

## Visible and IR polarizers increase insights from FTIR microscopy analysis

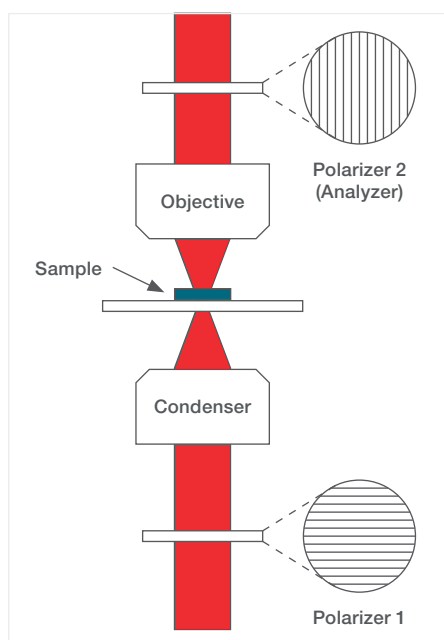


Figure 1. Schematic representation of crossed polarizer configuration in a microscope.



Figure 2. Thermo Scientific Nicolet RaptIR+ FTIR Microscope.

### Introduction

Infrared microscopy is a valuable tool to characterize small samples (<100  $\mu\text{m}$ ) and to understand the spatial distribution of chemical compounds within a sample. However, an additional level of insight is provided by using polarizers in microscopy. We discuss in this note the use of polarization in both visible and infrared applications. The former allows for visual discrimination between samples or within a sample even before the collection of spectra, while the latter enables better understanding of the orientation of molecular structures in materials such as polymers. Two separate pairs of polarizers are used for visible and infrared polarization. One polarizer between the light source and sample is called the polarizer, while a second polarizer placed after sample is called the analyzer (see Figure 1). The polarizer and analyzer can be rotated together or independently. Polarization studies can be done with the polarizer alone to produce plane-polarized light, or with both the polarizer and the analyzer, for cross-polarized light.

One well-established technique involving visible polarizers is the use of crossed polarizers. As shown in Figure 1, this involves the use of both a polarizer and analyzer. Since the polarizers are oriented at ninety degrees to each other, all the light passing through is normally blocked, resulting in a black field. However, when samples exhibiting birefringence are viewed, they will be visible. This occurs since light at different polarizations will travel at different velocities through birefringent materials, resulting in a phase difference which can produce different observed colors and thereby allowing rapid classification of samples by visual inspection, even before evaluation by FTIR spectroscopy.

Alternatively, when used with polarized IR light, infrared spectroscopy has the capability to probe molecular orientation within a sample. This ability results from the selection rules for infrared activity which require that there must be a dipole moment change and that the electric field vector of the light must align with the change in dipole moment. For unpolarized light consisting of randomly orientated electric field vectors, the portion of the light that aligns with the bond axis will cause absorptions in the IR spectrum. But if an IR polarizer is used, the IR band intensity will be maximized when the light is polarized in the same direction as the oscillating dipoles of specific molecular vibrations.

Images and spectra collected for this application note were obtained using a Thermo Scientific<sup>™</sup> Nicolet<sup>™</sup> RaptIR+<sup>™</sup> FTIR Microscope (Figure 2) coupled to an Thermo Scientific<sup>™</sup> Nicolet<sup>™</sup> iS50R FTIR Spectrometer. The RaptIR+ was configured with completely automated polarizer control, including insertion/removal of the filters from the light path as well as setting of the polarizer angle through the OMNIC<sup>™</sup> Paradigm Software interface.

### Crossed Visible Polarizer Examples

To illustrate the effects of birefringence, samples were presented for visual analysis. Three individual textile fibers of polyester, nylon, and cotton were positioned on a glass slide, then viewed in normal transmission mode. These were found to be visually similar when no polarizers were selected, as shown outside of the blue rectangle in the center of Figure 3. Once the option for crossed polarizers was selected through Paradigm software, the image in the center of the Figure 3 was obtained. As expected, most of the image is now black, since the crossed polarizers block any light that has not passed through birefringent sample material and glass from the slide itself is known to be a highly isotropic material, exhibiting no birefringence. The crossed polarizer view in Figure 3 (center) shows that the polyester fiber (top) is almost not visible, exhibiting very low birefringence. In contrast, the middle nylon fiber (middle), can be clearly seen in the crossed polarizer image indicating a higher level of birefringence. The cotton fiber (bottom) is the brightest of the three fibers, exhibiting the most birefringence. This natural fiber contains high levels of cellulosic material in its secondary cell wall which is directionally aligned with the cotton fiber, resulting in a high degree of orientation and therefore birefringence.

