microhardness.

The volume fraction of polybutadiene of the starting blend components ST2 and LN4 is 26% and 35%, respectively (see table 1). If we represent the obtained H-values in the light of the additivity law of the single components, a straight line (dashed line in Fig 4b) with two limiting values for the corresponding homopolymers, $H_{\text{PS}} = 177$ MPa and $H_{\text{PB}} = 0$, is obtained. The experimental hardness of the blends show, however, much lower H-values than those predicted from the additivity law. This finding is similar to the results obtained for microphase separated styrene/butadiene block copolymers [7]. The linear variation of the experimental H values obtained shows a very steep slope. Hence, it should be stressed that the volume fraction of styrene and butadiene phases in the block copolymer blends used in this study does not reflect the effective hard/soft phase volume ratio owing to the modified copolymer architecture and microphase separated morphologies.

Correlation of Microhardness with Yield Stress and Young's Modulus

Fig 5a shows the plot of H as a function of the tensile yield stress σ_y for the ST2/LN4 blends. The data points may be fitted to a straight line which yields a slope of approximately 1.9, a value which is significantly lower than that predicted by Tabor's relation ($H/\sigma_y \sim 3$, [15]) for a perfectly plastic material. The observed deviation from the theoretical prediction might be due to the larger deformation rate used during tensile testing (50 mm/min) in contrast to that used in microhardness testing. In previous studies we showed that Tabor's relation applies for yield stress experiments in which the deformation rate is similar to the indentation rate (2mm/min) [16]. A good agreement between the experimental H/σ_y data and Tabor's equation was obtained in molded and extended chain PE samples on performing the tensile testing at a cross head speed of 0.5 mm/min [17].

Fig 5b illustrates the H vs. E values for the investigated block copolymer blends. In agreement with the results observed in other semi-crystalline [17] and amorphous materials [5], the microhardness values of the ST2/LN4 blends show a general tendency to increase with Young's modulus as derived from tensile testing. The data points approximately fit into a straight line passing through the origin yielding a slope of $E/H = 30$. This linearity is similar to the experimental results for PE [17] and Struik's prediction for other polymers [18], however, the experimental value of $E/H = 30$ measured in the binary block copolymer blends is significantly larger than that obtained by Struik [18] and Flores et al. [17].

These results demonstrate that the deviations in the microhardness behavior and the relations E/H and H/σ_y for the block copolymer systems are larger than those observed in other polymeric systems, such as homopolymers and polymer blends. This difference could arise from the length scale effect of the block copolymers, where the heterogeneity is in the range of the gyration radius of the copolymer molecules. In these length scales, different micromechanical mechanisms are observed which allow very intense plastic yielding

processes that are not observed in ordinary polymer blends (the so called ‘thin layer yielding mechanism’ [4] and ‘chevron morphology’ [9]).

CONCLUSIONS

- The microhardness behavior of the binary block copolymer blends investigated is mainly determined by the nature of the microphase-separated morphology. The overall phase composition plays only a secondary role. The experimental H values measured were always found much smaller than those expected from the additivity law over the whole composition range.
- The hardness was found to correlate to the yield stress of the binary blends following the relationship $H/\sigma_y \sim 2$.
- Due to the depression of the H values with respect to Tabor’s relation, a deviation of the E/H ratio from Struik’s prediction is obtained as, $E/H \sim 30$.

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Table 1

Characteristics of the blend components.

Blend component	* M_n (g/mol)	* M_w/M_n	§ Φ_{styrene}	Morphology (TEM)
ST2-S74	109,200	1.69	0.74	Lamellar
LN4-S65	116,000	1.20	0.65	PS domains in random PS/PB copolymer matrix

* Number average (M_n) and weight average (M_w) molecular weights determined by the gel permeation chromatography (GPC)

§ Total styrene volume content determined by Wijs double bond titration

Table 2

Microhardness H, glass transition temperature of PS ($T_{g\text{-PS}}$) and PB ($T_{g\text{-PB}}$) phases, microhardness, yield stress σ_Y and Young's modulus E of the investigated blends.

LN4 content (Wt.-%)	* $T_{g\text{-PS}}$ (°C)	* $T_{g\text{-PB}}$ (°C)	§ $T_{g\text{-PB_calc}}$ (°C)	H (MPa)	σ_Y (MPa)	E (MPa)	E/ σ_Y	+ Φ_{PB} (%)
0	104	-74	-	44	24	1205	50	26.0
20	104	-68	-64	28	16	1000	62	27.8
40	103	-53	-54	24	10	750	75	29.6
60	100	-31	-43	16	7	450	64	31.4
80	87	-25	-30	12	4.5	300	67	33.2
100	70	-15	-	8	3	80	27	35.0

* $T_{g\text{-PS}}$ and $T_{g\text{-PB}}$ measured by the DMA

§ $T_{g\text{-PB}}$ calculated using the Fox's equation (Eq. 2)

+ total polybutadiene content assuming volume fraction ~ weight fraction

LEGEND TO FIGURES

Figure 1. Scheme showing the architecture and morphology of the block copolymers used.

The white and dark colors correspond to the hard and soft phase, respectively

Figure 2. TEM micrographs showing the microphase separated morphology of the binary block copolymer blends in injection moulds; injection direction vertical, OsO₄ staining. (Numbers give the percentage of the LN4 component in the block copolymer blends)

Figure 3. Glass transition temperature of the butadiene phase (T_{g-PB}) as a function of composition in ST2/LN4 blends.

Figure 4. Microhardness vs. composition in ST2/LN4 system as a function of: a) LN4 content and b) total PB content (assuming volume fraction $\sim$ weight content; dashed line represents the additivity law)

Figure 5. Microhardness H plotted against the parameters derived by uniaxial tensile testing in ST2/LN4 blends: a) yield stress σ_Y and b) modulus of elasticity E

Figure 1

Figure 2

Figure 3

a)

b)

Figure 4

a)

b)

Figure 5