

# Effect of the finishing oil of acrylic fibers in the optical rotation of the Raman scattered light

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**Abstract:** Polarized Raman spectra have been obtained from polyacrylonitrile copolymers fibers with vinyl acetate Poly(AN-co-VA), and methyl acrylate Poly(AN-co-MA) with finishing and without finishing, in order to show the effect of the finishing in the optical rotation of the Raman scattered light. The polarized Raman spectra were used to calculate the depolarization ratios for both fibers. These values reveal that there is antisymmetric Raman scattering in the form of anomalous depolarization for some bands due to a dipolar interaction between the polar headgroup of the finishing with the polar nitrile group of the fiber causing changes in the orientation of fiber polymer chains, or pseudo antisymmetric Raman scattering due to planar hydrocarbons of the oil finishing which are optically active and are aligned when they are applied to the acrylic fibers during the spinning process. Although the finishing should not affect the physical or chemical properties of the fibers, in this work is shown that the finishing could introduce optical activity in the different wavenumbers of the Raman signal and this effect is proportional to the finishing content. According to the results obtained in this work, Raman polarized spectroscopy can provide an express method to identify acrylic fibers with finishing and without finishing agents.

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## 1. Introduction

The polyacrylonitrile (PAN) is a semi-crystalline vinylic homopolymer whose monomer is  $-(CH_2-CH_2-CN)-$  and is usually found in atactic form. PAN is one of the most versatile polymers that are widely used for making membranes and offers good resistance to a wide range of organic solvents. PAN shows good mechanical strength as film and is thermally stable [1]. Fibers produced with the homopolymer of PAN are rather difficult to dye and have poor mechanical performance. PAN has high concentration of nitrile dipoles ( $C\equiv N$ ), but the helical structure of the polymer chains causes the antiparallel radiating dipoles to cancel each other; the incorporation of vinyl monomers with bulky side chains, such as methyl acrylate (MA) and vinyl acetate (VA) into PAN chains disrupts the intermolecular bonding due to the polar nature of their carbonyl ( $C=O$ ) side chains, reducing the parallel between chains in the ordered regions [2,3] and causing the reorientation of nitrile dipoles.

Commercial acrylic fibers used by the textile industry consist of no less than 85% acrylonitrile (AN), and the sum of additives and comonomers cannot exceed 15% [4]. Polyacrylonitrile copolymers fibers with vinyl acetate, Poly(AN-co-VA), and methyl acrylate, Poly(AN-co-MA), are usually used in textile industries. Poly(AN-co-VA) and Poly(AN-co-MA) fibers have a helical structure with alternated amorphous and crystalline regions [5,6]. These copolymers form long thin chains whose length is many times its diameter. These chains have a high degree of molecular cohesion; they are oriented in a single axis and are easily bent. Physicochemical properties of these copolymers as thermoplasticity, elasticity, polarizability and crystallinity, strongly depend on their VA or MA content [1,7,8]. Fibers of Poly(AN-co-VA) and Poly(AN-co-MA) are usually used for fabric production and for final products such as clothes, outdoor garments and also for biomedical applications [9–11].

Finishing on the textile fibers is added as a thin film to reduce the friction between fibers and the hard surface of the spinning equipment [12,13]. The finishing can contain starch, waxes, mineral oils, grease and oleochemical derivatives, among others [13–20]. Finishing consists mainly of fatty acids (carboxylic acids with long hydrocarbon chains) [13,21]. The finishing of the acrylic fiber filaments is applied during the spinning process, usually, after stretching thereof and frequently prior to subsequent processing. The finishing is applied to the filaments at the bottom of the spinning tube. This guarantees extremely uniform distribution of the lubricant film on the surface of the individual filaments [19,22].

Blanco and Pagès report a classification and quantization of finishing oils by near infrared spectroscopy [21]; which is one of the most useful non-extractive reported methods for examining chemical finishes [13]. Although the capability of polarized Raman spectroscopy to investigate the structure of thin organic films has been reported [23], and could be a non-extractive effective method to classify and quantify finishing oils; recent research has shown that planar hydrocarbons are more optically active than their isomeric helicenes [24].