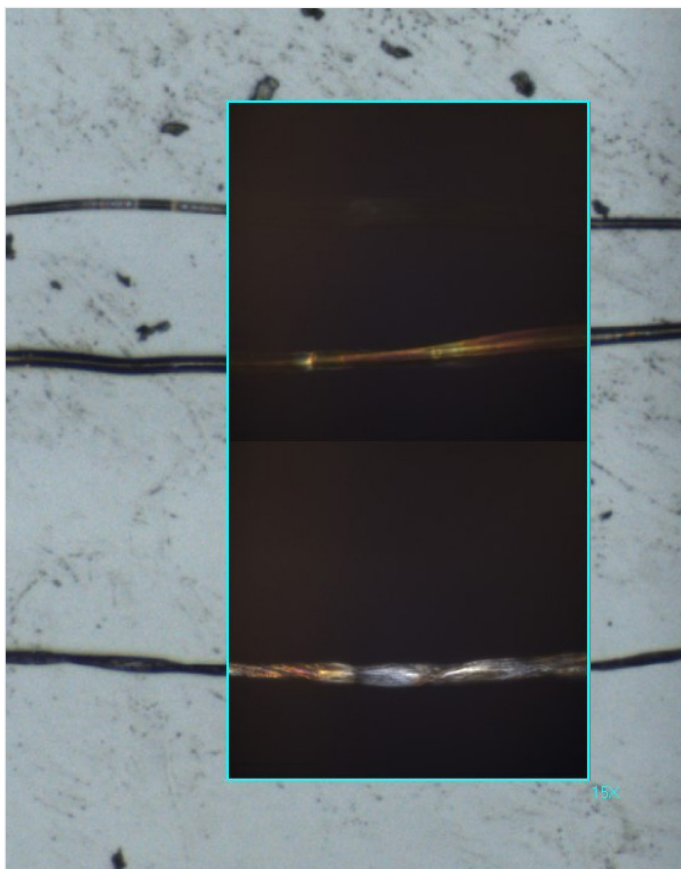


Figure 3. Fibers showing varying degrees of birefringence. The image observed with crossed polarizers (black area) is shown superimposed over the view with no polarizers used. Fibers top to bottom: polyester, nylon, cotton.

Figure 4 illustrates the cross section of a polymer laminate sample when crossed visible polarizers are applied. The cross section was essentially uncolored in the normal view. When viewed through crossed polarizers, however, individual layers can be seen with varying brightness and interference colors, indicative of the different compositions of each layer. The interference colors seen with crossed polarizers relate to a material's thickness, molecular structure, amount of orientation and crystallinity. For polymers, the degree of straightness of a polymer chain and the presence of side groups on the polymer chain can also impact the overall observed birefringence. In this case, the appearance of the sample under cross polarizers helps guide the ensuing FTIR analysis in terms of the number of layers as well as the thickness of each layer, which can be difficult to assess with normal visual inspection.

