Effect of compatibilizer on the interphase boundary of polymer blends of PS and natural rubber compatibilized with SBS

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Abstract: The microhardness (H) technique has been used to quantitatively characterize the quality of the interphase boundary of blends of atactic polystyrene (PS) with natural rubber (NR) and their compatibilizer styrene-butadiene-styrene (SBS) block copolymer. Qualitative conclusions for the same purpose from scanning electron microscopy (SEM) observations on the surface indentation are drawn. Cast films of neat PS and the blends PS/NR, PS/SBS and PS/NR/SBS were prepared from a common solvent (toluene). While the neat PS shows a constant H value of 175 MPa, the PS/SBS blend exhibits a gradual decrease starting from $H = 130 - 140$ MPa at about a distance of 100 μm from the phase boundary up to the final H value of 25 MPa. For the PS/NR blend this hardness decrease starts at about 50 μm reaching the same final value. Owing to the elastic recovery no indentations on the NR or SBS particles surface can be detected as confirmed also by the SEM observations. The compatibilized blend PS/NR/SBS is characterized by the thinnest phase boundary (of about 25 μm) and a final H value of 75 MPa which demonstrates that the compatibilizer SBS is distributed just on the phase boundary between PS and NR. Results confirm previous findings in incompatible blends of poly(methyl methacrylate)/NR, highlighting that microindentation is a sensitive tool for studying the breadth and quality of the interphase boundary in non- or compatibilized polymer blends and other non-homogeneous materials. This technique allows, in addition, the localization of the compatibilizer distribution in the polymer blends.

Key words: phase boundary, polymer blends, compatibilizer, microhardness, SEM

Introduction

Polymer blends attracted the attention of academia and industry some decades ago as an alternative of the new polymers synthesis for satisfying the steady increasing demands of polymer materials with new exploitation properties profile [1]. Similarly to the copolymers, polymer blends offer the possibility to combine in one material the properties of the individual components. However in contrast to copolymers where the chemically different monomer units are linked by chemical bonds, blending and particularly the achieving and preservation of a desired final degree of dispersion creates serious problems. This is valid for polymer partners that are not thermodynamically miscible. In order to enhance the dispergation process, and mostly to stabilize the reached degree of dispersion, which in turn assures the constancy of the desired blend properties, a third component (compatibilizer) is used [2]. This third blend component is expected to be distributed on the phase boundary between the two components. The compatibilizer, usually in an amount of few percents, not only enhances the blending and stabilizes the blend but also contributes to the improvement of the adhesion between the blend components, as the coupling agent in the case of glass fibre reinforced composites does, and in this way improves significantly the mechanical properties of the blend material. This last task of the compatibilizer can be fulfilled only if it is actually distributed over the surface boundary. For this reason, it is important to find appropriate techniques to introduce the compatibilizer, as well, as methods for localization of its distribution. For blends of condensation polymers, in which the compatibilizer represents a copolymer of blended components and usually is created during melt blending, the distribution is perfect because the copolymer is synthesized just on the phase boundary where the two components are in contact and chemically reacting. For the rest of the polymers this is not the case and for this reason appropriate techniques for analysing the compatibilizer distribution have to be used.

The microhardness test has become a common technique due to its simplicity and appears as a promising tool for the micromechanical and microstructural investigation of polymer blends and composites [3-7]. Specially, we have demonstrated that the microindentation hardness (H) is a very sensitive tool for testing the phase boundary doubly injection moulded glassy polymers [8]. For this

purpose microindentation scanning across the contact surface has to be performed. In case of glassy polystyrene (PS) and polycarbonate (PC), depending on the temperature of the melt fronts within the mould, a well-defined weld line can be identified [8]. This weld line is distinguished by a drop in H when scanning across to it. The hardness drop is followed by an immediate increase, thus defining a weld line width of 0.2 – 0.4 mm.

Microhardness indentation measurements have been recently used in the blend of glassy poly(methyl methacrylate) (PMMA) and natural rubber (NR) prepared by means of a common solvent [9]. These measurements revealed that when approaching the phase boundary between the two immiscible partners the microhardness value drastically drops (by 30%) in a narrow phase boundary (around 0.75 mm thick). This strong decrease in the H value very close to the rubber particle surface indicates the existence of a narrower or wider phase boundary between the two components.

From the foregoing it looks interesting to try to characterize by means of micro indentation hardness and scanning electron microscope (SEM) the change in the phase boundary between two immiscible polymers in presence and in absence of a compatibilizer. For this purpose solution blended PS and NR as well as styrene-butadiene-styrene (SBS) block copolymer as compatibilizer were used. The aim of the present study is to characterize the cast films of the respective solutions by means of SEM and microhardness measurements.

