Exploring Layered Structure of Composite Films Using FTIR Microscope

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Introduction

Multi-layered materials are commonly used in various industries such as packaging, construction and medical industries. Multi-layered structures may alter mechanical, acoustic and optical properties of materials. Identifying the chemical composition of different layers by studying the cross section of a multi-layered film is important in research and development of composite materials. With the aid of the Shimadzu AIM-9000 FTIR microscope, infrared spectra can be acquired with special resolution on the order of 10 microns along the cross section of composite films. Analysis of the FTIR spectra help to understand the formulation of different layers the polymer film is composed of.

Experimental

The AIM-9000 FTIR microscope was setup in combination with the IRTracer-100 FTIR spectrophotometer. The AIMsolution and LabSolutions IR software suite were used to maneuver the microscope and to set the experimental parameters. The optional mapping software allowed for scanning and measuring samples in the points, line or area modes. The "line" mode was particularly useful in the investigation of cross section of a film sample. By setting an appropriate aperture size, optimal signal was obtained while maintaining high spatial resolution over the cross section of composite films.

Parameter	Value
Instrument	Shimadzu AIM-9000 FTIR Microscope Shimadzu IRTracer-100 FTIR Spectrophotometer Ge ATR accessory for AIM-9000 FTIR Microscope
Optical Mode	Absorbance, Reflectance, ATR
Detector	Mid-band MCT detector with liquid nitrogen cooling
Spectral Range	4000-700 cm^{-1}
Resolution	8 cm^{-1}
Number of Scans	64

Table I: Experimental Parameters

Sample preparation is of vital importance in this experiment. The composite film under study was received from a commercial source. It was white in color and laminated on both sides. The sample was first cut to a smaller size of approximately 0.5 cm x 0.5 cm. It was then loaded onto a microtome and cut into thin slices appropriate for cross section study under an optical microscope. The cut thin slices of the polymer film were subsequently loaded onto a diamond window under a binocular optical microscope. Cares were taken in the placement of the sample such that the cross section can be observed in the field of view. The sample was then transferred to the AIM-9000 FTIR microscope for infrared investigation.

Figure 1. The composite film was loaded onto a microtome and cut into thin slices for cross section studies. The cut slices were loaded onto a diamond window and transferred to the AIM-9000 FTIR microscope

The front and back side of the film have different chemical composition. FTIR spectra of both sides were acquired by using ATR attachment with Ge crystal. Individual peak analysis and the search software revealed that one side of the film is polyethylene, the other side is 84% petrothene NA 117 (mixture of polyethylene and monomer) and 16% polyamide.

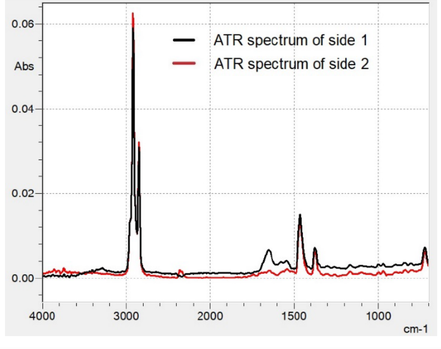

Figure 2. FTIR spectra of the two sides of the polymer film sample. One side (red) is polyethylene; the other side (black) is 84% petrothene NA 117 and 16% polyamide

The Shimadzu IRTracer-100 is a versatile FTIR bench that is capable of measuring in the Mid-IR, NIR and FIR range. When used as the light source to drive the AIM-9000 FTIR microscope it is measuring in the Mid-IR Range. It utilizes a 30º interferometer, the mirror speed is set at 9 mm/s.
The AIM-9000 FTIR microscope measures the sample in the transmittance, reflectance or ATR mode. A wide-field camera and an 15x objective are installed allowing convenient sample image zooming from macro size (10x13 mm) to micro size (300x 400 µm) The sample stage can move in a 70 x 30 mm area.

Figure 3. The Shimadzu AIM-9000 FTIR microscope system used to measure cross section of the polymer film samples

FTIR spectra of the film cross section were acquired using the Shimadzu AIMsolution software. Using the "line" mode of the optional mapping software, a series of measurement spots were placed along the direction of a preset line. The aperture sizes were set as 10x50 µm to allow for fine spatial resolution across the cross section while maintaining sufficient signal level (Figure 4).
Spectral difference from one side of the film to the other can be identified by comparing peak intensities of a few IR modes.