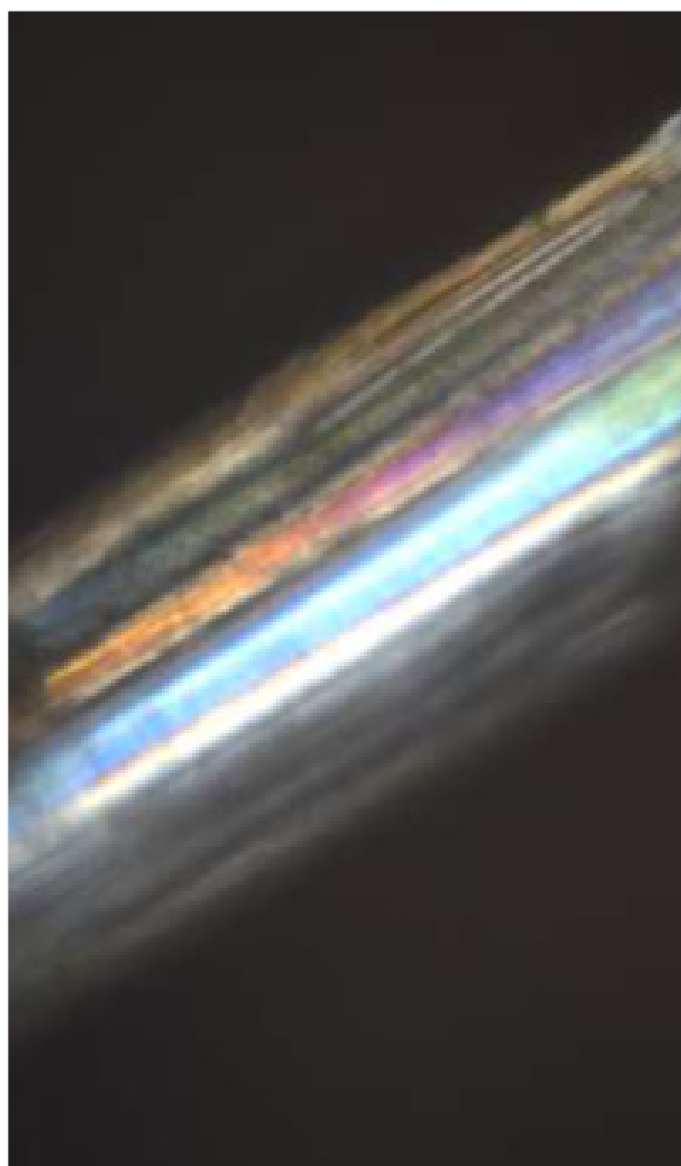