In this work, the results of the PS/NR blend compatibilized with SBS will be reported. In a following study, we will discuss the hardness results of the PMMA/NR blend compatibilized with epoxydized natural rubber (E-NR).

Experimental part

The blend cast films were prepared using common solvent (toluene). Commercial grade of atactic polystyrene (PS), of natural rubber (NR), and of styrene-butadiene-styrene (SBS) block copolymer (as compatibilizer) were separately dissolved in

boiling toluene, filtered and appropriately mixed under continuous stirring at elevated temperatures for removing of the major part of the solvent within 40-60 min. The complete drying at room temperature (constant weight of the film) takes place within a couple of days. The dried films were of the following composition (by wt %): PS/NR = 95/5, PS/SBS = 95/5 and PS/NR/SBS = 95/4.5/0.5.

The microhardness of the film surface was measured using a microindentation tester with a Vickers square-based diamond indenter. The hardness value (in MPa) was derived from the residual projected diagonal impression, using $H = kP/d^2$, where P is the applied force in N, k is a geometrical constant equal to 1,854, and d is the length of the projected indentation diagonal in μm . A load of $P = 0,15$ N and a loading cycle of 6 s were used. In order to obtain a larger number of reliable measurements close to the interphase boundary the measurements were performed not on a straight line across the interphase boundary (the radius of the spherical particles) but on a curved trajectory gradually approaching the dispersed sphere. Since the dimensions of the indentation diagonals are comparable to the thickness of the interphase boundary, the lengths of the diagonals at the interphase are slightly different. The measured H was derived from the average value of the diagonals.

A JEOL JSM 5400 scanning electron microscope with an accelerating voltage of 20 kV was used for studying the surface samples. The samples were coated with a thin gold layer prior to SEM analysis.

Results

SEM observations on the PS/SBS film surface (Fig. 1a) show that SBS is dispersed in the PS matrix in the form of nearly mono-dispersed particles (spheres of about 20 - 40 μm diameter) that are too small to study the interface boundary between the two components (the diagonals of indentation are of about 40 μm). For this reason much larger, rarely observed SBS spheres (diameters ~ 250 μm , Fig. 1a) were selected for this purpose. Only those SBS spheres that "emerged" on the surface of the PS matrix could be used for this purpose, i.e. those particles that are not in the bulk of the film or covered by the thin PS layer. While Fig. 1a illustrates such a SBS spherical particle surrounded by many indentations, on the lower half of Fig. 1b one can

appreciate a section of such a large SBS sphere being in contact with the dominating PS matrix occupying the upper half of the SEM micrograph (Fig. 1b).

The two polymers used can be easily identified because of the completely different nature of their surfaces. While the surface of the glassy PS is quite smooth, the SBS shows a “wavy” surface that is typical for elastomers. Furthermore, for the correct interpretation of Fig. 1 it is important to mention that glassy PS is a hard material that shows well shaped indentations (Fig. 1), in contrast to SBS which, owing to its very low glass transition temperature ($T_g = -110^\circ\text{C}$ [10]), and to the fact that its elastic deformation is practically reversible, does not show any indentations on its surface. (It should be noted that SBS as a block copolymer exhibits two glass transition temperatures [11].)

This very large difference in the microhardness behaviour of the two polymers allows one to make an estimate about the phase boundary extension between the two materials. A careful analysis of the SEM micrographs at higher magnifications (1000 x instead of 200 x as in Fig. 1) allows one to derive the following qualitative conclusions.

Quantitative information about the broadening and “depth” of the phase boundary can be gained after calculation of the indentations from the H data. The variation of H as a function of the distance z from the interphase boundary is plotted in Fig. 2 for the neat PS, blends PS/NR, PS/SBS and PS/NR/SBS.

One sees that the neat PS shows the highest and more constant H values (around 175 MPa). The H values obtained for the neat PS are in accordance with previously reported ones [12].

The blend of PS with the compatibilizer SBS (Fig. 2b) shows a completely different behaviour. Far away from the interphase particle boundary the microhardness is rather constant (around 130–140 MPa) though showing a gradual decrease when approaching the phase boundary (ca. 100 μm from it) and reaching a final value of $H = 25$ MPa (Fig. 2b).

Quite similar is the trend for the binary blend PS/NR curve (Fig. 2c) reflecting again the observed variation of H and the distance from the interphase boundary. The only difference here is the fact that the H values far away from the phase boundary are slightly lower as compared to the previous ones (PS/SBS, Fig 2b). In addition the decrease of H is here much steeper (starting at distance of about 50 μm from the boundary instead of 100 μm as in Fig. 2b) and reaches the same final H value of about 25 MPa.

