A Novel Method To Detect the Increase in the Rubber Concentration at the Interface between the Poly(vinyl chloride) (PVC) and Styrene−Butadiene Copolymer (SBR) Phases in Compatibilized PVC/SBR Blends

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Introduction. The adhesion between the phases in immiscible blends is one of the most important parameters for producing materials with practical significance.[1−5] The strength of the bond between the immiscible phases influences the mechanical properties of the blends such as tensile modulus, elongation-at-break, and impact strength. The bond strength at the interface can be enhanced by the migration of a compatibilizer to the interface during processing of the blends. For example, Schaffer et al.[1] have shown that the adhesion between a homopolymer and a blend can be enhanced by the segregation of one of the components in a blend to the interface between the two phases. Therefore, it is extremely important to obtain detailed information about the distribution of the compatibilizer in the blends.

In our previous work, we have developed a method to compatibilize poly(vinyl chloride) (PVC) and styrene−butadiene copolymer (SBR) by using acrylonitrile butadiene rubber (NBR) as a compatibilizer, which is miscible with PVC.[4−6] Being miscible with PVC, NBR is uniformly dispersed in the PVC phase; however, the butadiene group in NBR will be attracted to the SBR phase. Therefore, it is possible that the concentration of NBR at the interface between the PVC and SBR phases will be enhanced. In addition, we have found that the addition of a curing agent in the blends will further enhance the mechanical properties. We believe that this improvement is caused by the covulcanization of the SBR and NBR at the interface. The covulcanization at the interface will further enhance the rubber (SBR and/or NBR) concentration at the interface. The objective of this paper is to present a novel method for detecting the increased rubber concentration at the interface.

It is known that the radiation stability of polymers can be improved by blending with a radiation-insensitive polymer.[7−11] For example, the blending of miscible polymers—poly(methyl methacrylate) (PMMA) and styrene−acrylonitrile copolymer (SAN)—can reduce the rate of scission of PMMA upon γ irradiation in a vacuum.[7] When immiscible polymers are mixed, intimate contact between the two phases is required for the radiative-sensitive polymer to be protected by the radiation-insensitive one. PVC is known to be very sensitive to electron irradiation[12−15] due to the cleavage of the C−Cl bonds and the formation of polyene on the backbone of the macromolecules. It is possible that when PVC is mixed with NBR, the dehydrochlorination rate of PVC may be reduced because of the high reactivity of the double bonds in the butadiene segments. If SBR can be mixed well with PVC (providing intimate contact between these two phases), it is also reasonable to assume that the dehydrochlorination rate of PVC will be reduced because the styrene group in SBR is very effective in absorbing the energy from the energetic electrons. Our objective is to show that when PVC is mixed with rubber, the dehydrochlorination rate is reduced. This special feature is utilized in the TEM study to determine the increase in the rubber concentration at the interface between the PVC and SBR phases.

Experiment. Fifty parts (by weight) of PVC (K value = 67 (Fikenstcher: DIN 53726)) and fifty parts of SBR (Zeon, Nipol 1502) were blended in a Haake mixer. Ten parts of NBR (Zeon, Nipol 1053, acrylonitrile content 29.5 wt %) was used to replace SBR as a compatibilizer. The curing system contains sulfur as a primary cross-linking agent, mercaptobenzothiol (MBT) as an accelerator, and ZnO as an activator. The Banbury rotor was operated at 30 rpm, and the chamber wall temperature was controlled at 150 °C. The actual temperature was measured to be about 160 °C. The compounds were mixed for 22 min and hot-pressed for 10 min at 160 °C.

Thin sections (approximately 80 nm thick) of the samples were cut by a diamond knife with a cryo-ultramicrotome (Ultracut R, Leica) and collected on copper grids. The samples were coated with a 100 Å thick carbon layer to prevent charging during the TEM study. TEM micrographs were obtained with a JEOL JEM 100 CXII transmission electron microscope. An electron beam at an accelerating voltage of 100 kV was used. TEM micrographs were obtained as a function of irradiation time.

