SHORT COMMUNICATIONS

SIMS Chemical Imaging on Fractured Surface of Polymer Blend

Satoru HOSODA

*Sumitomo Chemical Co., Ltd., Chiba Research Laboratory,
Anesakikaigan 5-1, Ichihara-shi, Chiba 299-01, Japan*

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Recently modification of polymer materials by means of a polymer blend has been progressively carried out to endow a new performance to raw polymers, and blends obtained which are lately called "polymer alloy" have been continuing to make inroads into various industrial materials. Meanwhile, localization of component polymer, chemical composition and its distribution at a surface or interface of polymer blend are considered to be key factors that strongly influence the properties of a product. Therefore, characterization of polymer surface and interface has increasingly become important to evaluate the degree of modification.

Among various physical techniques for polymer surface characterization, X-ray photoelectron spectroscopy (XPS) is still dominant because of its easy applicability to insulating materials and very low radiation-damage effect. However, as Briggs¹ suggested, the XPS technique has several severe problems, such as very poor spatial resolution, ambiguity of binding energy based on small dynamic range of core level chemical shift, and limited surface sensitivity. On the other hand, secondary ion mass spectrometry (SIMS) has been widely used for surface analysis of electric conductors and semiconductors²⁻⁴ taking advantage of their high spatial resolution and

excellent surface sensitivity. Further, by the use of both a charge neutralisation technique and a very low beam current of primary ion, it has gradually come to be applied to organic insulating materials.⁵⁻⁸

As for the application of SIMS to polymer surface characterization, Briggs *et al.*⁹⁻¹² have studied the mass spectra of various kinds of polymers and suggested that it is possible to assign a polymer from peaks characteristic to each kind of polymer ("fingerprint species"). In addition to this type of utilization, both depth profiling and chemical imaging for polymer material are considered to be powerful techniques of SIMS, in which the fundamental peculiarity of SIMS is effectively withdrawn as shown in a few reports on polymers.¹³⁻²⁰ As for polymer blends, very little has been reported so far. Chujo *et al.*¹⁶ revealed a vertical composition distribution from the very surface to inner portion for a polyvinylidene fluoride/polymethylmethacrylate (PMMA) miscible blend by depth profiling. Chemical imaging on the film surface of PMMA/polystyrene blend prepared by solvent cast method was reported by Simko *et al.*,¹⁹ using a magnetic sector type SIMS equipped with Cs⁺ primary ion source (beam diameter; 100—200 μ m). Wirth *et al.*²⁰ obtained the chemical imaging of the polymer extrudate of polyethersulphone containing 6%

of dimethylsiloxane, using a time-of-flight type SIMS with a liquid Ga^+ ion source (beam diameter; $0.5\ \mu\text{m}$).

In this paper, the author reports briefly the results of chemical imaging by a quadrupole type SIMS on a fractured surface of polypropylene/nylon immiscible blend lately developed as a polymer alloy useful for industrial materials.

EXPERIMENTAL

SIMS experiments were carried out using a VG Ionex SIMSLAB MK-I system fitted with MM12-12 quadrupole mass spectrometer with a mass range of m/z 800. Mass spectra and chemical images were obtained using a 10 keV Ga^+ ion beam from a liquid metal source (MIG 100, beam diameter; $5000\ \text{\AA}$) with an absolute current of 200 pA. Ion beams were rastered in an area of $50 \times 50\ \mu\text{m}$. The current density of $8\ \mu\text{A cm}^{-2}$ in this measurement seems too high for general static SIMS, but it was indicated¹³ that fast data acquisition makes it possible to get clear chemical imaging even under high current density. Data acquisition for imaging was thus possible within 20 seconds for each sample. Charge neutralisation has been achieved with a static flood of 600 eV electrons.

Polymer blend samples were prepared by extruding a polymer pellet mixture using 30 mm ϕ extruder at 280°C and injection-molded into a sheet of 3.2 mm thickness and 12.7 mm width. A fractured surface of a notched Izod-impact test specimen (ASTM D256, temp; 23°C) was subjected to SIMS measurement.

RESULTS AND DISCUSSION

Mass spectra of negative ions from the fractured surface of polymer blend samples A and B are shown in Figure 1. Sample A is a simple binary blend of polypropylene (PP) and nylon 6 (Ny6) (weight ratio; 60/40), and sample B is composed of PP, Ny6 and acrylic

Figure 1. Negative SIMS spectra of (a) sample A (polypropylene/nylon 6, 60/40) and (b) sample B (polypropylene/nylon 6/compatibilizer, 50/40/10).

polymer as a compatibilizer (50/40/10). Strong peaks common to both samples were observed at m/z 24 and 26, and assigned to C_2^- and CN^- ions, respectively, though the peak at m/z 26 has a very small contribution from C_2H_2^- . C_2^- is known to be a fragment characteristic of organic polymers and independent on the kind of polymer. CN^- is representative of an organic compound containing nitrogen, in this case Ny6. In the spectrum of sample B, a strong peak at m/z 16 due to O^- ion was observed, indicating considerable compatibilizer used in the sample B to exist at the fractured surface. Additional experiments such as depth profiling measurement might be necessary to elucidate whether the compatibilizer is localized at the fractured surface or not.

Further, the chemical imaging of the fragment ion of CN^- was carried out and indi-

Figure 2. Chemical images of (a) C_2^- and (b) CN^- ions for sample (A), induced by 10 keV Ga^+ primary ion.

cated a two dimensional distribution of Ny6 component at the fractured surface, and the results are shown in Figures 2 and 3. Chemical image of C_2^- ion which gives a very good indication of the topography of the surface is also shown in Figure 2(a). At the fractured surface of sample A, PP makes a continuous phase and Ny6 aggregates as a spherical domain of diameter of 3–10 μm , indicating a low affinity between PP and Ny6. In contrast, Ny6 in sample B is widespread over the whole fractured surface as an irregular continuous phase, though the concentration distribution of Ny6 at the surface is not completely homogeneous in this case either. The difference be-

Figure 3. Chemical image of CN^- ion for sample (B), induced by 10 keV Ga^+ primary ion.

tween Figure 2(b) and Figure 3 suggests that the wettability of Ny6 to PP is enhanced by the action of the compatibilizer used here.

It is considered that the improved impact strength of the sample (b) (6.9 kgcm cm^{-2}) compared to the sample (a) (2.0 kgcm cm^{-2}) might be due to enhanced wettability at the interface of component polymers.

In the case of an immiscible polymer blend system, a compatibilizer which increases affinity among component polymers is generally used to stabilize phase separation. The chemical imaging on an interface disclosed by such methods as trimming and fracture should become an important technique of SIMS for evaluation of compatibilizing ability of various actual polymer blend systems. Furthermore, recent advances of liquid-metal ion sources²¹ should provide a higher spatial resolution of chemical imaging, and the SIMS image with high spatial resolution may therefore be used a powerful "chemical microscopy" for polymer surface and interface characterization.

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