

Quantitative Measurement of Interdiffusion at Polymer–Polymer Interfaces with TEM/EDS and EELS

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SYNOPSIS

Transmission electron microscopy and energy dispersive spectroscopy (TEM/EDS) were used to map the concentration profile at the interface of a poly(vinyl chloride) and poly(methyl methacrylate) bilayer. Thin sections in the order of 800 Å were cut using an ultramicrotome, examined with TEM, and the concentration profile was mapped with EDS. The intensity of fluorescence X-rays was adjusted for sample thickness variation by measuring the relative thickness across the interface with electron energy-loss spectroscopy (EELS). The interfacial thickness of the bilayer after 6 h at 120°C was 1.5 μm, whereas the interdiffusion coefficient was determined as 8.0×10^{-14} cm²/s. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Adhesion at the interface between two polymers affects the interfacial strength and mechanical properties of composites in multilayered polymer systems.^{1,2} Diffusion at polymer interfaces has been examined with a variety of techniques including neutron scattering,^{3,4} high-energy ion spectrometry,^{5,6} scanning electron microscopy,⁷ ellipsometry,⁸ infrared spectroscopy,⁸ and optical spectrometry.^{10,11} Of these techniques, only electron microscopy allows visual observation of the interface to directly map the concentration profile along the interfacial region. Combination of scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS) have been used to map the concentration profile across the interface between a polymer–polymer pair.¹² The major disadvantages of this technique are the limited spatial resolution due to the large interaction area between the electron beam and the polymer sample, and the uncertainty in the penetration depth of the beam across the interface caused by the difference in electron density between the two polymers.

In a previous article,¹³ we used a combination of TEM and EDS to map the concentration profile

across a poly(vinyl chloride) (PVC) and poly(ethyl methacrylate) (PEM) interface with enhanced spatial resolution of 100 nm compared to SEM, which was on the order of 1 μm. We observed that the thickness of the bilayer film varied across the interface after sectioning, due to the differences in viscoelastic properties of the two polymers. Here, we report on the use of TEM/EDS in combination with electron energy-loss spectroscopy (EELS) to map the concentration profile and measure interdiffusion at a polymer–polymer interface. EELS was used to measure the relative thickness of the interfacial layer. A polymer pair consisting of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) was used in this investigation.

EXPERIMENTAL PART

The PVC and PMMA samples were obtained from Scientific Polymer Products (Ontario, NY) as secondary standards. Gel permeation chromatography (GPC, model 6000A, Waters Associates, Milford, MA) was used to measure the molecular weight and molecular weight distribution of the samples. The experiments were carried out with tetrahydrofuran (THF) as the mobile phase; μStyragel[®] columns with 10⁶, 10⁵, 10⁴, and 10³ Å pore sizes were used, and the flow rate was 1 mL/min. The PVC and

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PMMA samples had \bar{M}_w of 1.22×10^5 and 1.01×10^5 with polydispersity indices of 2.1 and 2.0, respectively. The PVC and PMMA films were cast on silicon wafers from 6 wt % and THF and 4 wt % methyl ethyl ketone solutions, respectively. As a stabilizer, 1 wt % of di-*n*-octyltin-5,5'-bis(iso-octylmercaptoacetate) (Atochem North America, Philadelphia, PA) was added to PVC. Differential scanning calorimetry (DSC, model 2910, TA Instruments, Wilmington, DE) was used to measure the glass transition temperature, T_g , of the polymers at a scanning rate of $10^\circ\text{C}/\text{min}$. The T_g of the PMMA sample was 118°C . The T_g of the PVC sample with stabilizer was 74°C .

The following procedure was adapted for drying the polymer films quickly and without bubble formation: treatment for 1 week at room temperature, then in a vacuum oven with the time-temperature cycle of 1 week at room temperature, 2 days at 45°C , 1 day at 55°C , 1 day at 70°C , and, finally, 1 h above the T_g of each polymer. This time-temperature cycle insured the removal of all the solvent, as monitored with differential scanning calorimetry, without the formation of any bubbles inside the film. The surface roughness of the polymer films was examined in the direction parallel to the interface with a profilometer (Alpha step 200, Tencor Instruments, Mountain View, CA). The stylus tip radius was $5 \mu\text{m}$ and the stylus force was 4 mg. The surface roughness of the PVC and PMMA films was less than 100 \AA . After drying, the two polymer films were brought in contact, placed between two microscope slides, sandwiched between two steel plates, and placed in the vacuum oven preheated above the T_g of the two polymers (usually at 120°C). The steel plates served as a constant temperature heat source for controlling temperature during the experiment. Samples from the bilayer were removed from the vacuum oven as a function of time for analysis.

