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Distribution of clay platelets in blend nanocomposites by molecular mapping in energy-filtered transmission electron microscopy (EFTEM)

E. M. Linares, M. M. Rippel and F. Galembeck*

Physical-Chemistry Department, Institute of Chemistry, University of Campinas – SP, Brazil
*fernagal@iqm.unicamp.br

Abstract – Molecular mapping by low-energy-loss in energy filtered transmission electron microscopy (EFTEM) imaging was applied to analyze the morphology of natural rubber/poly(styrene-butyl acrylate) latex blend and its clay nanocomposites. The micrographs shows domains of P(S-BA) dispersed in a natural rubber matrix while clay platelets are concentrated in the P(S-BA) phase. Thus, clay particles are partitioned in the two-polymer-phase system suggesting that other nanosized particles may show similar behavior.

Molecular mapping by low-energy-loss in energy filtered transmission electron microscopy (EFTEM) imaging is possible due to the differences in the low-energy-loss spectra of the sample constituents. Slight changes in the molecules produce intensity variations in molecular spectra that are in turn expressed in sets of low-energy-loss images. This technique allows the observation and distinction of domains in polymer blends without staining the sample, thus avoiding the introduction of artifacts and producing accurate molecular distribution maps. [1]

In this work, thin cuts of natural rubber (NR)/poly(styrene-butyl acrylate) P(S-BA), 7:3 (% wt) blend and its nanocomposite containing 5 phr (per hundred of resin) montmorillonite clay were analyzed by EFTEM in the low-energy-loss range, 25 to 90 eV range. Latex blend and clay nanocomposite were prepared by mixing the aqueous dispersions at room temperature and air-dried at 60℃ for 24-48 hours. Images were acquire d using a Carl Zeiss CEM-902 transmission electron microscope equipped with a Castaing-Henry-Ottensmeyer filter spectrometer. Ultrathin (ca. 60-nm) sections were cut at -150 ºC using a cryoultramicrotome.

Figure 1 (left) shows bright-field and low-loss EFTEM images taken from a cut of the NR/P(S-BA) blend. The bright-field image shows clearly one phase dispersed through a darker matrix. The spectra from the two polymers are dominated by peaks between 20 and 30 eV and are very similar, but they present some qualitative differences that are responsible for the excellent contrast in the low-energy-loss images and also allows the identification of the two polymer phases. P(S-BA) spectrum presents higher intensity below 40 eV than natural rubber spectrum. Above 40 eV, the spectral intensity for natural rubber decreases as the energy increases, slower than in the P(S-BA) spectrum. Thus, the NR domains are darker than P(S-BA) domains in the image at 25 eV, but they become brighter above 70 eV loss. The set of images from the nanocomposite (Fig. 1 at right) shows that clay is well dispersed in the blend, but it accumulates in some areas forming oriented array within P(S-BA) domains. The image in the crossing point, 40 eV, shows clearly the array of the clay inside the material thanks to the low contrast between the two polymer phases.

To conclude, molecular mapping based on EELS spectral differences in the low-energy-loss range provides unmatched information on complex polymer nanostructured systems.

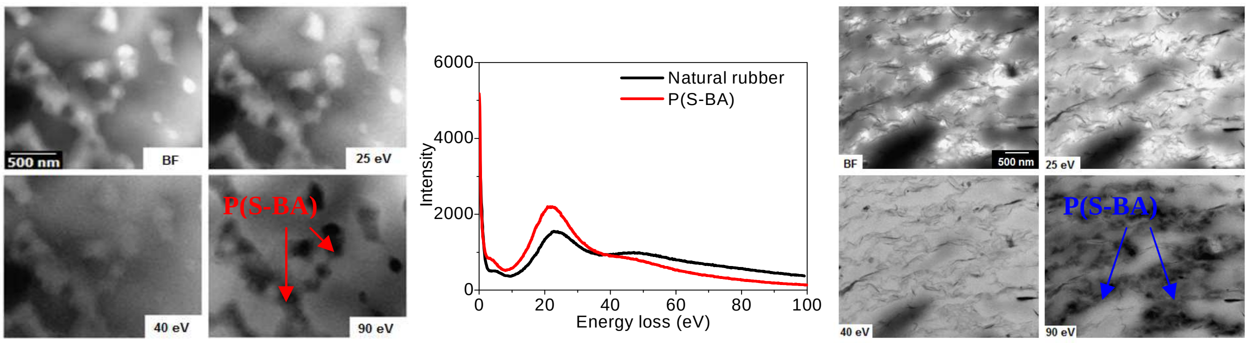

Figure 1: Bright-field and low-loss EFTEM images (25 to 90 eV) of thin cuts from (left) NR/P(S-BA) 7:3 (% wt) blend and (right) NR/P(S-BA) 7:3 (% wt) blend containing 5 phr of clay. EEL spectra of the NR and P(S-BA).

References

[1] Linares, E. M.; Leite, C. A. P.; Valadares, L. F.; Silva, C.; Rezende, C.; Galembeck, F. *Anal. Chem.* **2009**, *81*, 2317-2324.