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Characterization of Orientation at Polyester Fiber Surface by Modified Infrared Reflection Technique

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Abstract

The surface orientation of polyester fibers has been studied by a modified sampling technique using Fourier transform infrared (FT-IR) diffuse reflectance spectroscopy. The fiber axes were arranged parallel to incident radiation first, and then perpendicular to it. The differences in total absorbance and relative intensity changes in the spectra obtained show the features of specular reflection. The technique has the advantage over ATR that there is no optical contact problem.

Introduction

Diffuse reflectance FT-IR spectroscopy has been recently developed into a technique capable of handling a variety of samples. Theories for diffuse reflectance were originally developed for particulate absorbing particles dispersed in a particulate non-absorbing medium (1). The light incidents upon a powdered surface will be reflected in all directions. The reflected light is collected with ellipsoid mirrors and directed to the IR detector for analysis. For non-particulate samples a large portion of the radiation will be specularly reflected.

We have now taken the advantage of the collection efficiency of the diffuse reflectance optics, and extended its use to in-situ study of fiberic samples. Both stretched and undrawn samples were used to determine the sensitivity of the technique towards the molecular orientation effect.

Experimental

Spectra were obtained by a Nicolet 170SX FT-IR spectropho-

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tometer equipped with a MCT detector. A Harrick Scientific Corporation reflectance cell was placed inside the the spectrometer to collect the reflection radiation. 100 scans were co-added at a resolution of 4 cm^{-1} throughout the range of 3800—700 cm^{-1}. All reflection spectra (R) were obtained by ratioing the sample single beam reflection spectra against a potassium bromide single beam backgroud spectrum. The polyester (PET) fibers were not altered chemically or physically prior to the IR analysis other than to wind them around a square frame. The winding was performed by hand such that the axes of fiber were parallel to each other. Samples were put above a cell filled with potassium bromide power. The schematic diagram of the fiber reflection IR experiments is shown in figure 1. The plane of incidence is usually defined as the plane which contains both the normal vector and the propagation vector. In this experiment we define the normal vector as being perpendicular to the tangent plane of fiber. Therefore an infinite number of surface normal vector exist. In figure 1P the fiber axes are arranged to be parallel to the plane of incidence, and all of the incident angles are relative large. After the spectrum was taken, the sample cell was rotated by 90 degrees. In figure 1V the fiber axes are vertical to the plane of incidence, and the incident angles are variable. Figure 1D shows the normal diffuse reflectance measurement for chopped fibers which were randomly mixed with potassium bromide powder.

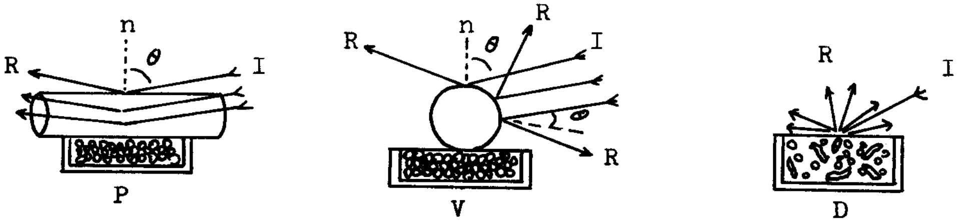

Figure 1. Schematic diagram of fiber reflection experiment. P:fiber axis parallel to the incident plane; V:fiber axis axis vertical to the incident plane; D:fiber chopped into small piecesaand randomly mixed with KBr powder.

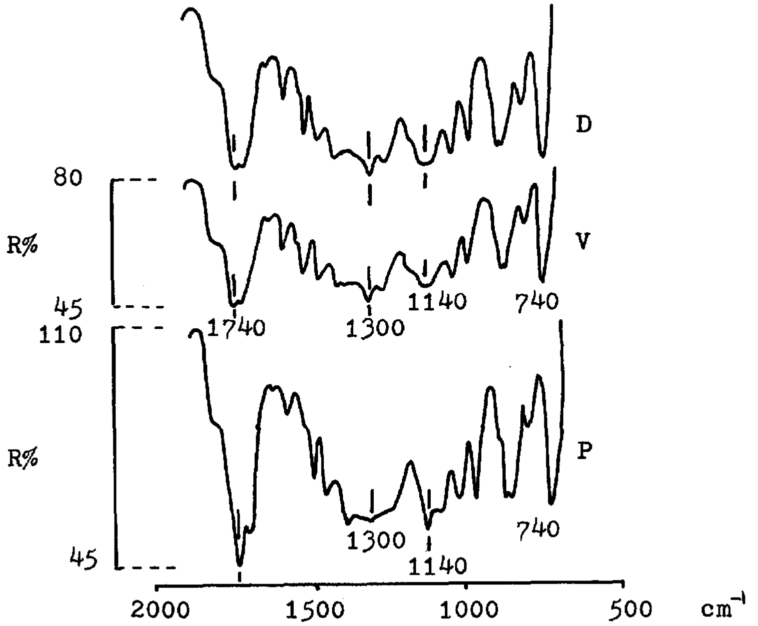

Figure 2. Reflection spectra of stretched polyester fiber.

