



Examining Molecular Orientation Using ATR Spectroscopy

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Many plastics and polymers are drawn or machined to produce slightly different physical and chemical properties by orienting the molecules therein. The orientation of the molecules within the material can effectively be examined using infrared ATR spectroscopy.

Oriented materials are characterized by chemical bonds aligned along a particular axis. Polymers and plastics are not inherently oriented, but some production methods induce an orientation of the molecules along a certain direction. Analyzing these oriented samples to correlate their properties with the degree of orientation is important both in materials development and for quality control.

For internal reflectance (ATR) measurements, absorption results from the interaction between the sample and the evanescent wave. The electric field of the evanescent wave for different directions depends on the incident polarization and angle. For s-polarized light, the incident light has an electric field oscillating perpendicular to the plane of incidence. This electric field can excite only those dipoles in the sample that have components in that direction. Dipoles oriented in the other two perpendicular directions cannot be excited by this electric field. Rotating the sample around the normal to its surface changes the orientation of the dipoles, allowing investigation of all dipoles parallel to the sampling plane.

This note explores using ATR measurements to probe orientation. In particular, the Seagull variable angle accessory is for fixed 67° measurements of an oriented plastic.

Experimental

The ATR measurements were carried out using Harrick's Seagull™ with its ATR Rotator (see Figure 1) and wire grid polarizer (KRS-5 substrate) on a highly oriented sample. The Seagull was configured for an incident angle of 67° with a ZnSe hemispherical ATR crystal. Such a high angle of incidence was necessary to eliminate spectral distortions that occur close to critical angle. The Seagull pressure applicator was hand-tightened to compress the sample against the ATR crystal. S-polarized radiation was used for all orientations of the sample, so the electric field direction and strength were identical for all measurements.

All spectra were recorded on an FT-IR spectrometer with a DTGS detector, set for 32 scans at an 8 cm^{-1} resolution.

Results and discussion

Figure 2 shows the spectra of the sample, taken in 10° increments, representing a 90° rotation of the sample. This allows one to quickly see which bonds exhibit orientation. For instance, the bond at 1000 cm^{-1} exhibits a large degree of orientation while the bond at 760 cm^{-1} appears largely unaffected. In this particular sample, most of the major bonds are oriented in the



Figure 1: The Seagull Variable Angle Reflectance Accessory shown with ATR Rotator.

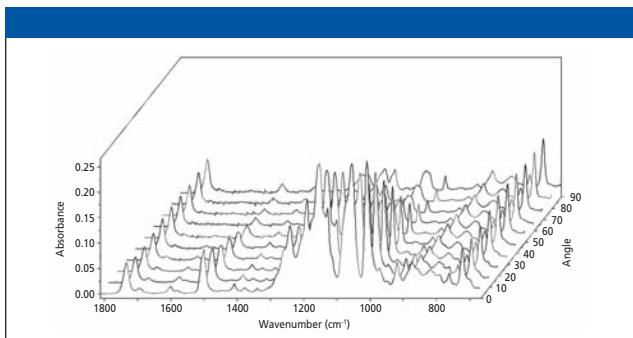


Figure 2: ATR Spectra of an oriented sample, measured in 10° increments over the 90° rotation of the sample.

same direction, that defined by the electric field at the sample rotation angle labeled 80°.

Conclusion

In conclusion, it is clear that ATR, using the Harrick Seagull with its ATR Rotator, enables detailed analysis of oriented samples. A study of bond orientations referenced to the external sample dimensions is straightforward.

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