FUNCTIONAL GROUP IMAGING OF A COATED INTERFACE AND POLYMER BLENDS
USING FOURIER TRANSFORM INFRARED MICROSCOPYTOSHIKATSU NISHIOKA *¹ and NORIO TERAMAE*²

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Abstract Fourier transform infrared microspectroscopic functional group imaging was applied for characterization of a coated interface and a polymer blend. The sample investigated was prepared by coating a polyurethane layer on EAA/EEA copolymer. A mixed phase of the two polymers could be detected clearly at the interface region. As for a polymer blends prepared by mixing polypropylene and polycarbonate, the spatially specific compositional heterogeneity could be easily identified.

Key words Fourier transform infrared microspectroscopy, functional group imaging depth profiling, coated interface, polymer blends

INTRODUCTION

In recent years, there has been considerable growth in the use of infrared microspectroscopy as an analytical tool. This technique has proven to be powerful for identifying very small samples and contaminants in a host material¹⁾⁻³⁾. Taking advantages of its spatial resolving power, we have studied inhomogeneities in polymers by using a microtoming technique⁴⁾⁻⁶⁾. In an industrial field of polymer, mechanism of adhesion between two different polymers is one of the problems of interest. Although there are some investigations⁷⁾⁻⁸⁾ about the adherent mechanism at a polymer-polymer interface in the paintings, few studies have been reported for obtaining information on structural changes caused by the adhesion. In order to develop a new adherent polymer, it is important to clarify a relation between the peeling strength of adherent samples and the details of interaction at the adherent interface. In the present paper, Fourier transform infrared microspectroscopy was applied to investigate a coated polymer-base polymer system by using a microtoming technique, in order to obtain information about the adherent mechanism. It was demonstrated that the existence of a mixed phase in a polymer-polymer system and the mode of interaction between molecules belonging to different polymers were easily clarified by functional group imaging in which an image of a material can be generated based on infrared absorptions by the specific functional groups.

EXPERIMENTAL

Instrumentation Two kinds of spectrometer systems were used. One was a Digilab FTS-40 Fourier transform infrared spectrophotometer, a Digilab universal microscope UMA-300A and a Digilab x-y computer-controlled mapping stage. The microscope is equipped with a narrow-band MCT detector. The other was a JEOL JIR500 Fourier transform infrared spectrophotometer, a JEOL microscope MAU110 equipped with a narrow-band MCT detector, and a JEOL x-y computer-controlled mapping stage.

Sample preparation An EAA/EEA (ethylene-acrylic acid copolymer/ethylene-ethyl acrylate copolymer) base plate contains 2.5 wt% acrylic acid and 2.5 wt% ethyl acrylate. The sample investigated was made by coating a polyurethane on the EAA/EEA. A polymer blend containing 60 wt% polycarbonate was made from injection molding. The sample were

prepared as microtomed cross sections by means of a LKB 2088 microtome.

RESULTS AND DISCUSSION

Figure 1 shows infrared spectra of polyurethane and EAA/EEA measured by a micro-transmittance method. As shown in the upper spectrum, characteristic absorptions by N-H and C=O stretching vibrational modes of polyurethane are observed at 3381 and 1738 cm^{-1} . The lower spectrum in Fig.1 shows two kinds of carbonyl absorption bands, one of which appears at 1737 cm^{-1} ascribed to a ester group in a ethyl acrylate part, and the other appears at 1707 cm^{-1} ascribed to a carboxylic group in a acrylic acid part. For the

Table 1 Shifts of adsorption bands in the ethylene acrylic acid copolymer/ethylene-ethyl acrylate copolymer layer.