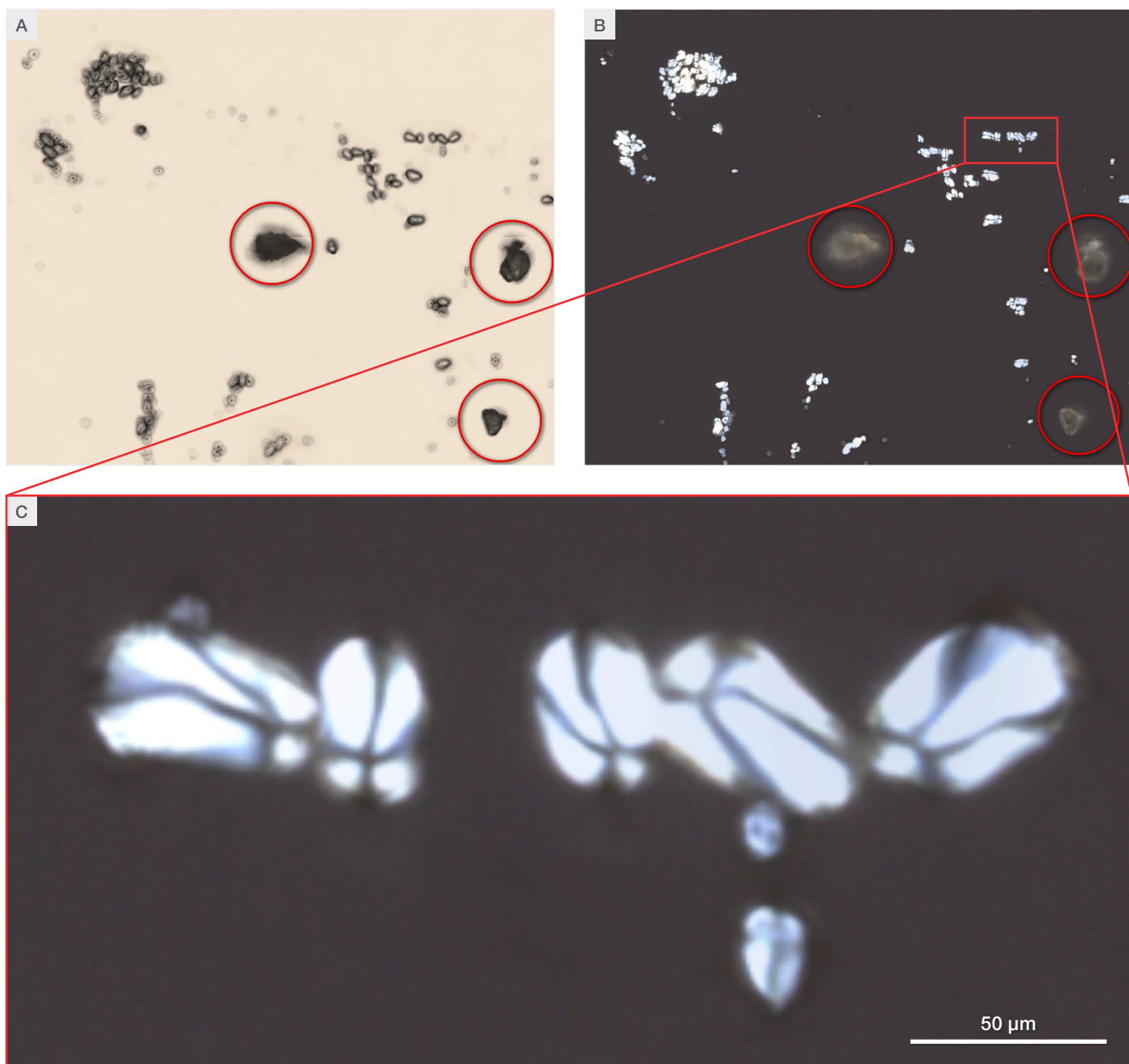


