

Mapping the concentration profile at the poly(vinyl chloride)/poly(ethyl methacrylate) interface

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Summary

The combination of transmission electron microscopy and energy-dispersive spectroscopy is used to map the concentration profile across the interface and measure the mutual diffusion coefficient for a compatible poly(vinyl chloride) and poly(ethyl methacrylate) polymer pair in the melt state. Preliminary results indicate that this technique has enhanced spatial resolution of 100 nanometers.

Introduction

Polymer/polymer interdiffusion affects the mechanical properties of polymers at interfaces with major applications in encapsulation of microelectronic devices, copolymer-enhanced adhesion for incompatible polymer composites, and welding of polymer interfaces (1). In these applications the final properties of the polymer are determined by the thickness of the interface or the concentration profile of the two polymers across the interface. Voyutski (2) proposed that after intimate contact is established between two polymer films, adhesion takes place by interdiffusion of polymer segments across the interface and the extent of interdiffusion depends on the compatibility parameter between the two polymers. Later, de Gennes (3) showed that interdiffusion coefficient is directly proportional to the Flory-Huggins interaction parameter for compatible polymer pairs.

A number of experimental techniques has been developed to study interdiffusion in compatible polymers. Laurence and collaborators (4) pioneered the use of electron microscopy to measure interdiffusion coefficients in polymers. They used the combination of scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS) to map the concentration profile of poly(vinyl chloride) (PVC), with chlorine as the label, across the interface between PVC and poly(ϵ -caprolactone) (PCL). The major disadvantage of this technique is the limited spatial resolution for polymers, in the order of 3–5 μm , due to the large interaction volume between the electron beam and the sample.

Raghava and Smith (5) have used transmission electron microscopy (TEM) to image the interface between poly(ethyl methacrylate) (PEM) and poly(vinylidene fluoride) and show qualitative evidence for interdiffusion. Koizumi et al. (6) have used TEM to show mutual diffusion of a poly(styrene-*b*-isoprene) copolymer in a polystyrene matrix by using a TEM micrograph to count the number of spherical polyisoprene microdomains across the interface. Their results showed the excellent spatial resolution of TEM for interdiffusion studies which is in the order of 50 nm. However, this technique is only useful for the diffusion of polymer

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microdomains in an incompatible polymer matrix.

Here we present a technique using the combination of transmission electron microscopy and energy-dispersive spectroscopy (TEM/EDS) to map concentration profiles and measure interdiffusion in compatible polymer pairs with enhanced resolution of 100 nm.

Experimental

The PEM sample used (Aldrich Chemical Co., Milwaukee, WI) had number and weight average molecular weights of 126,000 and 340,000, respectively. The PVC sample (Firestone Plastic Co., Pottstown, PA) had a number average molecular weight of 95,000. These two polymers are compatible as reported by Paul and Newman (7). Polymer films were cast from a 5% solution in tetrahydrofuran (THF) in petri dishes. As a stabilizer, 1 wt% of di-*n*-octyltin-5,5'-bis(iso-octylmercaptoacetate) (Atochem North America, Philadelphia, PA) was added to PVC.

The following procedure was used for drying the polymer films without bubble formation: one week at room temperature, then drying in vacuo with a time-temperature cycle of one week at room temperature, two days at 45 °C, one day at 55 °C, one day at 70 °C, and finally ten hours at 85 °C. This time-temperature cycle insured the removal of all the solvent, monitored with differential scanning calorimetry. The surface roughness of the polymer films was examined in the directions perpendicular and parallel to the interface with a profilometer (Alpha 200, Tencor Instruments). The theoretical spatial resolution was 200 Å as determined from surface roughness measurements perpendicular to the interface.

After the films were cast from THF and dried, the two polymer films were contacted along the side next to the Petri dish, placed between two micro-slides, and pressed firmly together by a small clamp. The assembly consisting of the polymer films between the micro-slides was placed in the vacuum oven preheated to the desired interdiffusion temperature which was in all cases above the glass transition temperature of the two polymers. Samples from the polymer/polymer film were removed from the vacuum oven as a function of time for analysis. The interface between the two polymer films was exposed by fracturing the film at liquid nitrogen temperatures and embedded in an epoxy matrix for microtoming.

For SEM/EDS experiments, the embedded sample was microtomed with a glass knife at room temperature to reduce the surface roughness to less than 0.2 μm, sputter-coated with gold, and examined in a JOEL-35CF SEM and Trecor Northern TN55 X-ray analyzer using an accelerating voltage of 15 kV. For TEM/EDS experiments, thin sections in the order of 800-1000 Å were cut using an ultramicrotome (Reichert Ultracut C) with a diamond knife at room temperature. The thin sections were placed on a 100 mesh copper grid, and examined in a JOEL 2000FX TEM and LINK analytical X-ray spectrometer using an accelerating voltage of 200 kV. The chlorine atom of PVC was used as the label for interdiffusion studies. The X-ray spectrum was integrated over the K_{α} and K_{β} bands of chlorine and this integrated intensity was set proportional to the concentration of PVC in the sample as a function of spatial position.