Excluding higher-order, non-linear processes, natural optical activity involving electromagnetic radiation consist of three principal classes of phenomena, two of which are closely related. The classical forms of optical activity are optical rotation and circular dichroism. Optical activity into vibrational spectrum, such as Raman spectroscopy [25], could provide more detailed and reliable stereochemical information because a vibrational spectrum contains many more bands sensitive to the details of the molecular structure [26].

In Raman spectroscopy, for a vibrational mode to be Raman active, the vibrational motion must cause a change in the polarizability of the molecule. The depolarization ratio ( $\rho$ ) is the intensity ratio between the perpendicular component and the parallel component of the Raman

scattered light [27]; this value can further provide information about chain conformations as well as the secondary structures such as molecular orientation [28,29].

Although there are many methods by which the depolarization ratio may be obtained, the standard procedure involves the measurement and comparison of the intensities of scattered light whose polarizations are parallel and perpendicular to that of the incident radiation. Different methods for determining the distribution of molecular orientations have been developed based on the original studies by Bower [30]; S. Frisk *et al.* [31], compared four different methods based on the same Raman measurements in order to determine the degree of molecular orientation from polarized Raman spectroscopy based on the C<sub>1</sub>–C<sub>4</sub> ring stretching vibration of poly(propylene terephthalate) (PPT) at 1614 cm<sup>-1</sup>.

The  $\rho$  value of a Raman band depends on the symmetry of the molecule and the normal vibrational mode. A Raman band whose depolarization ratio is less than 3/4,  $0 < \rho < 3/4$ , is called a polarized band, and a band with a 3/4 depolarization ratio,  $\rho = 3/4$ , is called a depolarized band. Totally symmetric vibrations produce polarized bands and non-totally symmetric vibrations produce depolarized bands.

Polarization measurements can help to identify the type of vibration (symmetry) that produces a band. Theoretically, to a first approximation,  $\rho$  was found to be as is expressed in Eq. (1) [27–29,32]:

$$\rho = \frac{3\beta^2}{45\alpha^2 + 4\beta^2}, \quad (1)$$

where  $\alpha$  is known as the spherical polarizability being equivalent to the trace of the polarizability tensor, and  $\beta$  is called the first anisotropy.

A more complete expression for  $\rho$  was reported [32]:

$$\rho = \frac{3\gamma^2 + 5\delta^2}{45\alpha^2 + 4\gamma^2}, \quad (2)$$

where

$\gamma^2 = \frac{1}{2}((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2) + \frac{1}{2}(\frac{3}{2}((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2))$ , and  $\delta^2 = \frac{3}{4}((\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{yz} - \alpha_{zy})^2 + (\alpha_{zx} - \alpha_{xz})^2)$ . In Eq. (2), values greater than 3/4 but less than  $\infty$  are called anomalous polarization. For anomalous polarization to occur,  $\delta^2$  must be greater than (27/4)  $\alpha^2$ .

Experimentally,  $\rho$  is measured by using Eq. (3):

$$\rho = \frac{I_x(I_{\perp})}{I_z(I_{\parallel})}, \quad (3)$$

where  $I_{\perp}$  ( $I$  perpendicular) and  $I_{\parallel}$  ( $I$  parallel) are the Raman scattering intensities when the polarization direction of the collected light is perpendicular (cross-polarized) or parallel (co-polarized), respectively, to the polarization direction of the excitation light. Frisk *et al.* shown that simply ratioing the band intensity obtained with the polarization parallel and perpendicular to the unique axis of the sample provides a good qualitative method to observe the evolution of orientation in a series of similar samples [31].

Although polarization data are normally obtained for liquids and single crystals, it is possible to measure depolarization ratios of Raman bands from solids [33–35]. In this work, we used polarized Raman spectroscopy in the backscattering geometry in order to find an easy and non-extractive way to detect the presence of thin films of finishing oil in acrylic fibers by means a pseudo antisymmetric Raman scattering in the form of anomalous depolarization, due to polarization effects introduced by the finishing.

## 2. Experimental

### 2.1 Materials

In this work, we used Poly(AN-co-VA) and Poly(AN-co-MA) fibers with the same type of finishing. The nominal composition of the fibers for Poly(AN-co-VA) is 93% acrylonitrile (AN) and 7 wt. % of vinyl acetate (VA) and for Poly(AN-co-MA) is 93% of AN and 7 wt. % of methyl acrylate (MA). The extraction of finishing of the fiber was made using 50-50 wt. % mixture of benzene-toluene solvents during 2 hrs. in total reflux over 2 g of fiber at 80 °C in a *Soxhlet* equipment. The flask was weighted before and after the extraction in order to calculate wt. % of finishing.