Flat specimens for energy-dispersive X-ray analysis (EDX) were prepared by cutting the samples at −120 °C. The experiment was performed with a Philips XL30 model scanning electron microscope. The electron beam was operating at 30 kV. X-ray emission was detected by an energy-dispersive analyzer (lithium-doped silicon detector) at a takeoff angle of 35° with respect to the surface normal of the sample. The primary electron beam was scanned over an area of 100 × 100 μm, at a speed of 1.87 ms/line. Each frame contained 484 lines. To measure the current density, a Faraday cup was placed next to the sample. The beam currents before and after each run were measured. A small change in the current density was detected due to filament instability. The experimental parameters such as the working distance and spot size were adjusted to maintain the current around 1.02−1.09 nA. This was equivalent to a dose rate of 0.102−0.109 C/(m^2 s). The gun tilt, astigmatism, and working distance were optimized to give a photon count of 3000−6000 s^{-1}. An EDX spectrum was acquired after every 120 frames. The background was subtracted before the peak intensity in the spectrum was calculated by the software automatically. The Cl peak intensity at 2.26 keV was monitored as a function of electron irradiation time.

Results and Discussion. TEM Study. Our earlier study suggested that the rubber concentration at the interface between the SBR and PVC phases increases

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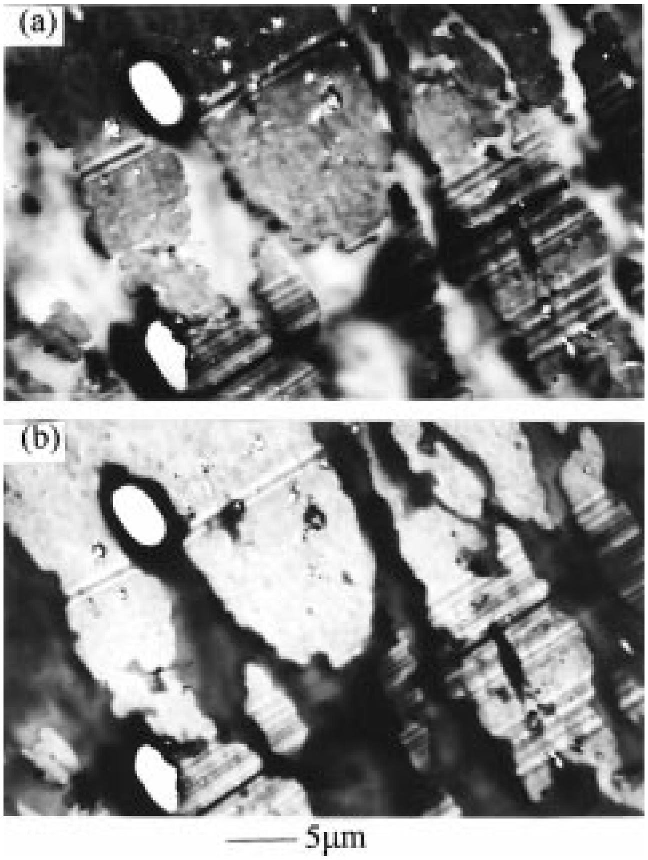

Figure 1. TEM micrographs of the unvulcanized PVC/SBR (50/50) blend taken at electron irradiation times of (a) 0.5 and (b) 1.5 min.

as a result of the addition of NBR and the covulcanization between SBR and NBR.[5] This conclusion is made on the basis of a series of TEM micrographs obtained on an unstained PVC/SBR sample as a function of electron irradiation time. The contrast observed in the TEM micrographs from the unstained sample comes mainly from the mass−thickness contrast. Figure 1 shows the TEM micrographs of the PVC/SBR (wt ratio = 50/50) blend. The micrographs were obtained from the same area at two different electron irradiation times. The dispersed dark regions in Figure 1a represent the PVC domains because of the presence of Cl, which scatters electrons more effectively than other light elements such as H, C, and O in the blends. SBR, which has only C and H, appears as the light areas because fewer electrons are scattered in this region than in the PVC domains. As the electron beam irradiation continues, the loss of Cl in the PVC domains reduces its scattering power, and hence the contrast between the rubber and PVC decreases. When most of the Cl disappears, the PVC regions will be thinner than the rubber regions because Cl in PVC accounts for 63 wt %. Consequently, a contrast inversion is observed due to the contrast caused by the difference in mass.

A series of TEM micrographs obtained from the same area of a sample of the PVC/SBR (50/40) blend compatibilized by 10 parts of NBR as a function of time are shown in Figure 2. Again, in these micrographs, the dark areas represent the PVC domains and the light areas represent the SBR phases. The PVC regions are still darker than SBR regions after prolonged exposures to the electron beam. No contrast inversion is observed even after 1.5 min of electron irradiation. The probable explanation is that the Cl concentration in the PVC regions for the compatibilized blend does not decrease at the same rate as the uncompatibilized blend.

