

Chemical and structural analysis of a single modacrylic fiber using polarized reflectance FTIR microscopy

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Keywords

FTIR, modacrylic fibers, polymer

Application benefits

The setup for the polarized experiments is easy to implement and allows for an effortless switch between normal and polarized FTIR microspectroscopic measurements. The methodology described in this note is generally applicable for the chemical and structural analysis of polymer fibers.

Thermo Fisher Scientific solutions

Nicolet iS50 spectrometer
Nicolet Continuum microscope

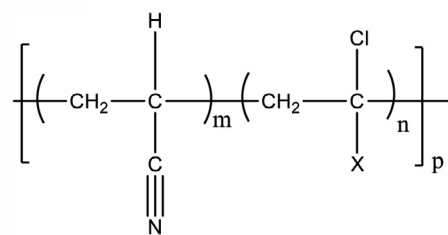
Abstract

In this application note, the workflow for the chemical and structural analysis of a single modacrylic fiber using FTIR reflectance microscopy is described. The FTIR spectrum provides a wealth of information on the chemical composition of the fiber. In addition, by placing a ZnSe wire grid polarizer in the beam path exiting FTIR spectrometer, a series of polarized FTIR reflectance measurements were successfully carried out. The results indicate that the C≡N groups exhibit a high degree of orientation whereas the C=O groups are randomly oriented. The nitrile bonds are oriented approximately perpendicular to the longitudinal fiber axis.

Introduction

Infrared spectroscopy is a commonly used analytical technique for the analysis of natural and synthetic fibers in forensics^{1,2}, textile manufacturing³⁻⁷, and art conservation and restoration⁸. By combining the power of FTIR spectroscopy and optical microscopy, FTIR microscopy can provide visual observations of microscopic samples and valuable chemical information about a single fiber. When coupled with polarized radiation, FTIR microscopy can also aid in understanding the molecular orientation and morphology of fibers, which has a profound impact on fibers' mechanical strength and processability³⁻⁷.

Modacrylic fibers (Figure 1) are synthetic copolymers containing 35-85% of polyacrylonitrile (PAN), 15-65% of comonomers such as poly vinyl chloride (PVC) and poly vinylidene chloride, and a variety of organic/inorganic additives. Because of the large magnitude of the dipole moment of the nitrile groups in PAN, there are strong intra-chain and inter-chain interactions through secondary bonding. As a result, modacrylic fibers contain discrete crystalline PAN domains and amorphous domains of comonomers and additives. While the high orientation of the crystalline molecular segments impart high tensile strength and modulus to the fibers, the amorphous phase gives rise to toughness and dyeability⁶.



X = H for poly vinyl chloride
X = Cl for poly vinylidene chloride

Figure 1. Representative chemical structure of modacrylic fibers.

In this application note, we describe the chemical and structural analysis of a single modacrylic fiber via FTIR reflectance microscopy. The principles and the general applicability of employing FTIR reflectance microscopy in single fiber analysis are also discussed.

Experimental

A single modacrylic fiber was isolated from a fiber swatch (Warp Stripe 13 Fiber Fabric, Testfabrics, Inc.) under a stereoscope, and pressed out with the back end of a roller knife onto a gold substrate.

A Thermo Scientific™ Nicolet™ iS50 FTIR Spectrometer, equipped with a KBr beamsplitter, was coupled to a Thermo Scientific™ Nicolet™ Continuum™ Infrared Microscope, which houses an MCT-A detector and a 15× objective.

All background and sample acquisitions were acquired at 8 cm^{-1} resolution with a minimum of 64 scans from $4000 - 800\text{ cm}^{-1}$ with a sampling aperture of $60 \times 30\ \mu\text{m}$. Background scans were acquired for each polarizer orientation on the bare gold substrate.

For the polarization experiments, a ZnSe wire grid polarizer was mounted in the beam path between the Nicolet iS50 and the microscope (Figure 2a). The polarizer, which has an adjustable wheel that controls the wire grid orientation, produces an electrical field that is perpendicular to the corresponding wire grid (Figure 2b). When the dial is set to 0° , the longitudinal grid affords an electric field with an east-west (EW) vector; conversely, a north-south (NS) electric field is generated at the 90° setting.