Depth/ μm	10	20	30	40	50	60	70
Carboxyl group/ cm^{-1}	1705.5	1705.5	1705.5	1706.0	1706.0	1706.5	1707.0

Fig.1 Micro FT-IR transmittance spectra of the polyurethane (top) and the ethylene-acrylic acid copolymer/ethylene-ethyl acrylate copolymer(bottom).

microtomed sample, the latter absorption band was found to increase in frequency on a depth from an interface. The frequency shifts for a carboxylic absorption bands are summarized in Table 1. This result suggests the existence of a long range interaction between polyurethane and EAA/EEA layers. Figures 2 and 3 show a compositional map of the coated sample (aperture dimensions: $x = 10\mu\text{m}$, $y = 50\mu\text{m}$, $10\mu\text{m}$ steps, 100 scans, 4cm^{-1} resolution) based on absorptions at 1707 and 1737 cm^{-1} , respectively. As shown in Figs.2 and 3, a mixed phase of the two polymers was recognized around the interface region; this phase was approximately $70\mu\text{m}$ in thickness.

Fig.2 Infrared microspectroscopic functional group image based on the 1707/1464 cm^{-1} ratio of absorption frequencies.

Fig.3 Infrared microspectroscopic functional group image based on the 1737/1464 cm^{-1} ratio of absorption frequencies.

A molecular interaction (about $60\text{ }\mu\text{m}$ in depth) was detected between secondary amine groups in the polyurethane and carboxyl groups in the ethylene-acrylic acid copolymer/ethylene-ethyl acrylate copolymer.

Another example of polymer blends demonstrates how similar images can be obtained with transmittance spectra. The material studied is a PP(polypropylene)/PC(polycarbonate) blend. We performed a two-dimensional map on the material in order to obtain a compositional map. The conditions for the map were: (1) the aperture size was $10\times 10\text{ }\mu\text{m}$ that allowed radiation to reach the narrow-band MCT detector; (2) we made $10\text{ }\mu\text{m}$ steps in the x- and y-directions when moving the stage to collect the spatially specific data; and (3) signal averaging times were 256 scans at 8cm^{-1} resolution to obtain spectra of good quality. An image of the sample based on the PP component of the blend (2840 cm^{-1}) and PC component of the blend (1773 cm^{-1}) was generated. Figures 4 and 5 show compositional maps based on the 2840 cm^{-1} absorption of PP/PC (40/60) blends. The image is represented as an axonometric plot in Fig.4, and is represented as a two-dimensional plot in Fig.5. As observed from the images, polypropylene or polycarbonate dominant regions can be easily identified. These maps demonstrate the capability of the technique for determination of the spatially specific compositional heterogeneity of a material. Quantitative treatment can be carried out by plotting out the spectrum at a position of interest, as shown in Fig.5. In the future, we believe that quantitative determination of the solubility or mixing of the phases in a blend can be determined by a study of the specific domains.

Fig.4 Infrared microspectroscopy functional group image based on the 2840cm^{-1} absorption of a polypropylene/polycarbonate(40/60) blend. The image is represented as an axonometric plot.

CONCLUSION

Infrared microspectroscopic functional group imaging can be used to investigate the coated interface in two polymers and the compositional homogeneity in polymer blends. Interpretation based simply on analysis of an optical and/or electron microscopic image

could misrepresent the chemical compositional homogeneity. The physical state/morphology of a sample and its preparation for the infrared microspectroscopic examination must be carefully chosen to avoid determining incorrect values for the solubility of one phase of a polymer blend in the other. Although the technique currently limits examination to phases that are larger than approximately $10\text{ }\mu\text{m}$, the potential of the method for obtaining direct information on the compatibility of two phases in a biconstituent polymer system has been demonstrated. We are confronted with the $10\text{ }\mu\text{m}$ spatial resolution limit and the concerns associated with sample preparation. This technique will be applied to the research of a variety of adherent products.

Fig.5 Two-dimensional functional group image based on 2840cm^{-1} absorption of a polypropylene/polycarbonate(40/60) blend: $10\times 10\text{ }\mu\text{m}$ aperture, $10\text{ }\mu\text{m}$ step size in x and y direction 256 scans for signal averaging, 8cm^{-1} resolution.

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