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Locating the Modifier in a Polymer Blend by Electron Energy-Loss Spectroscopy

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Introduction. Despite the significant use and importance of interfacial modifiers in polymer blend systems,[1-5] very little is known concerning the efficacy of a modifier for a given interface during melt mixing. It is generally believed that only a fraction of the modifier finds its way to the interface, but how much is actually lost in the matrix or the dispersed phase? Due to the very minute amounts of the modifier added, very little data have been generated in the scientific literature concerning this critical question. To address such a problem, a microanalytical technique that has both very high elemental sensitivity and spatial resolution is essential. Combining scanning transmission electron microscopy (STEM), which readily provides spatial resolution in the 10 nm range, and electron energy-loss spectroscopy (EELS) could be a very interesting approach. EELS is inherently sensitive to the detection of low atomic number elements and can provide localized elemental analyses in polymer blends. Its detection limit for a number of light elements in the first two rows of the periodic table is in the 100 ppm order of magnitude for metals and semiconductors which can withstand massive electron doses (as compared to polymers).[6]

The aim of this paper is to report on the applicability of the EELS technique for the detection and localization of the modifier in a polymer blend system and to show that, in some cases, the modifier may not find its way to the interface.

Experimental Section. Materials. A reactive matrix consisting of Dylark 232 polystyrene (PS) containing approximately 8% by weight of maleic anhydride functions is a random copolymer supplied by Arco. The dispersed phase is an X2 bromobutyl (BB) rubber containing approximately 2% by weight of bromine and is supplied by Polysar. The interfacial modifier is a (dimethylamino)ethanol (DMAE) supplied by Canada Wide Scientific. As proposed by Willis et al. in their reaction mechanism, DMAE, under the right conditions, will react at the interface and form a copolymer (BB rubber −DMAE−PS).[7] Interestingly, the DMAE molecule contains a nitrogen atom which can be used as an elemental tracer during subsequent EELS analyses. Finally, 0.1% by weight of antioxidants Irganox 1076 and 565 supplied by Ciba-Geigy were added respectively to the PS matrix and the BB dispersed phase before melt mixing.

Mixing Procedure. These constituents were blended in a Brabender mixing chamber in three different ways according to a PS/BB/DMAE weight fraction (where the DMAE weight fraction is reported with respect to the dispersed phase): NC was a 80/20/0 noncompatibilized sample, C1 was a 80/20/10 one-step simultaneously mixed sample, and C2 was a 80/20/10 two-step mixed sample where the DMAE was added to the dispersed phase initially and then subsequently mixed with the matrix. The temperature of the chamber was set to 180 °C, the rotor blade speed was set to 100 rpm, and the mixing chamber was kept under a continuous flow of nitrogen.

Scanning Electron Microscopy (SEM) and Image Analysis. The blend samples were microtomed to a plane surface using a Leica Jung RM2065 equipped with a glass knife, while the sample surface was cooled by a continuous flow of liquid nitrogen. The dissolution of the dispersed BB phase was achieved by immersing the samples in hexane at room temperature for 30 min. SEM micrographs of the polymer samples were taken using a Jeol JSM-820 operated at 10 kV. A semiautomatic image analyzer described elsewhere[8] was used to determine the number-average and the volume-average diameters (D_n and D_v, respectively) of the BB inclusions. These data were corrected by the Saltikov method[9] to obtain the true diameter values.

Staining and Ultramicrotoming. In order to prepare the samples for STEM and EELS, the classical staining technique developed by Kato[10] was used to stain the BB dispersed phase by immersing small blocks of each sample in a 1% OsO_4 solution for 7 days. The ultramicrotoming of the polymer samples was conducted on a Leica Reichert FCS Ultracut apparatus equipped with a diamond knife. The speed of the cut was set to 1 mm/s, and the nominal thickness of the sample cuts was set to 70 nm.

EELS Studies. The Philips Model CM-30 microscope was operated at 300 keV with either a W or LaB_6 source. The probe size diameter varied from 11 to 16 nm, and spectra were obtained by using a Gatan Model 666 electron energy-loss spectrometer. Elemental composition profiles were obtained by mapping 128 spectra, 1 spectrum/pixel, along a linear profile on each sample. A collection semiangle of 15 mrad was selected, and the readout time for the 1024 channels varied from 7.5 to 10.0 s. Elemental signals were integrated over either a 30 or 50 eV energy window. In order to minimize the contamination or significant degradation of the specimen, the samples were cooled to −170 °C using a cryogenic sample holder.