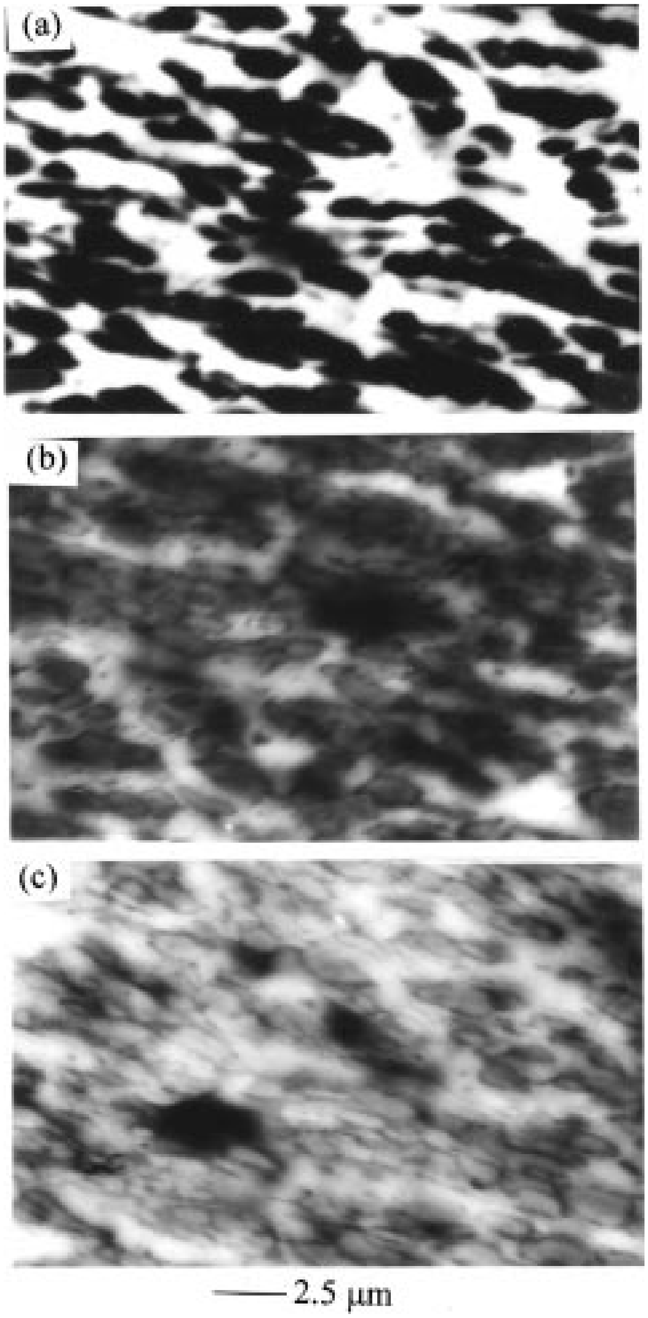

Figure 2. TEM micrographs taken at electron irradiation times of (a) 0.5, (b) 1.0, and (c) 1.5 min, respectively, for the PVC/NBR/SBR (50/10/40) blend.

Another important feature to be noted in Figures 2b,c is that the dark rings are observed at the interface between the PVC/SBR phases and become increasingly visible as irradiation continues. This phenomenon has not been observed for the uncompatibilized blend. These dark rings are darker than both the PVC regions and the rubber regions, indicating that the PVC at the interface is more resistant to the electron beam exposure. One of the possible explanations is that at the interface between the PVC and SBR phases there is a high rubber (NBR or SBR) concentration, which provides a more effective stabilization against electron beam irradiation. Consequently, the interphase regions are darker than both the PVC and SBR phases. To

