



Bridge You and Nano

## Exponential Business and Technologies Company

### Monitoring Polymer Orientation using Raman Microscopy

The orientation of polymers in a 3D arrangement plays important roles in determining not only the strength of the cured polymer but also affects a host of other physical properties like crystallization temperatures, glass transition temperatures, and wettability. Methods such as polymer extrusion are designed to assemble polymeric structures in a particular direction. Additional parameters such as the curing rate and downstream addition of additives all can critically affect the final polymer structure. As such, determining polymer orientation during product development, as a quality control check, and for failure analysis is critical.

The intensity of Raman scattering is dependent upon the angular relationship between the incident laser radiation electric field, the Raman scattering tensor (the functional group interacting with the laser radiation), and the polarization angle of the analyzer. By controlling the angle and orienting samples wisely, the analyst can obtain important information regarding the directional organization of molecules in the sample. This is well-suited for investigations into failure analysis, polymer extrusion, or confirming degrees of crystallinity or amorphousness.

To determine the relative orientation of functional groups present in a polymer, a sample of packaging tape was placed on a glass slide and imaged using a WITec 300RA Confocal Raman Microscope. The peak pattern indicates the transparent backing of the tape (not the adhesive) is made from polypropylene. The incident laser radiation was orientated parallel to the x-axis. The results of the experiment are shown in Figure 1. The polarization of the analyzer was first set to  $0^\circ$  (orange, Figure 1) and then increased in  $30^\circ$  increments to  $90^\circ$  (black, Figure 1).

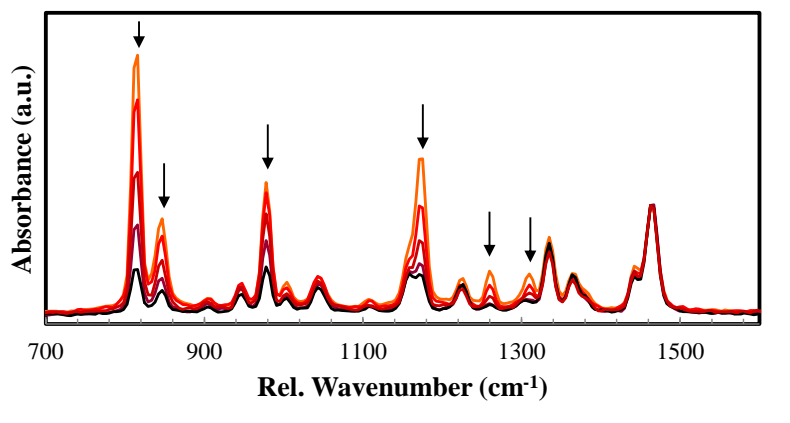


Figure 1. Polarized Raman spectra of transparent packaging tape. The angle between the incident laser light and the analyzer was set to  $0^\circ$  (parallel),  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ , and  $90^\circ$  indicated by the lines darkening from light orange to black, respectively. Arrows indicate the peak intensity shifts as the polarization analyzer was rotated.



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As can be seen from Figure 1, some absorption bands are sensitive to the angle of the polarization of the analyzer ( $840\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$ ,  $1180\text{ cm}^{-1}$ ), and some bands are not ( $1480\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$ ). This variation is expected for highly organized, rigid polymer structures in which absorption bands associated with the backbone of the polymer (C-C stretching bands) are polarization dependent, but the bands associated with less ordered, more symmetric side chains of the polymer ( $\text{CH}_3$  stretching bands) are not polarization dependent.

The relative heights of particular peaks can indicate the orientation of the polymer. The peaks can be analyzed for liquid crystalline polymers, amorphous polymers, or cured polymers and the interpretation is relatively straightforward so long as the spectral features for the ordered and amorphous reference states are known. In this example, the packaging tape was oriented in two directions: one in which the incident laser light and analyzer polarization were both parallel to the direction of the polypropylene (Figure 2, a) and one in which the incident laser light and analyzer polarization were both oriented perpendicular to the polypropylene strands (Figure 2, b). The results are summarized in Figure 2 and there are some immediately apparent spectral changes that occur as a result of the high degree of orientation of the polypropylene.

The molecular orientation of polymers significantly affects the resulting properties of the final product. Disoriented polymers have been implicated in a wide variety of failure analyses across almost all industries including the medical device, pharmaceutical, and automotive industries. Polarized Raman spectroscopy is a valuable tool used to monitor the macromolecular orientation of molecules as well as the molecular orientation of functional groups to assist with product development and optimization.

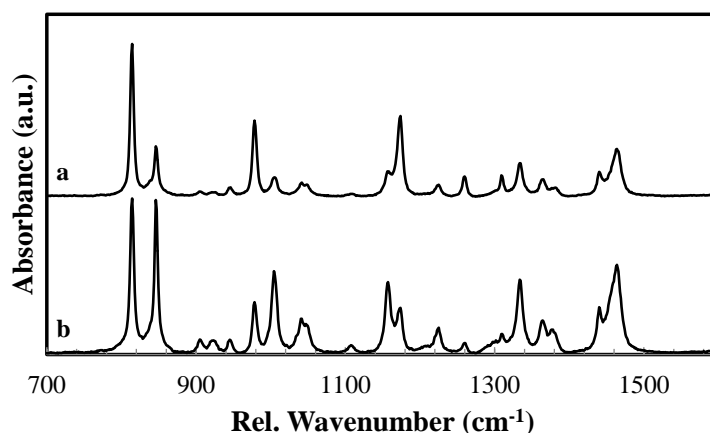


Figure 2. Polypropylene polymer oriented in two directions: (a) incident laser light and analyzer polarization both parallel to the direction of the polypropylene, and (b) incident laser light and analyzer polarization both perpendicular to the direction of the polypropylene.