### 2.2 Scanning Electron Microscope/ Energy Dispersive Spectrometry (SEM/EDS)

Fibers were observed by scanning electron microscopy, SEM-JEOL-5900-LV.

### 2.3 Raman characterization

Raman spectra of the fibers were obtained by using a Renishaw micro-Raman 1000 equipment with a backscattering geometry [36]. The system is provided with a 600 lines/mm grating, a CCD camera (Rem Cam 1024 × 256 pixels), and a diode laser emitting at 830 nm (the laser power at the sample was about of 25 mW). The laser beam was focused onto the sample with a 50 × microscope objective (Leica, model DMLM) with numerical aperture of 0.75. For this numerical aperture and wavelength, the cylindrical excitation volume has a diameter and length of about 7 and 187 μm, respectively [37]. The calibration of the Raman system was performed using the 520 cm<sup>-1</sup> Raman line of a silicon wafer.

To select the polarization vector of the scattered Raman signal for a determined angle, an arrangement of two polarizers were used. One of them aligned in parallel with the electric field vector of the laser, and the other, the analyzer, before the monochromator to select the polarization angle (parallel and perpendicular configurations) of the electric field of the Raman signal. Figure 1 shows a scheme of the Raman apparatus and the definition of the laboratory frame. The stretching of fiber axis was oriented along the z axis both parallel and perpendicular to the incident laser light.

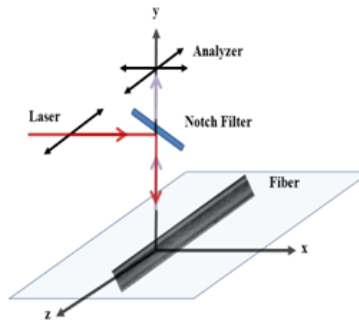


Fig. 1. Scheme of the Raman apparatus. The fiber orientation on the z axis and the laser electric field is both parallel and perpendicular to the incident laser light. The polarization analyzer is rotated to transmit the polarized Raman scattering.

## 3. Results and discussion

### 3.1 Finishing

By using the standard method of the extraction, it was found that the finishing content for Poly(AN-co-VA) is 9 wt. % and for Poly(AN-co-MA) is 2 wt. %. According to the reported [13,21], the finishing using in this work contains fatty acids, which chemically are hydrocarbon chains with a carboxylic group. Finishing exhibits high polar headgroup due to

the presence of C = O and OH polar group, and a nonpolar “tail” due to a long hydrocarbon chain [38]. When the finishing is applied to the fiber, these polar groups could interact with the nitrile group of the fiber. However, the fatty acids are achiral compounds and some kind of oriented achiral molecules can rotate the plane of transmitted polarized light incident in a general direction. Simple achiral compounds such as H<sub>2</sub>O and NH<sub>3</sub> provide general aspects of chiroptics that are not readily broached when considering chiral compounds exclusively [39].

### 3.2 SEM/EDS

The fiber diameter measurement (was about 20 μm) and the surface morphology with and without finishing, Fig. 2, was determined by SEM. In this Fig. it can be observed that the finishing produces a uniform smoothing on the fiber surface in the uniaxial axis.

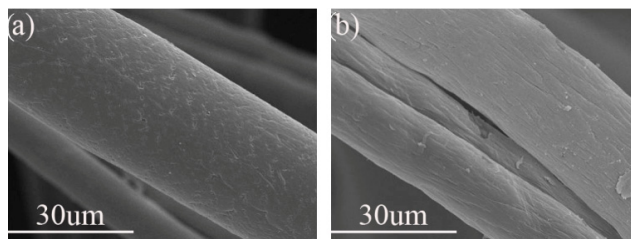


Fig. 2. Surface morphology of acrylic fibers. (a) With finishing (W/f) and (b) Without finishing (Wo/f).

### 3.3 Raman spectroscopy

The smoothing preprocessing of the Raman spectra was made numerically through a filter based on the Savitzky–Golay algorithm, and was carried out with the commercial software OriginPro 8. This smoothing was made using a second order polynomial function with a window of 5 points. The reduction of the fluorescence background, of each Raman spectrum, was made numerically following the methodology reported by Perez–Pueyo [40], where it was used mathematical morphology to remove the background of Raman spectra without modifying the Raman bands.

