

Nanostructured Epoxy Network Modified with Polybutadiene: Synthesis and Characterization

B. G. Soares^{(1)*}, Veronica D. Lima⁽¹⁾, Karim Dahmouche⁽²⁾

(1) Instituto de Macromoléculas– Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco J, Ilha do Fundão, 21945-970, Rio de Janeiro, RJ, Brasil (bluma@ima.ufrj.br)

(2) Universidade Estadual da Zona Oeste (UEZO), Rua Manoel Caldeira de Alvarenga, 1203, Campo Grande, Rio de Janeiro, RJ, Brasil

* Corresponding author.

Abstract – Epoxy resin was modified with functionalized polybutadiene containing isocyanate groups and cured with two types of hardeners: aliphatic amine and hexahydrophthalic anhydride. The resulting thermoset materials were transparent even with 20% of rubber. The transmission electron microscopy, atomic force microscopy and small-angle X-ray analysis revealed that the rubber particles are dispersed in nanometric scale when the material was cured with amine. The addition of the functionalized rubber resulted in a significant improvement on the mechanical properties without scarfifying the glass transition temperature.

The present work aims to modify epoxy resin with functionalized polybutadiene (PBD) and analyze the nano-scale rubber domain size in this system by using small angle X-ray scattering (SAXS) combined with transmission electron microscopy and to investigate the effect of the different curing system, based on amine (with cure at room temperature) and anhydride (which requires higher curing temperature). Isocyanate-terminated PBD was prepared according to our previous work.¹ The modified epoxy networks were prepared by adding stoichiometric amount of triethylenetetramine (TETA) as the aliphatic amine or tetrahydrophthalic anhydride.

The Small Angle X-ray Scattering (SAXS) study was performed at room temperature using synchrotron the beam line of National Synchrotron Light Laboratory (LNLS), Campinas, Brazil.

The ER-b-PBD-b-ER systems were cured with TETA and anhydride, respectively. Before and after curing, all they were transparent, indicating no phase separation. In spite of the homogeneous system, the values of the glass transition temperature were similar to that found with the neat epoxy network, in the case of TETA-cured systems or a little lower in the case of anhydride-based systems. All these results suggest that both rubber-modified epoxy thermosets presented phase separated structure in nano-scale. The TEM analysis shown in Figure 1 revealed that the system cured with anhydride presented larger rubber particle size with epoxy sub-inclusion. Contrarily, the system cured with TETA presented rubber particles in nanometric scale, confirming the presence of phase separated structure in nano-scale.

The SAXS profiles for the thermosets containing different amount of ER-b-PBD-b-ER presented no well-defined scattering peaks in both cured systems, indicating no great phase-separated morphology. The TETA-cured system containing 10% of the triblock copolymer presented a Guinier plateau indicating a diluted system. The average distance between the neighboring domains increased as the amount of rubber decrease, as expected. In TETA cured system, it is also possible to observe a small scattering peak at around $q = 1 \text{ nm}^{-1}$, indicating microphase-separate structure and a formation of micelle structure, indicating that the epoxy system behaves as a selective solvent for the triblock copolymer.

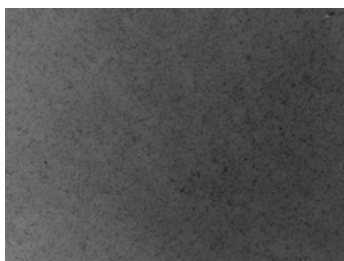


Fig 1. TEM micrograph of epoxy-PBD (10%) cured with TETA

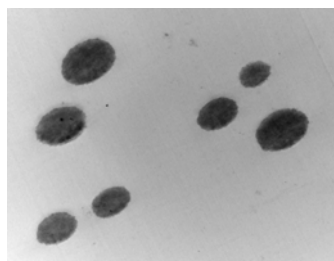


Fig 2. TEM micrograph of epoxy-PBD (10%) cured with anhydride

Aknowledgements

The authors thanks the financial support of CNPq, FAPERJ and PETROBRAS and the technical support of LNLS in Campinas- Brazil for the SAXS analyses.

References

[1] Barcia, F. L., Amaral, T. P., Soares, B. G., Polymer 2003, 44, 5811.