The interface between the two films was exposed by fracturing at liquid nitrogen temperature and embedding in an epoxy matrix for microtoming. The embedded sample was microtomed with a glass knife at room temperature to reduce the surface roughness to less than $0.2 \mu\text{m}$. Thin sections on the order of 800 \AA were cut at room temperature using an ultramicrotome with a diamond knife. The sections were placed on a 100 mesh copper grid, and examined in the transmission electron microscope (JEOL 2000FX, Analytical Electron Microscope) with an energy dispersive X-ray spectrometer (AN10000, Link Analytical EDS) using an accelerating voltage of 200 kV. The chlorine atoms of PVC were used to map the concentration profile of PVC across the

interface. The X-ray intensity was integrated over the K_α and K_β bands of chlorine and was set proportional to the PVC concentration as a function of spatial position. The X-ray intensities were corrected for variation in sample thickness with electron energy-loss spectroscopy (666 Gatan Parallel EELS) with an accelerating voltage of 200 kV.

ANALYSIS OF EXPERIMENTAL RESULTS AND DISCUSSION

The photon energy emitted from the chlorine atoms of PVC was used to map the concentration of chlorine across the polymer-polymer interface, which was directly proportional to the molar concentration of PVC. The number of X-ray counts occurring at a given energy is proportional to the number of atoms in the irradiated volume from which the X-rays originated. The detected count rate per unit interaction volume is¹⁴

$$N = \frac{J_e Q_k \omega_k \eta_d n}{V} \quad (1)$$

Here, N is the detected count rate of K_α and K_β X-rays, J_e is the electron flux, Q_k is the ionization cross-section for K shell excitation, ω_k is the fluorescence yield of K shell X-rays, η_d is the detector efficiency, n is the number of chlorine atoms, and V is the interaction volume between the beam and the sample. The intensity of X-ray fluorescence is calculated by integrating the detected count rate over the energy band for K_α and K_β X-rays and over the interaction volume:

$$I(x) = \frac{\iint N(\epsilon, x) P(V) \partial\epsilon \partial V}{V} \quad (2)$$

Here, $I(x)$ is the intensity of X-rays at distance x from the interface per unit interaction volume, and ϵ is the width of the K_α and K_β energy bands. The function $P(V)$ is the spread of the beam within the sample that makes the concentration profile more diffuse than the actual profile. Ideally, $P(V)$ should be decreased to a delta function to arrive at the actual concentration profile, but the interaction between the electron beam and the sample causes the incident beam to scatter into a pear shaped volume.

For polymers that have a lower atomic number compared to metals, the lateral spread of the beam is in the order of $2\text{--}3 \mu\text{m}$. This explains the low resolution of SEM for measuring the concentration

profile for polymeric materials. On the other hand, for TEM studies with samples of bilayer thickness on the order of 800 Å, the interaction volume is limited by the aperture size of the electron beam. Therefore, for thin sections, the spread function $P(V)$ becomes unity and eq. (2) reduces to

$$I(x) = \frac{\iint N(\varepsilon, x) \partial \varepsilon \partial V}{V} = \frac{I_m(x)}{V} \quad (3)$$

Here, $I_m(x)$ is the measured intensity of X-rays. For thin sections, the interaction volume becomes cylindrical, with the same cross-sectional area as the electron beam aperture, A_o , and length equal to the sample thickness, δ .

For polymer bilayers, the intensities can be normalized based on the intensities from each polymer phase far from the interface. Therefore, the normalized concentration profile is related to the X-ray intensity by

$$\psi(x) = \frac{C(x) - C_0}{C_1 - C_0} = \frac{I(x) - I_0}{I_1 - I_0} \quad (4)$$

Here, $\psi(x)$ is the normalized concentration, $C(x)$ is the concentration at distance x from the interface, and C_1 and C_0 refer to positions far away from the interface on the PVC and PMMA side, respectively. For constant aperture size, the normalized concentration reduces to

$$\psi(x) = \frac{\delta_1}{\delta(x)} \frac{I_m(x) - I_{m,0}(\delta(x)/\delta_0)}{I_{m,1} - I_{m,0}(\delta_1/\delta_0)} \quad (5)$$

Here, I_m is the measured X-ray intensity, and $\delta(x)$ is the sample thickness as a function of distance along the interface.

