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FINAL REPORT

Development/Applications of FT-IR ATR
and Photoacoustic Dichroism Techniques
for Structural Characterization of Polymer Surfaces

by

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This final report gives a summary of objectives, technical progress, reports, publications and student theses completed during the period of the contract.
Development/Applications of FT-IR ATR and Photoacoustic Dichroism Techniques for Structural Characterization of Polymer Surfaces

Objectives

The main objective of this project was to develop new techniques for the characterization of polymer surfaces and interfaces, based on Fourier Transform IR attenuated total internal reflection (ATR) and photoacoustic dichroism (PAS) methods. The project involved both development of FT-IR PAS and ATR dichroism techniques using a specially designed crystal and attachment, and the demonstration of these techniques for the molecular characterization of selected polymer surfaces.

Background

Measurement of bulk molecular orientation and degree of crystallinity by transmission IR dichroism is a well-established technique, but it is only applicable to very thin polymer films. For thick samples, ATR dichroism with its well-developed theoretical basis was potentially useful, but suffered from severe experimental difficulties. The initial goal of this project was to overcome such experimental difficulties to develop ATR dichroism for the use of the broad polymer community.

Technical Summary

The major effort during the initial period of the project was devoted toward developing a modified ATR attachment, using a symmetrical, double-edged internal reflection crystal (2,3). This modified attachment allows the sample to be rotated without disassembling and reassembling operations which change the contact area between the polymer sample and the ATR crystal. This eliminated the need for the correction of the reflectivities to an internal standard band. The usefulness of this attachment which provides information on two-dimensional orientation has been demonstrated on two types of polypropylene, uniaxially drawn and injection molded (3).

For polymer films which cannot have a good contact with the ATR crystal due to the brittle nature or the rough surfaces, FT-IR photoacoustic (PAS) dichroism technique can be employed either by rotating the sample or the polarizer. This was found to provide quantitative two-dimensional orientation values (4), in spite of weak signals and saturation on high intensity bands due to deeper penetration of the IR beam into the sample.

Toward three-dimensional surface structural analyses by FT-IR ATR dichroism technique, a new ATR attachment was designed and tested. The main feature of this new attachment is a rotatable ATR sample holder which was mounted on a rotating stage. The rotation axis was designed so that it coincided with the entrance plane to the crystal. The angle of incidence could be adjusted by a gear and worm-screw to precise angles (5). This new attachment was tested on well-characterized polymer films (uniaxial, biaxial polypropylene and uniaxial polyethylene terephthalate). From the four possible dichroic ATR spectra, all the necessary optical constants were calculated and used to estimate the surface degree of crystallinity and molecular orientation averaging about a micron in depth. The results on surface crystallinity agreed well with the values from x-ray and DSC studies.
The ability to alter the angle of incidence accurately with the new ATR apparatus allowed depth profiling from about 1 to 15 microns. The results revealed some subtle changes in orientation and crystallinity as a function of depth on the surface of uniaxially drawn polypropylene (5).

In order to overcome beam divergence and back reflection due to non-integer reflections with face-cut crystals when a wide range of incidence angles is used, as in depth-profiling, a new ATR attachment using a hemispheric crystal had been designed. In this attachment, the sample is held against the crystal surface at a fixed point in space. The goniometer has been designed so as to rotate the crystal horizontally as well as vertically. Under this condition, the resulting beam after a single reflection is always parallel at a precisely known angle of incidence with a constant incident beam energy, regardless of the incident angle. A preliminary study showed promising results (7,8).

In FT-IR PAS dichroism studies, we were able to obtain three dimensional orientation measurement by tilting the sample (45°) in a specially designed PAS cell. The experimental data will be analyzed by extending the theory for the photoacoustic effect on solid surfaces to anisotropic solids.

While we continue to improve and develop new ATR and PAS attachments, our first ATR attachment has been adopted by many laboratories in the world, (e.g. 3M, Rhone-Poulene, ICI, National Research Laboratory of Canada, University of Washington). Our 3-D ATR attachment has been adopted by Monsanto. They are being used to characterize a variety of polymers and composites such as PEEK and liquid crystalline polymers.


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