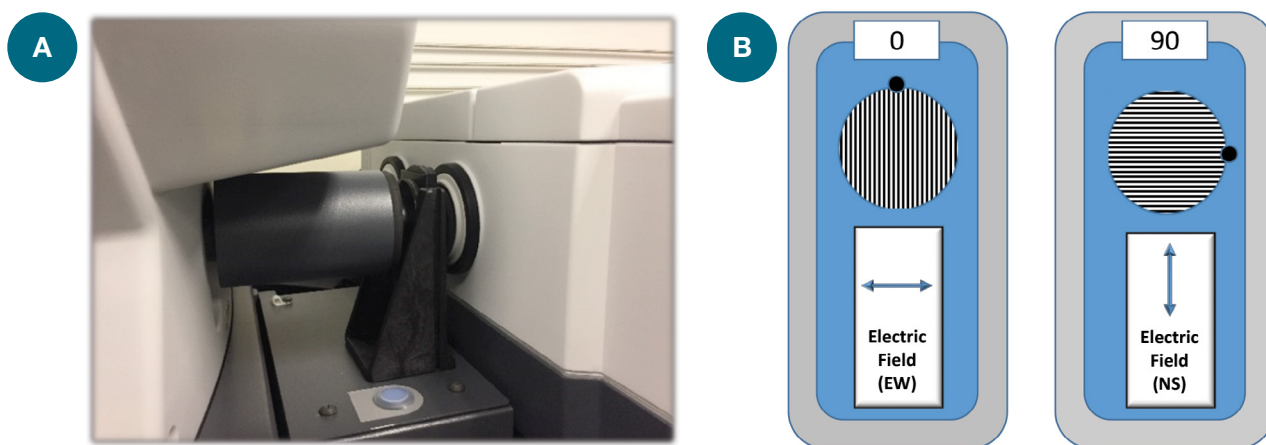


Figure 2. (a) A ZnSe-FTIR polarizer placed in the beam path between the Continuum microscope and Nicolet iS50 spectrometer for polarized FTIR reflectance microscopy experiments. (b) Orientation of wire grid in ZnSe polarizer and corresponding electrical field output.

Results and discussion

Figure 3 shows the FTIR spectrum of the modacrylic fiber without the polarizer. The rectangular illumination in Figure 3a represents the sample area of spectral acquisition. The bands at 2927 cm^{-1} and 2854 cm^{-1} (C–H stretching in CH_2), 1440 cm^{-1} (C–H bending in CH_2) and 1357 cm^{-1} (C–H bending in CH) are characteristics of aliphatic C–H groups along the PAN backbone. The weak feature at 1625 cm^{-1} is attributed to the C=C stretching, likely from the residual monomers. Of particular interest in

this study are the bands at 2243 cm^{-1} and 1732 cm^{-1} , which are ascribed to the $\text{C}\equiv\text{N}$ stretching of the acrylonitrile unit in the polymer chain and C=O stretching, respectively⁹. A library search of this spectrum yields a high correlation match (97%) with a modacrylic fiber that contains vinyl chloride, vinyl acetate, and antimony trioxide, although any carbonyl-containing comonomers and/or additives could contribute to the carbonyl band at 1732 cm^{-1} . It is worthy to point out that $I_{\text{C=O}}/I_{\text{C}\equiv\text{N}}$ was successfully used to compare and discriminate among acrylic fibers within the same subgeneric class in forensic applications¹.

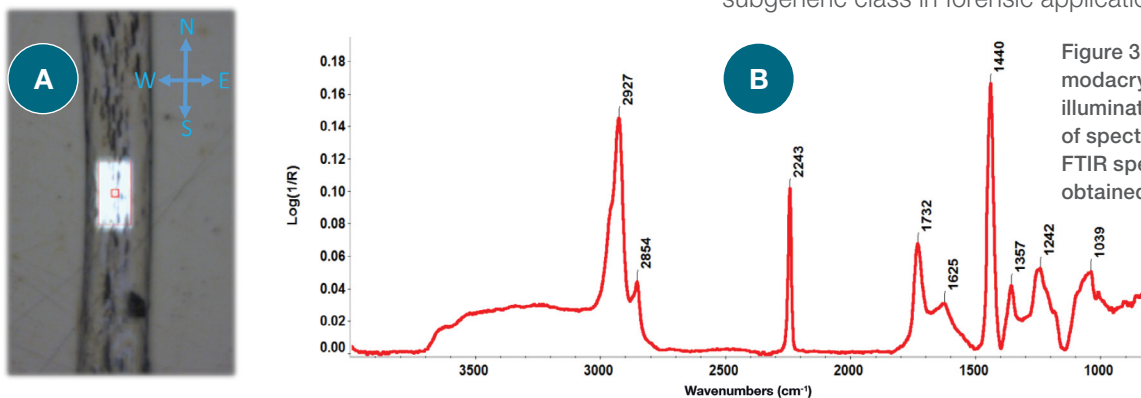


Figure 3. (a) Visual image of the modacrylic fiber. Rectangular illumination represents the sample area of spectral acquisition. (b) Reflectance FTIR spectrum of the modacrylic fiber obtained without polarizer.

Next, a polarizer was placed into the beam path and a series of spectra were obtained at varying grid angles (Figure 4). Radiation passing through a polarizer in the infrared beam path has a directional vector. If the resulting vector is biased towards the dipole moment orientation of a bond, signal intensity is augmented. Conversely, if the polarized electric field and the dipole moment orientation are crossed, the signal is hindered¹⁰. For PAN fibers, the intensity variation of the C≡N stretching band at 2243 cm⁻¹ in polarized FTIR measurements provides valuable insight to molecular orientation of the fibers⁵⁻⁷.