The behaviour of the last ternary blend PS/NR/SBS (Fig. 2d) is in contrast to the previous ones (Fig. 2b, c). First of all, the H values on the plateau of the curve are the smallest ones (around 100 MPa in comparison with 175 MPa for the neat PS, Fig. 2a, and around 130-140 MPa for the binary blends PS/SBS and PS/NR, Figs. 2b and 2c, respectively). Another striking observation for the compatibilized blend PS/NR/SBS is the fact that the H -decrease from the constant value of 100 MPa starts very near to the phase boundary between PS and NR (only 25 μm as compared to 50 and 100 μm in the cases for the binary blends). The second peculiarity of the PS/NR/SBS blend is the relatively high final H value of 75 MPa (Fig. 2d).

Discussion

What can be the reason for the observed differences in the behaviour of the binary and the ternary (compatibilized) blends, and more specifically in (i) the H values of the respective matrix (far away from the phase boundary), (ii) the distance from the latter where the H -decrease starts, and (iii) in the lowest final H values?

First of all it is convenient to note that the H value of the neat PS of 175 MPa is in agreement with the reported ones for glassy PS [10]. Taking into account that the second blend component represents a typical rubber (NR) or a rubber-like polymer (SBS), both of them with very low glass transition temperatures T_g (around -70°C for NR [10] and -110°C for the soft part of SBS [10]) one can expect a depression in H values for the blends far away from the phase boundary. This depression is the largest one for the compatibilized blend containing the two rubbery components (H = 100 MPa, Fig. 2d, against H = 175 MPa for the neat PS, Fig. 2a, and around 130 -

140 MPa for the binary blends, Fig. 2b, c). The slightly higher H values for the PS/SBS blend as compared with the PS/NR blend are due to the fact that in the block copolymer the styrene is dominant and thus, SBS has a higher T_g value and, consequently, a higher microhardness as compared with NR.

Most interesting is the behaviour of the blend of PS with the compatibilizer SBS (Fig. 2b). One can see that the transition zone between the two components is very smooth being the largest one among the blends studied (compare the horizontal arrows in Fig. 2). This observation is obviously related to the fact that SBS, being a compatibilizer for the blends of PS with natural and synthetic rubbers, contains PS (two of the three blocks are of styrene). The styrene blocks of SBS penetrate through the PS surface and, thus, ensure a smooth transition from one to the other blend partner across the interphase boundary.

Most important, with respect to the aim of this study, are the results from the non-compatibilized PS/NR blend and the compatibilized one (PS/NR/SBS) (Fig. 2c and Fig. 2d, respectively); the blend without compatibilizer showing a larger and “deeper” transition zone (Fig. 2d) (compare 25 with 50 μm and final H values of 25 with 75 MPa, respectively). A possible explanation for the observed differences could be that the SBS compatibilizer is distributed just on the phase boundary between PS and NR. In accordance with this assumption, parts of the SBS molecules admittedly penetrate in one of the components and other parts of the compatibilizer - in the second component. In this way SBS is completing its role to improve the adhesion between the two polymers through their compatibilization. When the “empty” space within the phase boundary in the blend PS/NR is filled up with other polymer (SBS) the microhardness in this transition zone has to be higher resulting in a higher final H value, as actually observed (compare Fig. 2c with Fig. 2d). This finding suggests that the compatibilizer is displaced just on the interphase boundary between PS and NR where it is expected. It should also be mentioned that the phase boundary ($z = 0$ in Fig. 2) is well defined by a few of H measurements on the surface of the dispersed particles (NR or SBS, Fig. 2b and c) showing a constant values of around 20-25 MPa. However, these latter values are somewhat questionable because of the elastic recovery of the material. The data cannot be regarded as a feature of the rubbery

material but they help us to define the phase boundary extension between PS and NR.

In conclusion, the microindentation hardness study performed reveals conspicuous differences at the interphase boundary of blends of PS and natural rubber compatibilized with SBS. In case of the PS/SBS and PS/NR blends the decrease of hardness through the phase boundary (50–100 μm thick) occurs very rapidly when approaching the soft phase, showing a drastic fall of the initial hardness value. On the other hand, the compatibilized PS/NR/SBS blend exhibits a thinner phase boundary of about 25 μm , showing a less drastic decrease of hardness. Thus, it is shown that the microhardness technique, particularly in combination with SEM, is a sensitive tool for the quantitative evaluation of the nature and quality of the interphase boundary in polymer blends.

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Figure Captions

Figure 1 SEM micrographs of PS/SBS blend surface: (a) – SBS particles emerging on the PS matrix, (b) – PS-SBS phase boundary

Figure 2 Variation of microhardness H as a function of the distance, z , from the phase boundary for the blends PS/NR, PS/SBS and PS/NR/SBS as well as for the neat PS.

a)

b)

Figure 1

Figure 2