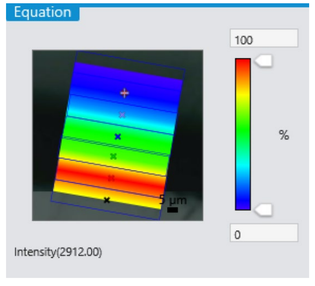

Figure 4. Heat map of the mode at 2912 cm^{-1}. The aperture size of 10x50 µm ensures fine spatial resolution across the sample.

The peak at about 2912 cm^{-1} was attributed to symmetric and antisymmetric stretching of C-H bond. Since a concentration gradient of $–CH_2-$ exists over the cross section, the peak intensity of this IR mode serves as a good indicator of varying chemical compositions. A monotonic change of the peak intensity was observed from one side of the sample to the other (Figure 5). Peak intensity analysis can be applied to other IR modes as well.

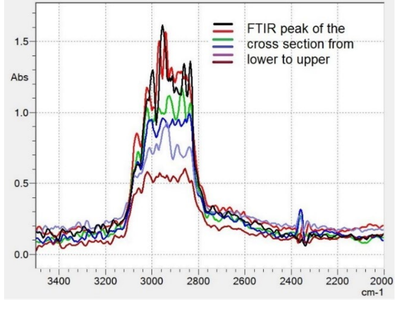

Figure 5. IR mode at about 2912 cm^{-1} over the cross section of the sample. A monotonic intensity decrease was observed from the lower side to the upper side of the sample.

In Figure 6 and Figure 7 peak intensity analysis was applied to the C=O bond at about 1640 cm^{-1}. The monotonic peak intensity change was not as obvious as that of the $–CH_2-$ stretch mode, probably because of the relatively low concentration of the polyamides (16%). It's worth mentioning that in addition to intensity analysis shown in the figures, the AIMsolution software allows for various types of analysis such as intensity ratio, peak height, peak height ratio, peak area, peak area ratio and purity analysis.

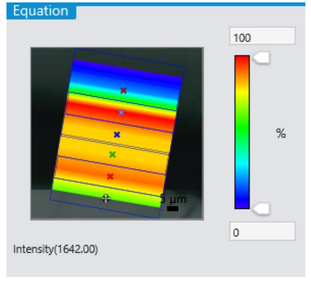

Figure 6. Heat map of the mode at 1640 cm^{-1}. over the cross section of the polymer film sample.

All the different types of analysis can be conveniently edited within the AIMsolution software. These analysis features and the high sensitivity of the liquid nitrogen cooled MCT detector make the AIM-9000 FTIR microscope an ideal tool in the investigation of cross section of polymer films.

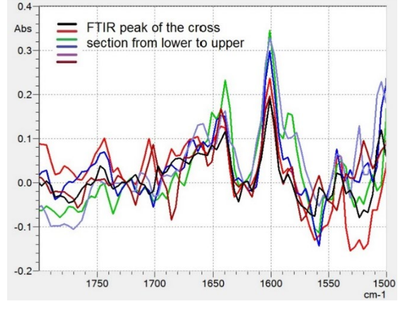

Figure 7. IR mode at about 1640 cm^{-1} over the cross section of the sample. Intensity increase was observed from the lower side to the upper side of the sample.

Conclusion

Shimadzu's IRTracer-100 FTIR spectrophotometer combined with the AIM-9000 FTIR microscope can be used to analyze the layered structure of composite films. The microscope system allowed measurement in the transmission, reflection and ATR modes. Sample preparation played an important role in the successful investigation of the film cross section. The AIMsolution software with the optional mapping software proved an indispensable tool in the cross section analysis. Experimental parameter setup proved equally essential in achieving satisfactory results. Even with the high sensitivity of the liquid nitrogen cooled MCT detector, it might have been difficult to obtain meaningful FTIR spectra had we not carefully selected the proper aperture dimension. Sampling, measurement and analysis were easily achieved with software control. Chemical composition variation was observed with spatial resolution of sub-10 microns level on the cross section of film samples.

References

- Application News No. FTIR-1901, *Characterization of Polymer Film Cross Section Using the Shimadzu AIM-9000 FTIR Microscope* (Shimadzu Scientific Instruments, Columbia, MD, December, 2018).