Considering a fiber parallel to the z axis, see Fig. 1, the normalized, baseline corrected, and nonpolarized Raman spectra of Poly(AN-co-VA) and Poly(AN-co-MA) fibers with and without finishing are shown in Fig. 3. Fibers of Poly(AN-co-VA) and Poly(AN-co-MA) used in this work contain the same amount of polyacrylonitrile and the corresponding vinyl acetate (VA) or methyl acrylate (MA) comonomer.

The physical and chemical behavior of both VA and MA are very similar, this can be observed in nonpolarized Raman spectra, shown in Figs. 3(a) and 3(b), where no significant changes were detected between the two spectra. These Figs. show that both spectra are comparable; however, there are some differences in the relative intensities of bands particularly near 260 (Aliphatic Nitriles [10,41]), 1600-1500 cm<sup>-1</sup> (C = C associated with chemical finishes [13]) and 1739 cm<sup>-1</sup> (C = O Stretching [10,41]); the relative intensity of the band at 1080 cm<sup>-1</sup> (Stretching modes of CC skeletal) of Poly(AN-co-VA) W/f and the band at 1080 cm<sup>-1</sup> Poly(AN-co-VA) Wo/f is almost the same. At this point, it is not totally clear which Raman spectra may be assigned to the acrylic fibers and which are ascribable to fibers with finishing, with the exception of small differences in the 1596 cm<sup>-1</sup> band for Poly(AN-co-VA) fiber. So far, the only difference between the two fibers is the amount of finishing present in each fiber.

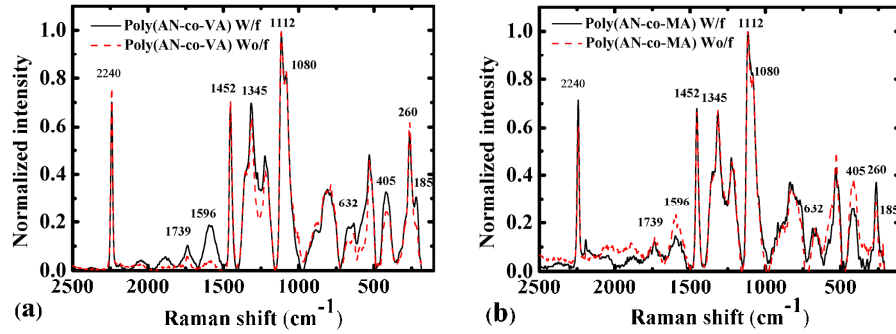


Fig. 3. Normalized nonpolarized Raman spectra of fiber With (W/f) and Without (Wo/f) finishing. (a) Poly(AN-co-VA), (b) Poly(AN-co-MA).

### 3.3 Polarized Raman spectroscopy

Since polarized Raman spectra of the fiber oriented both parallel and perpendicular to the incident laser have similar results; in this work, we are just considering  $I_{\perp}$  and  $I_{\parallel}$ , obtained by rotating the analyzer while the fiber is still aligned along the z direction, the electric field of the incident radiation polarized parallel to the z axis and the scattered radiation recorded along the y direction.  $I_{\perp}$  is the measured intensity when the incident electric field is polarized in the z direction and the Raman scatter is observed in the x direction. If the Raman scatter is observed along the z direction, the intensity will be  $I_{\parallel}$ . Figure 4 shows the linearly polarized and baseline corrected Raman spectra of Poly(AN-co-VA) fiber, (a) with finishing (W/f) and (b) without finishing (Wo/f); Fig. 5 shows the same for Poly(AN-co-MA) fiber. For each case, the Raman signal was obtained from different points and fibers until obtain 20 measurements. After the fluorescence background was subtracted, and in percentages of the maximum intensity, the standard deviation was about of 2.8%. In all measurements the same tendency was observed and due to this, for each case, a representative example is reported.

