Polymer Bulletin 32, 693–696 (1994)

Polymer Bulletin

The role of sample preparation on the study of the microstructure of rubber-reinforced polymers

V. M. Castaño[1,*], E. Oliva[1], A. del-Real[1], P. Mexia[1], S. Víquez[1], E. Rivera[1], and E. Martínez[2]

[1]Instituto de Fisica, U.N.A.M., Apartado Postal 20-364, 0100 Mexico, D.F., Mexico
[2]Industrias Negromex, S.A., Bosques de Ciruelos 180, Mexico, D.F., Mexico

Abstract

Transmission electron microscopy of thin sections of rubber-reinforced polystyrene commercial specimens was performed. The importance of an adequate sample preparation technique to obtain reliable microstructural information is demostrated through the observations and analysis of samples prepared by variuos methods. The relevance of carefully selecting preparation method is emphasized.

Introduction

Polymer blending has become a fashionable and very active area of research and development for engineering applications of high-tech polymer-based composites. Natural and synthetic elastomers are of special interest as modifying agents for many engineering plastics. High-Impact Polystyrenes (HIPS) are a good example of the adventageous use of dissimilar polymers and, the high degree of sophistication in designing microstructures [1-3].Generally speaking, HIPS are two-phase materials in which the rubber component is dispersed in the polystyrene matrix. The key parameters that control high-performance are the morphology and the particle size distribution of the rubber phase. Accordingly, many methods, including transmission electron microscopy (TEM) complemented with digital image processing[4], ultrasonic degradation combined with nuclear magnetic resonance[5] , etc., are routinely used by many manufacturers to monitor the evolution of the above parameters.

In this work, commercial HIPS with different morphologies were studied by TEM. As has been previously demonstrated [6-8], TEM could easily lead to erroneous results if not enough care in the corresponding preparation technique is taken. In the present case specimens were prepared by different methods and totally different morphologies were observed. A discussion on the relevance of this effect is included.

Experimental

Commercial HIPS specimens designed for automotive engineering applications were obtained from Negromex, S.A. All the samples were known to have a cellular structure, in wich polystyrene domains are enclosed by polybutadiene membranes wich, in turn, are dispersed in a polystyrene matrix. The samples were prepared for TEM observation by

*Corresponding author

ultramicrotomy in a RMC-MT-6000-XL machine, wich produces very thin and uniform cuts with diamond knives. Prior and after the microtomy, HIPS were subjected to either of three preparation procedures, as follows:

a) Without previous treatment, the thin cuts were exposed to a 2% OsO_4 solution for half an hour. b) Before cutting, HIPS pellets were frozen by immersion in liquid nitrogen for half an hour. After microtomy, the thin sections were then exposed to a 2% OsO_4solution for half an hour. c) HIPS pellets were immersed in a OsO_4 solution (2%) for 48 hours, then frozen in liquid nitrogen for half an hour and finally cut into thin sections.

In all cases, the cuts were deposited onto Cu, 100 mesh microscope grids and TEM observatios were carried out in a JEOL-100CX machine at 100 KeV, under bright field imaging conditions.

Results and discussion

Figure 1 shows a typical result of samples prepared by procedure (a). As can be observed, the cellular structure of these composites is observed as a highly deformed collection of elongated particles. It is interesting to notice, however, that the material is working as designed, because no matter the high degree of deformation introduced by the microtomy process, the domains preserve their topology without breaking of the membranes.

Figure 2 now shows the same samples prepared by procedure b. The microstructure is more clearly observed, nevertheless, some degree of deformation is still detected.

Figure 1.- TEM Micrograph of HIP
prepared with method a.

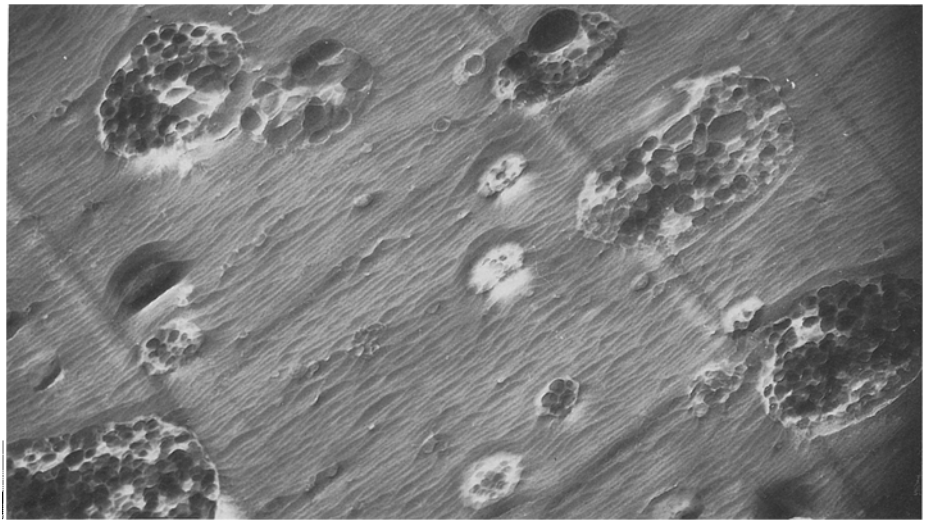

Figure 2.- TEM Micrograph of HIP
prepared with method b.