Electron energy loss spectroscopy was used to measure the sample thickness along the interface. EELS can reveal the energy distribution of electrons that have been transmitted through the sample. Figure 1 shows a typical EELS spectrum obtained from an arbitrary position across the PVC/PMMA bilayer at 200 keV accelerating voltage. The peak at zero energy loss is due to electrons that have been transmitted through the sample without loss in energy. The peak at approximately 20 eV of energy loss is the plasmon peak produced by the interaction of the beam with free electrons in the specimen, known as plasmon excitation. The probability of an electron exciting n plasmons is given¹⁴ by

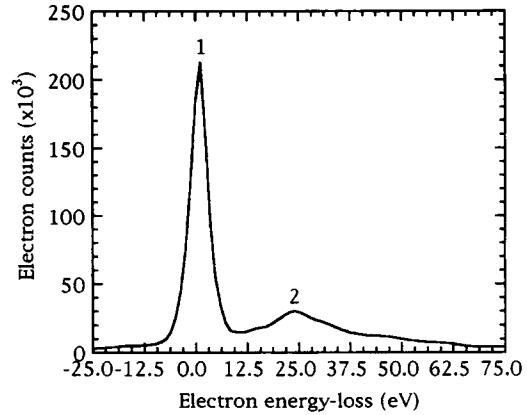


Figure 1 EELS spectrum of PVC/PMMA interface. Peaks 1 and 2 correspond to the zero-loss and plasmon peaks, respectively.

$$E(n) = \frac{1}{n!} \left[\frac{\delta(x)}{\lambda_p} \right]^n \exp \left(- \frac{\delta(x)}{\lambda_p} \right) \quad (6)$$

Here, $\delta(x)$ is the sample thickness as a function of distance from the interface and λ_p is the plasmon mean free path. The ratio of the probabilities of exciting no plasmon, $E(0)$, and one plasmon, $E(1)$, is the intensity of the plasmon peak, I_p , to the zero-loss peak, I_{ZL} , respectively. Therefore, the sample thickness is given by

$$\delta(x) = \lambda_p \frac{I_p}{I_{ZL}} \quad (7)$$

The plasmon mean free path is related to the concentration of free electrons in the specimen and can be regarded as a constant for polymers. Therefore, eq. (7) provides an accurate way to measure the relative thickness of the sample as a function of distance from the interface, x .

Figure 2 shows the TEM micrograph of the PVC/PMMA interface after 6 h at 120°C at 8000× magnification. At a lower magnification of 1500×, the PMMA side of the interface was ridged with shallow and dark regions, indicating that the thickness of the bilayer varied with distance across the interface. The dark dots in the micrograph are indications of sample damage by the technique. Chlorine X-ray counts are shown in Figure 3 as a function of distance for beam aperture diameters of 100 nm and 250 nm. According to this figure, the number of X-ray counts increased in proportion to the diameter of the beam aperture, verifying that the interaction volume was controlled by the beam diameter for thin sections.

EELS was used to correct the number of X-ray counts for sample thickness. Figure 4 shows the rel-

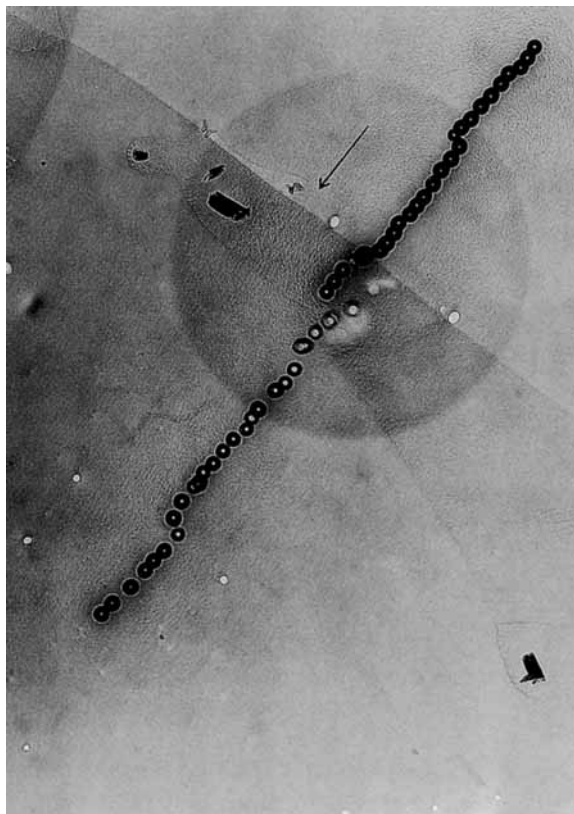


Figure 2 TEM micrograph of the PVC/PMMA interface at 8000 \times after 6 h at 120 $^{\circ}$ C. The position of the interface is shown by the arrow. The dark circular bullets in the micrograph are the locations across the interface where X-rays were collected.