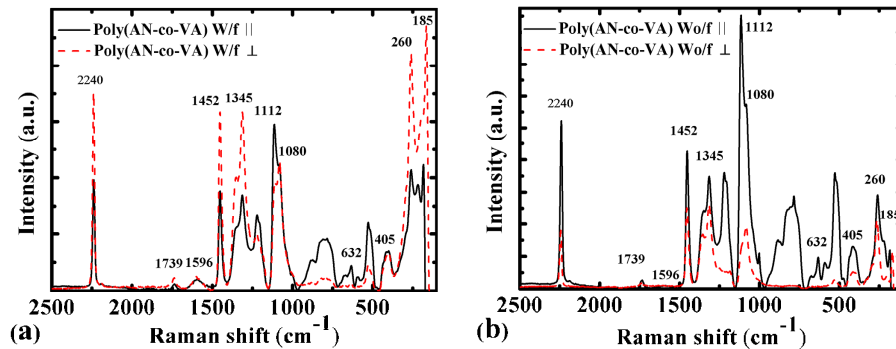


Fig. 4. Parallel and perpendicularly polarized Raman spectra of Poly(AN-co-VA) fiber, (a) With finishing (W/f) and (b) Without finishing (Wo/f).

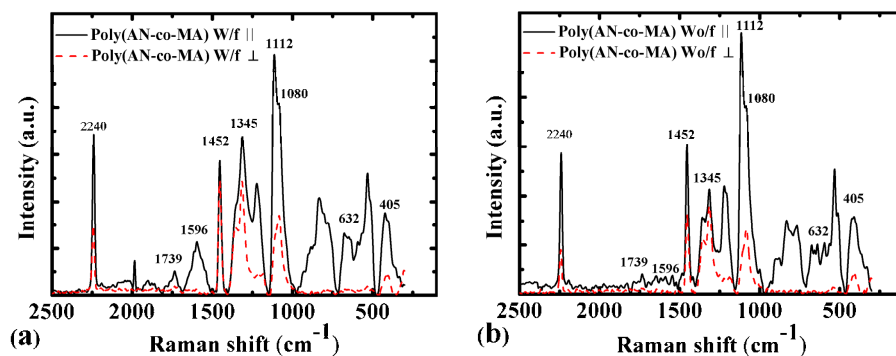


Fig. 5. Parallel and perpendicularly polarized Raman spectra of Poly(AN-co-MA) fiber, (a) With finishing (W/f) and (b) Without finishing (Wo/f).

The polarized Raman spectra in the backscattering geometry, Figs. 4 and 5, show that there is no shift in the wavenumber of the bands, indicating there is not a chemical modification, since Raman bands are sensitive to the chemical composition and structural orientation of the material. However, these spectra present differences in the relative intensities bands for fibers W/f and Wo/f. Table 1 show the variation of  $\rho$  values for these Raman bands. The  $\rho$  values for Poly(AN-co-VA) Wo/f vary in the range of 0.17-0.70, performing a totally symmetric vibration, meanwhile, for Poly(AN-co-VA) W/f,  $\rho$  values vary in the range of 0.63-2.00, indicating anomalous depolarization according to Ec. 2, which arises when isotropic and anisotropic scattering contribute to the same band [42].

The  $\rho$  values for Poly(AN-co-MA) Wo/f vary in the range of 0.26-0.69, performing a totally symmetric vibration; while for Poly(AN-co-MA) W/f, almost all the  $\rho$  values vary in the range of 0.26-0.71, performing again a totally symmetric vibration. However, the band at  $1452\text{cm}^{-1}$  ( $\rho_{1452} = 0.85$ ) exhibits anomalous depolarization, which means that the oil finishing arises anisotropic Raman scattering.

For Poly(AN-co-VA) fibers W/f, the intensity of the following depolarization ratios increased respect to Poly(AN-co-VA) fibers Wo/f:  $\rho_{2240}$  (C≡N stretching),  $\rho_{1739}$  (C = O stretching),  $\rho_{1452}$  (CH<sub>2</sub> and CH<sub>3</sub> bending deformation),  $\rho_{1345}$  (C-H bending),  $\rho_{1080}$  (C-C skeletal stretching),  $\rho_{405}$  (C-CN nitrile deformation),  $\rho_{260}$  (aliphatic nitrile), and  $\rho_{185}$  (C-CN deformation vibration). The changes in the  $\rho$  values in the form of anomalous depolarization for those bands cannot be ascribed to changes in the orientation of fiber polymer chains due to the treatment with the solvent organic mixture used in the standard method of the extraction. So, those changes in the  $\rho$  values could be attributable to the presence of oil finishing