Elemental Quantification. It is possible to identify elements from the presence of ionization edges in the high-energy-loss spectrum situated above the approximate value of 50 eV.[11] Major elements in the PS/BB/DMAE polymer system, i.e., in this case C, O, and N, were quantified by extrapolating the pre-edge background by means of an inverse power law and measuring the integrated intensities of the edges in a selected energy window above the extrapolated pre-edges[11] using the following expression:

$$\frac{N^x}{N^y} \approx \frac{\sigma^y{}_j(\beta,\Delta)\, I^x{}_k(\beta,\Delta)}{\sigma^x{}_k(\beta,\Delta)\, I^y{}_j(\beta,\Delta)} \tag{1}$$

where N is the absolute number of detected atoms, the superscripts x and y represent the elemental species, the subscripts j and k represent the type of edges (K, L, or M), σ is the atomic ionization cross section, β is the collection angle, Δ is the integration energy window, and I is the measured integrated intensity.

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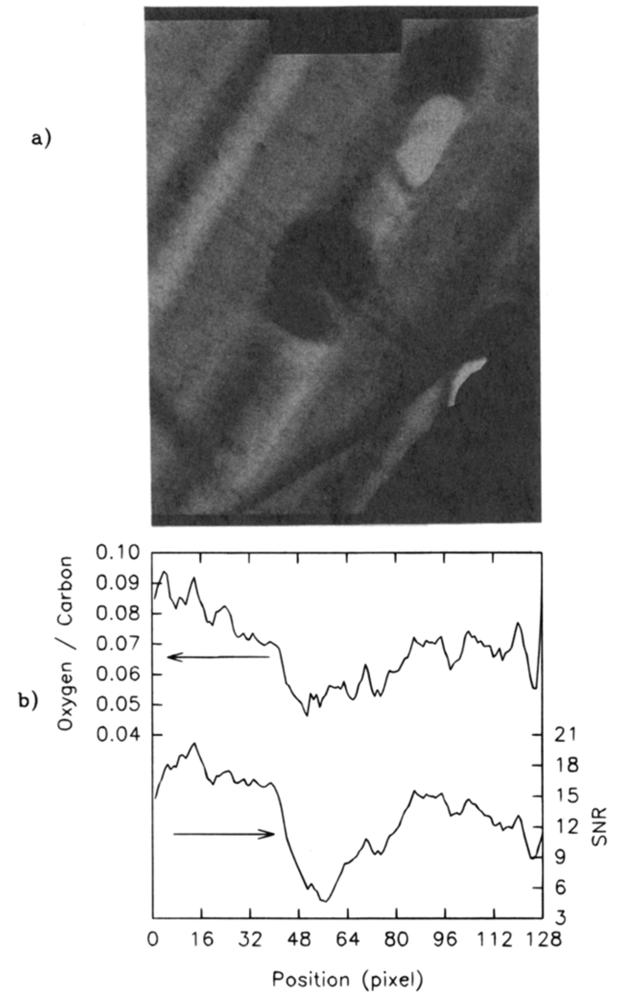

Figure 1. (a) Typical TEM micrograph (18300X) of sample NC after EELS analysis and (b) its corresponding EELS elemental and signal-to-noise ratio profiles. This sample contains no modifier.

Results and Discussion. EELS Elemental Profiles of the Binary Polymer Blend. A first objective was to obtain the EELS elemental profiles for the matrix and dispersed phase of the blend in the absence of tracing interfacial modifier. Profile spectra were obtained for the carbon and oxygen present in sample NC, and TEM micrographs of the sample were taken before and after the analyses. Figure 1a, which is a typical micrograph for all samples studied, shows traces of contamination from residual hydrocarbon chains in the TEM column represented by the two parallel dark lines on the sample surface indicating the precise electron beam course during the data acquisition. Figure 1b shows the corresponding elemental profile which exhibits the O/C atomic ratio versus position. In sample NC, a significant decrease in the O/C ratio which can be observed approximately between pixels 39 and 86 in Figure 1b corresponds to the relative position of the BB particle on the micrograph shown in Figure 1a. This significant variation in the O/C atomic ratio between the matrix and the dispersed phase undoubtedly comes from the combined absolute variations in O, which comes from the maleic anhydride groups present in the matrix and the OsO_4 present in the BB dispersed phase, and C in these locations. Similar distinct profiles distinguishing the matrix and dispersed phase were also obtained for C1 and C2. In some instances, significant variations in the O/C atomic ratio can be difficult to relate to precise positions in the profiles. In order to minimize this problem and as in Figure 1b, it is helpful to plot on the same graph the O/C atomic ratio along with the corresponding signal-to-noise ratio (SNR).

Table 1. Comparison of the Particle Diameters Obtained from the EELS Profiles and the TEM Micrographs

sample	diameter measd from the profile (nm)	diameter measd from the micrograph (nm)
NC	870	1090
C1	850	930
C2	490	500

Table 2. Image Analysis Results

sample	D_v (μm)	D_n (μm)	(D_v/D_n)
NC	6.7	2.0	3.4
C1	2.2	0.4	5.5
C2	10.0	2.7	3.7

By simply multiplying the constant step distance between the center of the pixels (approximately 15 nm for all experiments) by the number of pixels under the part of the plot showing a decrease in the O/C ratio, one can obtain a particle diameter. This value was compared to the one obtained from direct measurements of the particle diameter along the contamination traces on the TEM micrograph. Table 1 shows a comparison of the diameter values obtained from the profiles and TEM micrographs for all three samples. Discrepancies between the values obtained from the profiles and the ones from the micrographs are largely due to some physical drift of the specimen during the data acquisition and the calibration of the TEM.