ative thickness of the sample as a function of distance along the interface. The thickness of the PMMA side of the interface was approximately 20% less than the PVC side. The X-ray counts in Figure 3 were adjusted for sample thickness using eq. (7) and normalized using eq. (5). Figure 5 shows the normalized concentration profile for PVC/PMMA after 6 h at 120 $^{\circ}$ C. After 6 h, the concentration profile was diffuse but the interface was symmetric with thickness δ_0 of approximately 1.5 μ m. This thickness was determined from the fitting of the data of Figure 5 to the error function profile.

The data in Figure 5 were fitted to eq. (8), in which the diffusion coefficient is related to the slope of the concentration profile at the interface, according to the long-term approximation of the semi-infinite solution of the Fickian diffusion equation.

$$D = \frac{1}{16t(\partial\psi/\partial x|_{x=0})^2} \quad (8)$$

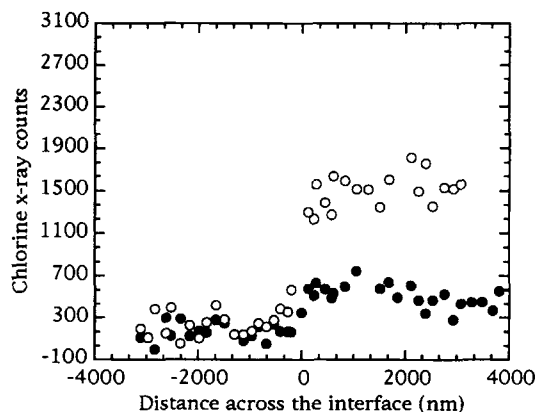


Figure 3 Normalized chlorine X-ray intensity across the interface for PVC/PMMA after 6 h at 120 $^{\circ}$ C. The open and filled circles correspond to aperture diameter of 250 and 100 nm, respectively.

Here, x is the distance from the interface, t is time, and D is the interdiffusion coefficient. Using eq. (8), an interdiffusion coefficient of 8.0×10^{-14} cm^2/s was obtained from the concentration profile of Figure 5, which agrees closely with the values reported in the literature for interdiffusion in bulk polymers.¹⁵

CONCLUSIONS

The concentration profile and interfacial thickness of a poly(vinyl chloride) and poly(methyl methacrylate) bilayer were measured with transmission electron microscopy and energy dispersive spectroscopy. Electron energy-loss spectroscopy was used to account for the variation in sample thickness across the interface. The interfacial thickness was 1.5 μ m after 6 h at 120 $^{\circ}$ C. The concentration profile

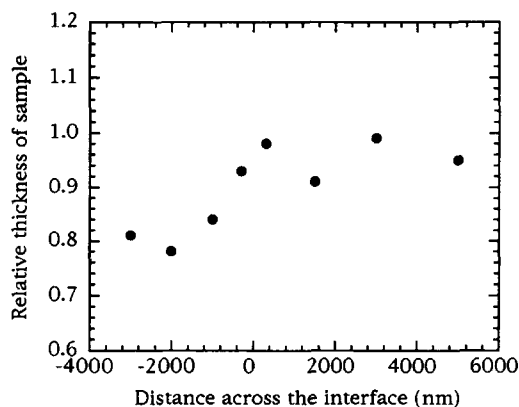


Figure 4 Relative thickness of the PVC/PMMA bilayer across the interface.

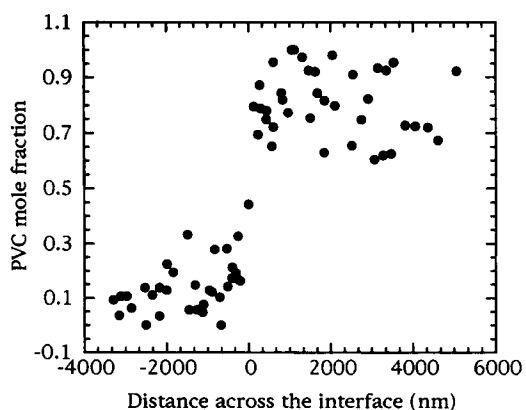


Figure 5 PVC mol fraction across the PVC/PMMA interface after 6 h at 120°C, corrected for sample thickness variation.

was fitted to the Fickian diffusion equation and an interdiffusion coefficient of 8.0×10^{-14} cm²/s was obtained.

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