Figure 4. Cross section of a multi-layer polymer laminate when viewed with crossed visible polarizers. The specific differences of the many layers are obvious due to differences in birefringence between the layers in the sample.



**Figure 5. Potato starch granules and gelatin powder with normal viewing (A) and with crossed polarizers (B) and (C). Granules of gelatin are shown circled.**

Figure 5 shows the images of potato starch granules and a few powdered gelatin (collagen) granules, mounted on a glass slide. In normal transmission viewing mode (5A) the starch granules appear featureless and are only differentiated from the gelatin particles by size. With crossed polarizers (5B), the starch granules appear much brighter, due to their birefringence resulting from the semicrystalline nature of the starch granules. A closer view of the starch grains (Figure 5C) shows the Maltese cross pattern normally associated with starch granules. The lack of crystallinity/birefringence of the gelatin makes them significantly darker than the starch granules. Thus, discrimination between these two particle types is readily accomplished even before the collection of FTIR spectra.

In the crossed polarizer examples shown above, images were obtained from samples mounted on glass slides. Subsequent IR measurement was performed by the Nicolet RaptIR+ FTIR Microscope in ATR mode. Alternatively, samples could be transferred to IR-transparent salt windows or gold coated slides for transmission or reflective measurements, respectively.

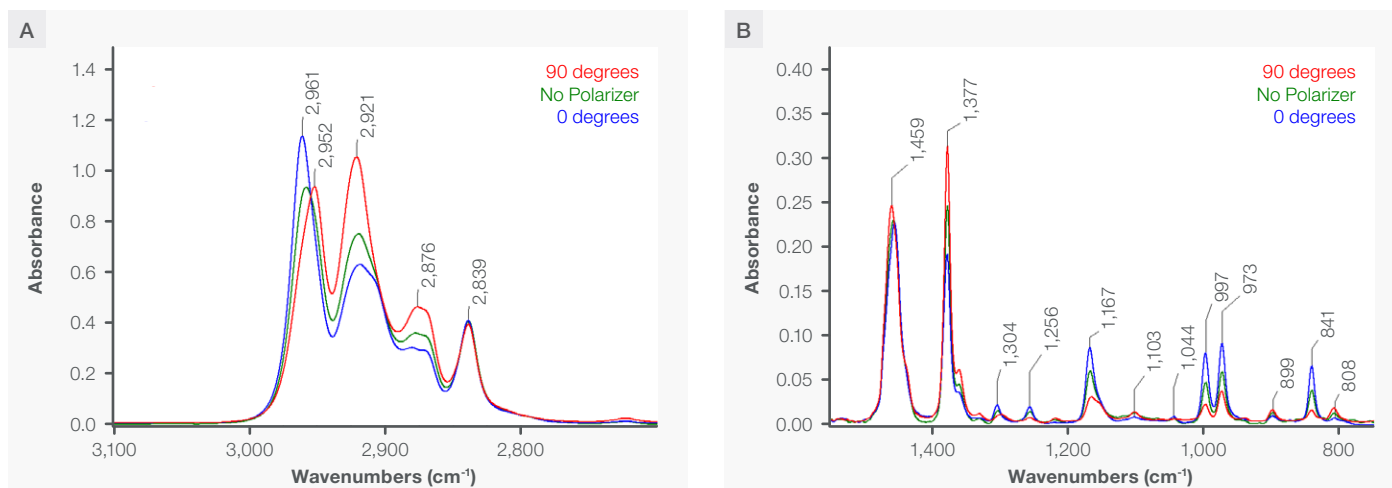


Figure 6. FTIR spectra of a polypropylene fiber obtained using IR light polarized at  $0^\circ$  and  $90^\circ$  degrees as well as with unpolarized IR light. Regions shown are the CH stretch region (A) and “fingerprint region” (B).

### IR Polarization and Orientation

Two polypropylene samples, one a single fiber, and the other a thin slice from a food container were measured by polarized infrared light in transmission mode. Despite their similar chemical composition, these two samples differ in their degree of alignment between the polymer chains within each sample because of different manufacturing processes. Fibers are usually created through an extensional process, which results in the polymer chains within the fiber being generally parallel to the axial direction of the fiber. On the other hand, food containers are often created through a molding process which results in polymer chains that are less consistent in their overall orientation. With an IR polarizer, the electric field vector of the IR beam can be adjusted through the polarization angle. Samples with polymer chains that tend to be aligned with each other experience more pronounced spectral intensity change with polarization angle, because the polymer chains align with the polarized light at certain angles. Conversely, samples of low alignment of polymer chains yield essentially the same spectrum independent of IR polarizer angle because there will be some chains that align with the incident light at any polarizer angle. Therefore, by using polarized IR light, the degree of alignment between polymer chains can be assessed. This knowledge is important since many physical properties of polymers, such as tensile strength, barrier strength and Young's Modulus strongly correlate to the degree of polymer chain alignment.<sup>1</sup>

The measurement of spectra from the polypropylene fiber sample was carried out as follows. A single polypropylene fiber was hand-rolled flat to approximately a 50 micron width. The fiber was mounted over an opening in a sample holder in “east-west” orientation to allow transmission measurements without the need for any IR window. Spectra of the fiber were collected with the Nicolet RaptIR+ FTIR Microscope under three different polarization conditions: first with no polarizer, second with the IR polarization set to  $0^\circ$  (electric field vector perpendicular to the axial direction of the fiber) and third with the IR polarizer set to  $90^\circ$  (electric field vector parallel to the axial direction of the fiber). An aperture setting of  $25\ \mu\text{m} \times 25\ \mu\text{m}$  and 128 scans co-addition were used for all measurements. As shown in Figure 6, the obtained spectra show dramatic differences depending on the orientation of the IR polarized light of each measurement. Also, the spectrum collected with no polarizers shows intermediate band intensities when compared to the  $0^\circ$  and  $90^\circ$  polarized IR light spectra, as expected. The observed results are in good agreement with previous work reporting the IR polarized spectra of isotactic polypropylene and containing band assignments to the spectra<sup>2</sup>.