At 45°, the electric field has equal contributions from both NS and EW orientations and consequently, the resulting peak (Figure 4, aqua curve) has a similar intensity as the one obtained without the polarizer (Figure 4, red curve). As the grid angle moves to 30°, the electric field has more EW contribution than NS, resulting in an increase in peak intensity (Figure 4, light green curve). The peak intensity reaches its maximum (Figure 4, blue curve) at 0° grid angle where the electric field is EW. Following the same trend, when the grid angle is set at 60°, the electric field has more NS contribution than EW, resulting

in a decrease in peak intensity (Figure 4, pink curve) from the one at 45° (Figure 4, aqua curve). The peak intensity reaches its minimum (Figure 4a, dark green curve) at a 90° grid angle where the electric field is NS. In contrast, the intensity of the carbonyl peak at 1732 cm⁻¹ remains relatively constant regardless of the grid angle. Most likely, the carbonyl bonds from the comonomers and/or additives are randomly oriented and reside in the amorphous phase of the fiber.

Clearly, the C≡N group exhibits a high degree of orientation. The intensity of the C≡N band reaches its maximum when the polarized electric field is in the EW direction, indicating that the nitrile bonds are oriented approximately perpendicular to the longitudinal fiber axis (NS), as illustrated in the upper right inset of Figure 4. This observation is consistent with the previous reports^{5,6}. Furthermore, the ratio of the peaks when the polarized electric field is parallel and perpendicular to the fiber axis, respectively, can be used to calculate the degree of molecular orientation of polymer fibers, a key determining factor of their performance. Detailed analysis of molecular orientation is beyond the scope of this technical note and can be found elsewhere⁵⁻⁷.

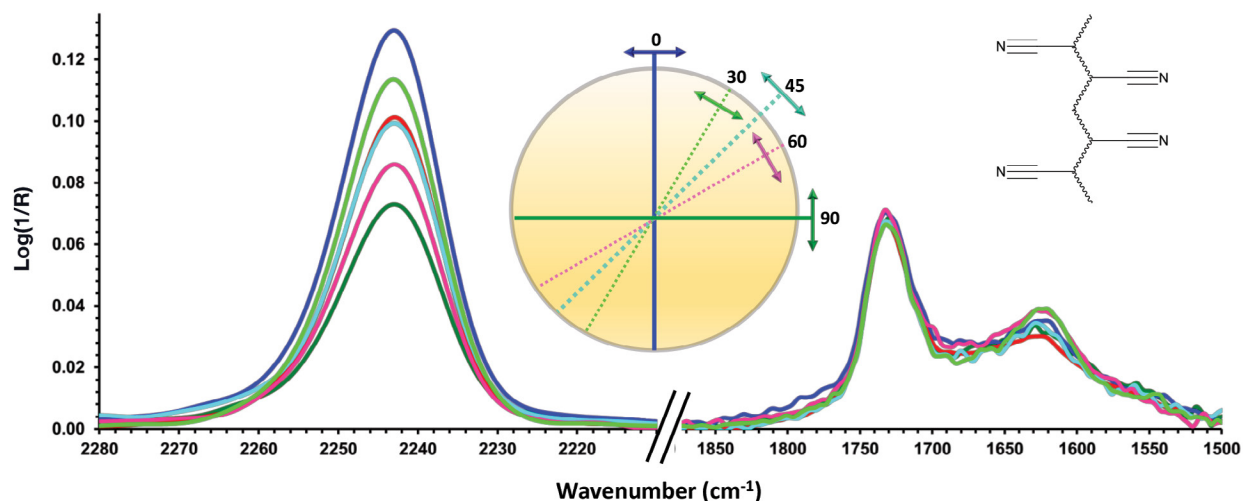


Figure 4. The C≡N stretching band at 2243 cm⁻¹ (left) and the C=O stretching band at 1732 cm⁻¹ (right) of the PAN fiber at different grid angle. The middle inset is the schematic of a polarizer with differing electric fields. The numbers denote the grid angle and the lines represent the wire grid orientation. The arrows correspond to the electric field orientation of the light passing through the polarizer. The upper right inset illustrates the C≡N orientation with respect to the polymer backbone.

Conclusions

In this application note, the workflow for the chemical and structural analysis of a single modacrylic fiber using FTIR reflectance microscopy is described. The FTIR spectrum provides a wealth of information on the chemical composition of the fiber. A library search of the spectrum yields a high correlation match (97%) with a modacrylic fiber that contains vinyl chloride, vinyl acetate, and antimony trioxide. By placing a ZnSe wire grid polarizer in the beam path exiting FTIR spectrometer, a series of polarized FTIR reflectance measurements were

successfully carried out. The results indicate that the C≡N groups exhibit a high degree of orientation whereas the C=O groups are randomly oriented. The nitrile bonds are oriented approximately perpendicular to the longitudinal fiber axis. The sample preparation is straightforward and nondestructive. The setup for the polarized experiments is easy to implement and allows for an effortless switch between normal and polarized FTIR measurements. The methodology described in this note is generally applicable for the analysis of polymer fibers.

References

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