The  $\rho$  values variations obtained in this work (Table 1) are according to the amount of finishing present in each fiber: Poly(AN-co-VA) fiber contain 9 wt. % of finishing and the Poly(AN-co-MA) contain 2 wt. %. This difference in the  $\rho$  values could be attributed to the oil finishing, planar hydrocarbons [24], which are optically active and are aligned when they are applied to the acrylic fibers during the spinning process. Molecules in the finishing thin film are predominantly oriented with their long axis parallel to the fiber as confirmed by Raman results. But also, anomalous depolarization could be explained by a dipolar interaction between the polar headgroup of the finishing with the polar nitrile group of the fiber causing changes in the orientation of fiber polymer chains. Also, from the Table 1, it can be observed that the difference between the  $\rho$  values for fibers with and without finishing is not a constant; this could mean that, in this case, the changes in the depolarization ratios depend on the type of vibration responsible for the scattering and the concentration of the active group of both, the fiber and the amount of finishing present in each fiber. Therefore, Raman polarized spectroscopy could be used as a non-extractive tool for identifying acrylic fibers with and without finishing and, also, could be used to quantify the amount of finishing



**Table 1. Depolarization ratios**

Functional Group	Raman Shift ( $\text{cm}^{-1}$ )	Poly(AN-co-VA)		Poly(AN-co-MA)	
		$\rho$ (Wo/f)	$\rho$ (W/f)	$\rho$ (Wo/f)	$\rho$ (W/f)
Nitrile Stretching	2240	0.29	1.85	0.29	0.40
C = O Stretching carbonyl group	1739	0.70	2.00	0.35	0.37
Methylene, $\text{CH}_2$ , methyl, $\text{CH}_3$ , bending deformation	1452	0.58	1.79	0.54	0.85
C-H bend from the macromolecular backbone	1345	0.65	1.72	0.69	0.71
Stretching modes of CC skeletal and also to $\text{CH}_3$ and $\text{CH}_2$ rocking	1080	0.34	1.03	0.35	0.42
C-CN Nitrile deformation	405	0.40	0.94	0.26	0.26
Aliphatic Nitriles	260	0.68	1.97	0.00	0.00
C-C = -N deformation vibration Aliphatic Nitriles	185	0.17	1.41	0.00	0.00

#### 4. Conclusions

The depolarization ratio  $\rho$  of Poly(AN-co-VA) and Poly(AN-co-MA) fibers without finishing and with the same type of oil finishing, was experimentally calculated using the intensity ratio between the perpendicular component and the parallel component of the Raman scattered light relative to the input laser polarization.

Since both fibers were subjected to the same treatment of finishing extraction and there is no evidence that the solvent mixture benzene-toluene had an effect on the molecular structure of the fibers, therefore, the only difference between the acrylic fibers is the finishing content, so that, the change in the depolarization ratio could not be ascribable to a fiber molecular change and could be attributable to the finishing. We have shown that although the finishing used in this work is just to provide lubrication on the surface of the fibers, it introduces changes in the optical properties of the acrylic fibers manifested as anomalous depolarization. These  $\rho$  values reveal that there is antisymmetric Raman scattering for some bands due to a dipolar interaction between the polar headgroup of the finishing with the polar nitrile group of the fiber causing changes in the orientation of fiber polymer chains, or pseudo antisymmetric Raman scattering due to planar hydrocarbons of the oil finishing which are optically active and are aligned when they are applied to the acrylic fibers during the spinning process.

The changes in the  $\rho$  values measured depends on the (i) the type of vibration responsible for the scattering, (ii) the amount of finishing present in each fiber, (iii) the alignment of the molecules in the finishing film and (iv) the concentration of the optically active substance in the thin film. The relative intensity of a peak and the thickness of the finishing film could be directly proportional because the results show that the optical activity increase with increasing concentration of finishing.

According to the results obtained in this work, Raman polarized spectroscopy using a single analyzer can provide an express method to identify acrylic fibers with finishing and without finishing oil and also quantify the amount of finishing oil. There are, however, still limitations to the calculation of the exact molecular orientation because we only used a single analyzer. We suggest a total determination of the Stokes parameters in order to obtain a full description about the polarization state of the Raman signal throwing the finishing.