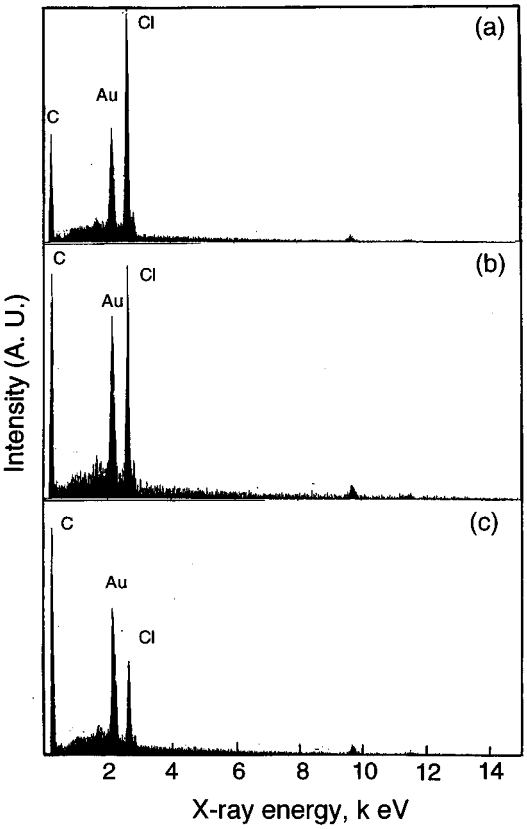

Figure 3. EDX spectra taken after (a) 2, (b) 30, and (c) 60 min, respectively, for the unvulcanized PVC/SBR (50/50) blend.

confirm that the dark rings are the result of a higher rubber concentration at the interface, we have to obtain additional evidence to show the stabilization effect of rubber on PVC. The enhanced stability of PVC due to the presence of rubber was studied by energy-dispersive X-ray analysis.

EDX Analysis. The X-ray excited by the electron beam can be analyzed by an energy-dispersive X-ray detector in a TEM or SEM. Linderberg et al.[16] used a TEM equipped with EDX to study the change in the Cl concentration for PVC and its blends under electron beam bombardment. Due to the difficulties associated with the sample preparation for the TEM study, SEM/EDX was used in the present study. The interaction volume of electrons in SEM will be significantly larger than that in TEM and so is the volume in which the X-ray is generated. Usually, the depth of the interaction volume is about 5−10 μm depending upon the energy of the primary electron beam.[12] Hence, monitoring the intensity of the Cl peak can provide an estimation of the Cl loss in the sample.

To demonstrate the stabilization effect of rubber on PVC, PVC/NBR (50/50) and PVC/SBR (50/50) blends were prepared. Because NBR is miscible with PVC, the stabilization effect should be easily observed. Parts a−c of Figure 3 show the EDX spectra of the PVC/SBR (50/50) blend after 2, 30, and 60 min of electron beam irradiation, respectively. Three peaks at 0.227, 1.42, and 2.62 keV are assigned to the excited X-ray emissions of the carbon K lines, gold M lines (from the coating used to prevent surface charging), and the chlorine K lines, respectively. The Cl peak intensity is much higher than the other two peaks. As the electron beam exposure increases, the Cl peak intensity decreases in comparison with those of the gold and carbon peaks. After an irradiation time of 60 min, the Cl peak intensity decreases to the extent that it is lower than that of the gold. Because the Cl peak intensity is proportional to the Cl concentration in the interaction volume, the Cl intensity decay is a direct indication of the decrease in the Cl concentration as a result of the electron bombardment.

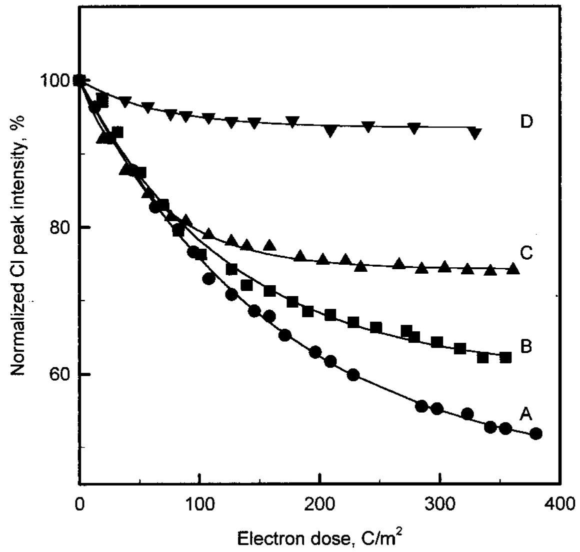

Figure 4. Normalized Cl intensity as a function of electron irradiation time for the uncompatiblized and compatiblized blends: (●) PVC/SBR (50/50) blend; (■) PVC/NBR/SBR (50/10/40) blend; (▲) PVC/NBR/SBR (50/10/40) vulcanized blend (S/MBT/ZnO = 0.5/0.5/1.0 phr); (▼) PVC/NBR (50/50)blend.

