Study of the phase boundary in PS/SBS blends as revealed by microindentation analysis

M. BOYANOVA*, F.J. BALTA CALLEJA**, S. FAKIROV*

Instituto de Estructura de la Materia, CSIC, Serrano 119, Madrid, Spain

Key words: Phase boundary, PS/SBS blend, microhardness, SEM

Paper submitted to *J. Mater. Sci. Lett.*

May, 2003

*Permanent address: *Laboratory on Polymers, University of Sofia, 1126 Sofia, Bulgaria*

**Author for correspondence: *imtb421@iem.cfmac.csic.es*

Polymer blends are an alternative to meet the steady increasing demands of polymer materials with new exploitation properties profile paralleling the synthesis of new polymers. The mechanical behaviour of these multicomponent materials, in relation to their formulation, composition and phase has been the subject of much work [1]. Similarly to polymer composites [2], the blend properties strongly depend on the adhesion at the interphase boundary between the blend components. In order to enhance the dispersion and to stabilize the degree of dispersion reached, as well as to improve the adhesion, a third component (compatibilizer) is commonly used [3]. The compatibilizer has to be distributed on the phase boundary between the two components. For this reason it is important to have appropriate techniques for introduction of the compatibilizer as well as methods for proving of its distribution on the phase boundary. Very recently [4-7] it was demonstrated that microindentation hardness can be successfully used for testing polymer phase boundaries.

The aim of this study is the attempt to demonstrate by means of microhardness indentation in combination with scanning electron microscopy (SEM) the changes in the phase boundary between a polymer (polystyrene) and its compatibilizer (styrene-butadiene-styrene).

Blend cast films were prepared using a common solvent (toluene). Commercial grade atactic polystyrene (PS) and styrene-butadiene-styrene (SBS) block copolymer (as compatibilizer) were separately dissolved in boiling toluene. Finally, they were filtered and appropriately mixed under continuous stirring at elevated temperature to remove part of the toluene in order to obtain a 5% solution of SBS in PS. Complete drying of the sample takes place within a couple of days at room temperature, as verified from the constant weight of the film.

The microindentations were made by means of a Vickers square-based diamond indenter. Further details about the microhardness technique used in polymer are given elsewhere [8].

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

The SEM observations on the film surface (Fig. 1a) show that SBS is regularly dispersed in the PS matrix in the form of nearly monodispersed (spheres diameter of about 20 - 40 μm) that are too small for studying the interface boundary between the two components (diagonals of indentation are of about 40 μm). For this reason much larger rarely observed spheres

(diameters ca. 250 μm , Fig. 1a) were selected for this purpose. Only those spheres that 'floated' 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 layer of PS. While Fig. 1a illustrates such a SBS spherical particle surrounded by many indentations, on the lower half of Fig. 1b one can only appreciate a section of such a large SBS sphere being in contact with the dominating PS matrix occupying the upper half of the electron-micrograph (Fig. 1b).

The two different polymers 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 the elastomers. Furthermore, for the correct interpretation of Fig. 1 it is important to mention that the glassy PS is a hard material that shows well shaped indentations (Fig. 1), in contrast to SBS which, owing to his very low glass transition temperature, and to the fact that its elastic deformation is practically reversible, does not show any indentations on its surface.

This very strong difference in the microhardness behaviour of the two polymers allows one to make an estimate about the phase boundary extension between the two polymers. While indentation A in Fig. 1b shows symmetric diagonals of the same length, the indentation B (Fig. 1b), which is much closer to the phase boundary and possibly touches it, is distinguished by asymmetric diagonals (shorter vertical diagonal as compared to the horizontal one). The last observation is very well expressed in the last indentation C (Fig. 1b) that covers the interface boundary. One can easily observe that only the horizontal diagonal shows symmetry with respect of the centre of the indentation. The vertical diagonal shows only the upper part arising from the PS matrix. The expected lower part of the diagonal from the SBS component, due to the complete elastic recovery of this polymer, is missing.

The most striking observation in the present case is the fact that no sharp edges of the two polymers on the contact region are observed. This contrasts with the finding on glassy poly(methyl methacrylate)/natural rubber (PMMA/NR) blend films [5] prepared in the same way as described above for PS/SBS blends. In Fig. 1b one can also see that the transition zone between the two polymers is rather smooth. 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 surface of PS and thus ensure a smooth transition from one to the other polymer material across the phase boundary.

In conclusion, it should be stressed that microhardness techniques, particularly in combination with other techniques as SEM in the present case, is a sensitive tool to accurately characterize the quality of the interphase boundary in non- or compatibilized polymer blends and other inhomogeneous materials. The next step of this study will be the quantitative evaluation of the microhardness changes close to- and across the phase boundary of the present and another polymer blends.

Acknowledgements

Grateful acknowledgement is due to the MCYT, Spain (Grant BFM2000-1474 for the generous support of this investigation. One of us (S.F.) deeply appreciates the financial support of NATO – Spain for the award of a fellowship making possible his stay at Instituto de Estructura de la Materia, CSIC, Madrid, where this study was carried out. S.F. and M.B. acknowledge also the hospitality of the same Institute.

References

1. D. R. PAUL and C. B. BUCKNALL, eds. "Polymer Blends," Vol. 1 and 2 (John Wiley & Sons, Inc. New York, 2000).
2. D. HULL, "An Introduction to Composite Materials" (Cambridge University Press, Cambridge, 1981) Chapter 5, p. 81.
3. R. D. DEANIN and M. A. MANION, in "Polymer Blends and Alloys," edited by G. O. Shonaike and G. P. Simon (Marcel Dekker, New York, 1999) Chapter 1, p. 1.
4. M.C. GARCIA GUTIERREZ, D.R. RUEDA, F.J. BALTA CALLEJA, I. KUEHNERT and G. MENNIG, *J. Mater. Sci. Lett.* **18**, (1999) 1237.
5. M. BOYANOVA, F.J. BALTA CALLEJA, S. FAKIROV, I. KUEHNERT and G. MENNIG, *Adv. Polymer Technol.* (submitted).
6. G. MENNIG, T. NGUYEN-CUNG, M. BOYANOVA, F.J. BALTA CALLEJA and S. FAKIROV, *J. Polym. Eng.* (submitted).
7. M. F. MINA, F. ANIA, F.J. BALTA CALLEJA and T. ASANO, *J. Appl. Polym. Sci.* (in press).
8. F.J. BALTA CALLEJA and S. FAKIROV, "Microhardness of Polymers" (Cambridge University Press, Cambridge, 2000) Chapter 2, p. 11.

Figure Caption

Figure 1 SEM micrographs of PS/SBS blend surface: (a) – overview, (b) – closer to PS-SBS phase boundary