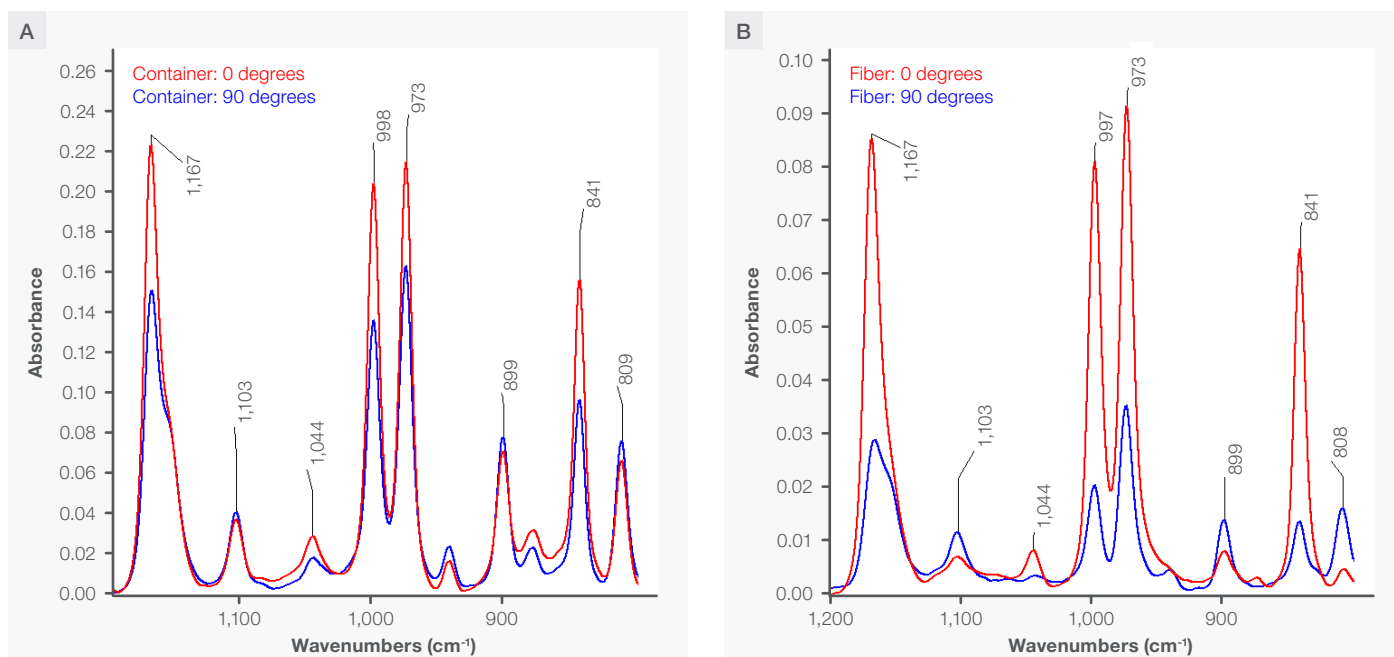


Figure 7. Comparison of IR polarized spectra of (A) a thin slice from a polypropylene food container and (B) a polypropylene fiber.

Sample preparation for the food container sample consisted of simply slicing a thin strip of material, about 5 mm long and less than 50 microns thick for transmission analysis. The polarized IR spectra of this strip were collected in the same manner as the fiber; however, a wider range of polarization angles were collected since, unlike the fiber sample, there were no obvious indicators which sample orientation would correspond to polarized light falling parallel or perpendicular to the overall polymer chain direction. Results for the polarization angles displaying spectral extremes and 90 degrees apart are shown above in Figure 7A in the 1200-800  $\text{cm}^{-1}$  region. These spectra can be compared to the spectra from the fiber sample in the same spectral region (Figure 7B). The two samples show overall intensity differences simply due to variance in the thickness of the two samples, but the higher degree of orientation in the fiber sample is demonstrated by it displaying significantly more change in spectral intensity between extreme polarization angles. For example, in the fiber spectra the peak at 841  $\text{cm}^{-1}$  was reduced 81% when comparing the 0° polarization spectrum to the 90° polarization spectrum, whereas the same comparison yielded only a 32% intensity reduction for the container sample spectra.

## Conclusions

The use of visible and infrared polarized light, although used for different purposes, are both valuable tools for FTIR microscopy analysis. As demonstrated here, the use of crossed visible polarizers reveals differences in birefringence within a sample instantaneously. This can be particularly useful for samples that appear uniform in normal visible viewing mode but have distinct regions of different birefringence, as the technique provides information on characteristics such as ingredient distribution, crystal form, and sample structure. On the other hand, by taking advantage of the different IR spectra obtained using IR polarized light at different angles relative to the sample, the application of IR polarization measurements can be used to establish the degree of chain alignment within a sample. This is important since the degree of alignment of polymer chains can be a significant indicator of processing effects and material performance.

## References

1. N. Overall "Using Polarized Vibrational Spectroscopy to Characterize Molecular Orientation in Polymers." Spectroscopy Vol. 15 Issue 9 Sept (2000) pp. 38-46
2. C.Y. Liang and F.G. Pearson "Infrared Spectra of Crystalline and Stereoregular Polymers. Part I. Polypropylene." Journal of Molecular Spectroscopy 5, (1960) pp.290-306

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