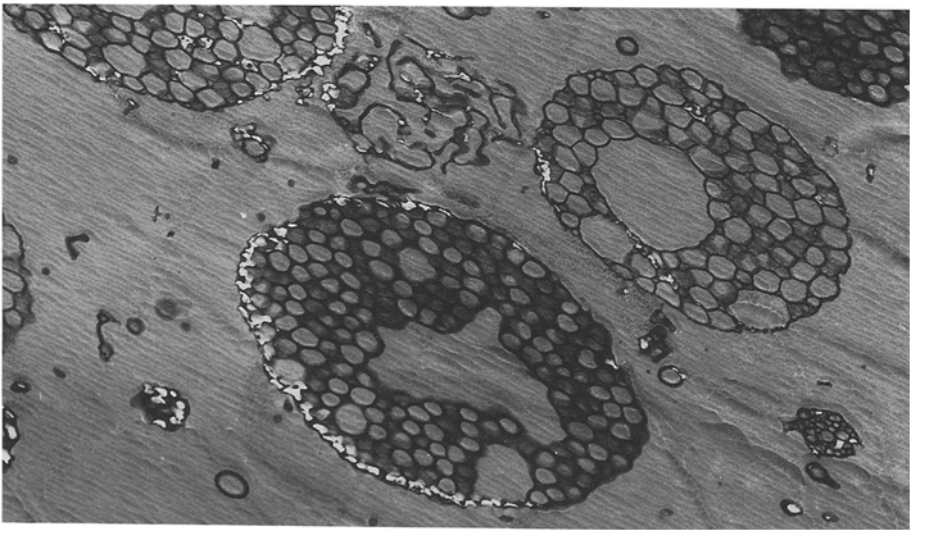

Figure 3.- TEM Micrograph of HIP
prepared with method c.

Thus, the microtomy of rubber samples well below their Tg apparently constitutes a good choice for more or less preserving the original microstructure. The nature of elastomers, however, in terms of their containing of double bonds, leads to introducing some method to account for this. Therefore, some ways have to be devised for ensuring that the morphology is preserved to yield reliable microstructural analysis. Accordingly, OsO_4 is known to oxidize unsaturations and provide, not only for better TEM contrast, but also a more stable structure.

Figure 3 shows the result of applying procedure c to the same HIPS specimens. The clasical "salami" morphology is clearly noticed (figure 3). Particle size distribution was obtained form the calibrated TEM micrographs and the results were in excellent agreement with those obtained by scattering techniques.

Conclusion

A number of lessons can be learned from the experiences described in this article: First, the key role of the particular preparation on the results of morphology by TEM. Second, the need of knowledge of both Tg and chemical structure of specimens to be analyzed to design a suitable technique. Third, the need of alternative methods, when possible, to compare and cross-check the TEM results. In the case of HIPS, where morphology is the key parameter to control, these recommendations are of extreme relevance.

Acknowledgements

The technical support of Mr. Roberto Hernández and Edilberto Hernández is gratefully acknowledged. The HIPS specimens were kindly provided by Mr. Tomás Acevedo (Industrias Negromex, S.A.)

References

1. R. J. Young, Strength and thoughness in comprehensive Polymer Science, Vol. 2 Pergamon Press, New York (1989).
2. R. J. Cerezo, Block and graft copolymers, Butterworths, London (1962).
3. M. J. Rivera-Gastelum, O. Robles-Vazquez, J. E. Purg, M. J. Garcia-Garduño, V. M. Castaño and V.M. Monroy, Mat. Lett. **17**, 84 (1993).
4. V. M. Castaño, R. Velázquez, R. Rodríguez and V. M. Monroy, Mat. Lett. **12**, 199 (1991).
5. R. Rodríguez, V. M. Monroy and V. M. Castaño, Mat. Lett. **12**, 448 (1992).
6. V. M. Castaño, A. González, J. Cardoso, O. Manero nad V. M. Monroy, Polym. Bull. **22**,617 (1989).
7. V. M. Castaño and F. A. Lagos, Mat. Lett. **8**, 137 (1989).
8. A. del-Real, R. Alexander, R. Hernández and V. M. Castaño, Mat. Lett. **15**, 118 (1992).

Accepted March 16, 1994 K