Localization of the Modifier. It was desired for EELS analysis to have different samples which display significant variations in the modifier distribution within the blend. In order to achieve this, two different types of mixing procedures were used when preparing compatibilized polymer samples. The influence of the mixing procedure (one-step and two-step mixing) was shown to have a significant influence on the emulsification and subsequent morphology of the blends. In order to evaluate the morphology of the modified samples the SEM was used. As shown in Table 2, the two-step mixing method used for sample C2 was found to be a poor technique for emulsifying the blend compared to the one-step mixing method. In fact, the particle size of C2 was not reduced at all in contrast to C1 which showed a significant reduction. As shown in Table 2, the latter sample displayed a dispersed phase D_v and D_n which decreased by factors of 3 and 5, respectively. This significant dispersed phase size reduction with interfacial modification observed with C1 is well-known and has been studied extensively.[1,3,4] It is directly related to an increase of interfacial interactions caused by the presence of DMAE at this location. It is interesting to note that the C2 particles did not display particle size reduction. In fact, some increase in the particle size was even observed. It is clear from the morphology data that in the case of C2 the addition of the DMAE modifier did not result in the emulsification of this blend. Samples C1 and C2 therefore constitute blends for which the state of mixing of the DMAE molecule is very different. The next step is to confirm this by using the EELS technique.

The following part of this study consists of tracing the nitrogen atoms which are present only in the DMAE. As shown in Figure 2, nitrogen was physically detected in the minor phase of C2, unambiguously indicating the presence of the interfacial modifier at this location. On the other hand, no trace of nitrogen was found in either

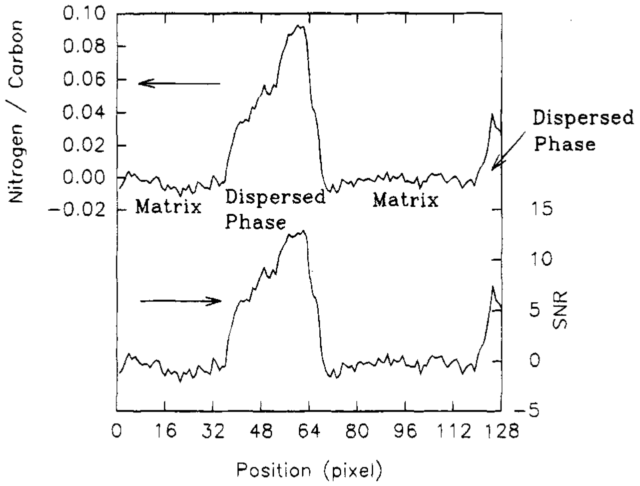

Figure 2. EELS spectra showing the N/C atomic ratio and its signal-to-noise ratio vs position for sample C2. This sample contains the modifier and was prepared by two-step mixing.

sample NC or C1. In this latter case, the nitrogen concentration is believed to be below the detection limit. All profiles shown throughout this paper are statistically significant since they exceed the signal-to-noise ratio value of 3.[12]

The EELS results have succeeded in showing that when DMAE is added to the dispersed phase via a two-step mixing process, it tends to remain in that phase. It appears therefore that DMAE has a very high affinity with BB rubber. This high affinity renders the migration of DMAE to the interface difficult and hence results in a poor emulsification of this system as compared to the one-step mixed system. This poor emulsification capability is confirmed by the morphological observations obtained by the classical SEM technique. A similar morphological demonstration of this phenomenon for other systems has been demonstrated in our laboratory.[13]

Future work should attempt to directly apply the promising EELS technique to the interfacial regions. For instance, combining TEM images with the EELS technique in optimal conditions and using smaller electron beam diameters (less than 10 nm) could potentially allow the evaluation of the thickness of the interfacial regions.

Concluding Remarks. The EELS technique was found to be a promising technique for the localization of an interfacial modifier in compatibilized polymer blends. EELS elemental profiles running across the PS matrix and the BB dispersed phase have been recorded. Relative positioning and dispersed phase particle size correspondence between TEM micrographs and EELS profiles were obtained. The samples studied were prepared by one- and two-step mixing processes to obtain a significant difference in the distribution of the interfacial modifier. For all samples studied by EELS, nitrogen was only physically detected in the minor phase of the sample prepared by the two-step mixing procedure, unambiguously indicating the presence of the interfacial modifier at this location. These results indicate that, in the single mixing step, the modifier was well distributed in the blend, whereas, in the two-step mixing process, the modifier to a large degree was trapped within the dispersed phase. Poor emulsification resulting from the two-step mixing process was confirmed by classical scanning electron microscopy followed by image analysis.

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