The normalized Cl peak intensity as a function of electron beam irradiation time for PVC/NBR (50/50) and PVC/SBR (50/50) blends is shown in Figure 4. The normalized Cl peak intensity is defined to be the measured ratio of the Cl peak intensity to that measured after 2 min of electron irradiation. The decrease in the Cl intensity for the PVC/SBR (50/50) blend is very fast because PVC and SBR are not miscible; hence, SBR cannot act as an effective stabilizer for PVC under electron beam irradiation. For the PVC/NBR (50/50) blend, the dehydrochlorination rate becomes very small. This result indicates that NBR, which is miscible with PVC, can provide a strong protection for PVC against electron beam degradation.

The normalized Cl peak intensity of the vulcanized and unvulcanized PVC/NBR/SBR (50/10/40) blends as a function of electron beam irradiation time is also shown in Figure 4. The results shown in Figure 4 clearly indicate that the addition of NBR in the blend decreases the dehydrochlorination rate by stabilizing PVC. When the ternary blend is vulcanized, the rate of dehydrochlorination is further reduced. This decrease in the dehydrochlorination rate is attributed to the additional stabilizing effect brought about by covulcanization between NBR and SBR, because covulcanization will effectively increase the rubber concentration in the interphase regions.

It has been shown previously[17] that the decay curves are given by

$$\frac{I}{I_0} = (1 - A)\mathrm{e}^{-kD} + A \qquad (1)$$

where I and I_0 are the Cl peak intensities at dose D and zero dose, respectively, and k and A are constants. The

Table 1: Values of *k* and *A* Determnined from the Best Fit to the Measured Chlorine Decay Curves

blend	k, C/m^2	A
PVC/SBR (50/50)	0.00595	0.460
PVC/NBR/SBR (50/10/40)	0.00785	0.600
PVC/NBR/SBR(50/10/40) (S/MBT/ZnO = 0.5/0.5/1.0 phr)	0.0158	0.742
PVC/NBR (50/50)	0.0146	0.935

value of k is polymer-dependent because different structures are formed by irradiation of the polymers.[17,18] The value of A is an indication of the chlorine concentration at high doses. The polymer blends that are more stable to electron irradiation will have higher values of A. The values of k and A were calculated from the best fit to the measured chlorine decay curves, and the results are summarized in Table 1.

There are three major mechanisms to absorb the electron energy in the blends. Upon electron beam irradiation, the C−Cl bonds are broken, forming carbon and Cl radicals. Subsequent abstraction of hydrogen leads to the formation of polyene or an allyl radical, making this chemical reaction thermodynamically favorable. The second phenomenon where the incident electron energy can be absorbed is the breaking of the carbon−carbon double bonds in the rubber (both NBR and SBR).[11] The third phenomenon is related to the phenyl ring in SBR. Polystyrene, which is a good example of a radiation-resistant polymer, has a very small G value (0.05) for cross-linking.[16] The incident electron beam energy is transferred to the aromatic rings where they can be dispersed in several ways, but without involving any chemical reactions. One of the ways for the energy to be dispersed is the formation of an excited triplet benzene ring, which is energetically favorable. The excited state can be returned to the ground state by fluorescence or other energy-transfer mechanisms. An alternative is that the evolved H, which plays a fundamental role in allowing two radicals to migrate and meet, is absorbed into the aromatic group and cannot react further.[16] Hence, the benzene rings in SBR can act as an effective energy sink competing for the incident electron energy.

When the blend components are well mixed, the three possible mechanisms will compete for the energy of the incident electrons. If PVC is in close proximity to NBR, the carbon−carbon double bonds will compete for the energy available from the electrons; thus the impact on the C−Cl bonds will be eased. The situation will further improve if SBR has been forced into the proximity of PVC via the covulcanization with NBR. The phenyl rings of SBR will be another energy sink for the incident electrons, providing additional shielding for the PVC.

Conclusions. A novel method has been developed to detect the enhanced rubber concentration at the interface between the PVC and SBR phases. This method is based on the fact that the dehydrochlorination rate of PVC can be reduced by the presence of NBR or SBR or both.

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