Results and Discussion

Figure 1 shows the TEM micrograph of the PVC/PEM interface after 5 days at 100 °C at 5000X. The lighter region on the left side of the micrograph is PEM and the darker region on

the right is PVC. The position of the interface is shown by an arrow. There is good adhesion at the interface between the two polymers. The circular dots in the micrograph show the positions across the interface at which X-ray analysis was done and are a measure of the interaction volume between the electron beam and the sample. The interaction volume is affected by the size of the electron beam and the sample thickness. Preliminary experiments with PVC/PEM indicate that spatial resolutions of the order of 100 nm is possible with this technique.

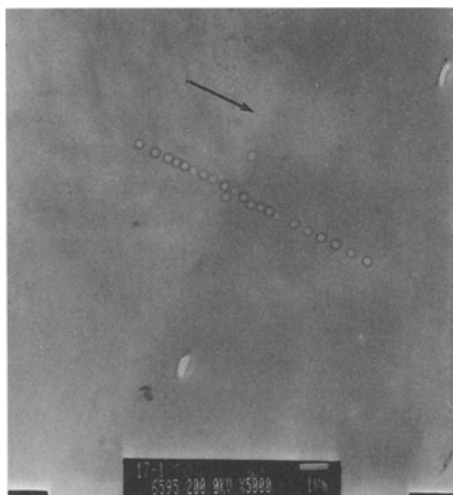


Figure 1. TEM micrograph of the PVC/PEM interface after 5 days at 100 °C

Figure 2 shows the normalized X-ray intensity versus distance from the interface for the PEM side of the interface for comparison of the spatial resolution of TEM/EDS with SEM/EDS.

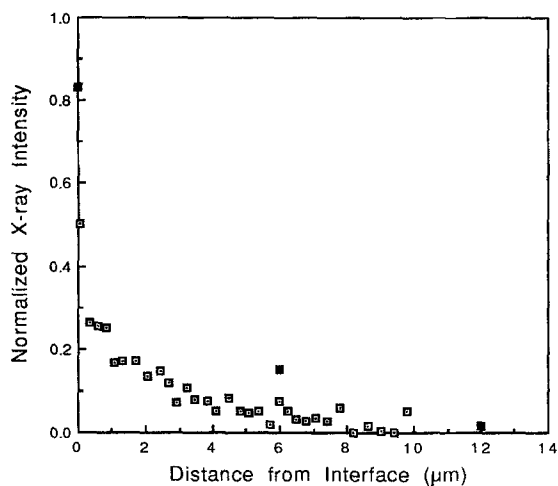


Figure 2. Comparison of the spatial resolution of TEM/EDS with SEM/EDS;
 □ (TEM/EDS); ■ (SEM/EDS)

Enhanced spatial resolution was observed with TEM/EDS as compared to SEM/EDS for interdiffusion studies. The X-ray intensity in Figure 2 was normalized based on the following equation:

$$\psi = \frac{I(x) - I_0}{I_1 - I_0} \quad (1)$$

Here, ψ is the normalized chlorine concentration, $I(x)$ is the chlorine X-ray intensity at distance x from the interface, and I_1 and I_0 are the chlorine X-ray intensities in the bulk region (away from the interface) of PVC and PEM, respectively. Figure 3 shows the plot of normalized chlorine concentration versus distance from the interface for the PVC/PEM polymer pair after 5 days at 100 °C.

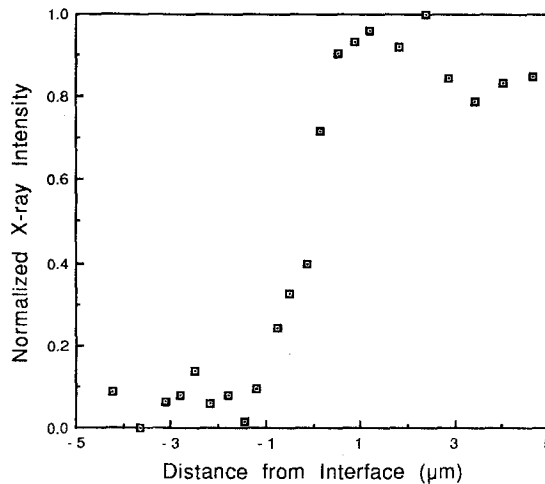


Figure 3. Normalized X-ray intensity versus distance from interface after 5 days at 100 °C

The chlorine concentration was directly proportional to the molar fraction of PVC across the interface. The concentration profile changes from a sharp interface at zero healing time to a diffuse interface, approximately 5 μm in width, after 5 days. The data of Figure 3 were fitted to the solution of the Fickian diffusion equation as shown below:

$$\psi = \frac{1}{2} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \quad (2)$$

Here, x is the distance from the interface, t is time, erfc is the complementary error function, and D is the interdiffusion coefficient. The interdiffusion coefficient obtained by fitting the data of Figure 3 to the above equation was $8 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. The diffusion coefficient is in close agreement with the values reported in the literature for interdiffusion in bulk polymers. Gilmore et al. (8) measured the interdiffusion coefficient for a PVC and PCL pair which is a system similar to the PVC and PEM. They reported a diffusion coefficient which is of the order of $10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. Therefore, this study shows that TEM/EDS is a viable technique for mapping the concentration profile and measuring interdiffusion coefficient in polymer pairs

with enhanced spatial resolution of 100 nm. The enhanced spatial resolution of TEM/EDS offers opportunity to investigate experimentally the effect of such parameters as polymer/polymer compatibility, molecular weight distribution, and the amount of plasticizer on the thickness of the interface between two polymers.

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