Results and Discussion

Figure 2 shows fiber reflection spectra of highly drawn polyester fiber. The fiber axis orientation with respect to the plane of incidence is shown next to each spectrum. The radiation was unpolarized. The noticeable aspects are the difference in total absorption intensity between spectra P and V, and the relative intensity changes which occur among the bands at 1740, 1300, and 740 cm^{-1}. These bands correspond to the C=O stretching, the C(O)-O stretching, and ring out-of-plane bending modes,respectively (2). They are shifted relative to their positions in a transmission spectrum due to optical distortion (3).

Gillbery and kemp have shown the difficulty of obtaining external reflection spectra of fibers (4). The quality of the spectra shown in figure 2 should be noted. Although the band positions are shifted, all the bands are readily identifiable.

In figure 2 the absorbance of spectrum V is weaker than spectrum P despite the fact that the same amount of samples were measured in both experimental arrangements. The same phenomena were observed by reproducing the spectra. This is mainly due to the relative positions between fiber axes and incident radiation. As the fiber axes were arranged vertical to the plane of incidence, the reflection was rather random, and the incident angles are variable (see figue 1). As the incident angle is near zero, the incident and the reflected waves combine to form a standing wave electric field, which has a node at the reflection surface. So little absorption can be observed by the surface materials (5). If the incident angles are larger than zero, but smaller than the critical angle, part of incidance radiation is reflected, part of it is refracted. The fact that spectra V are weaker than spectra P was found in the study of other fiberic samples, like glass fiber or nylon (6).

The relative intensity changes present in figure 2 seem to result from molecular level effect rather than the macroscopic arrangement of the fibers. This opinion can be supported by figure 3. The spectra were obtained in the same manner as figure 2 except that the fibers used were undrawn. In fact the relative band intensities in the spectra V and P (figue 3) are very similar despite the drastic change in the experimental geometry.

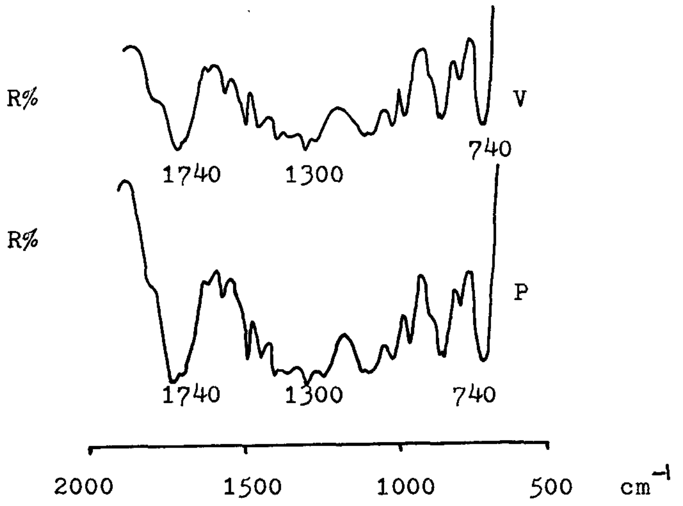

Figure 3. IR reflection spectra of undraw polyester fiber.

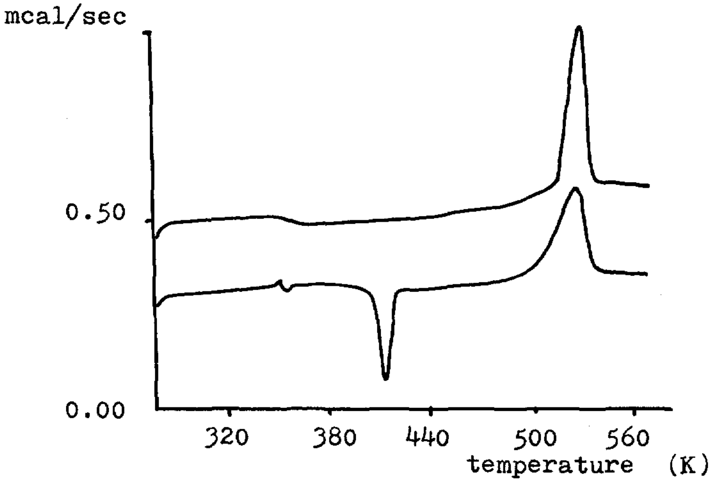

Figure 4. Differential scanning calorimetry curves for polyester fibers.
(upper:stretched fiber; lower:undrawn ones)

The thermogram for both stretched and undrawn polyester fibers in figure 4 shows the difference in crystallinity.

The spectra in figure 2 show molecular orientation effects although the incident radiation was unpolarized. This is possible, because as the incident angle is large (between 70 and 89 degrees) the radiation polarized parallel to the plane of incidence is more strongly reflected than the perpendicular radiation (5,7). The vibration modes with transition moments directing perpendicular to the reflection plane will be enhanced compared with the modes with transition moments parallel to it. H.Ishida and S.Yoshida confirmed that the spectra information with and without the polarizer is the same in their study on the orientation of imidazoles on copper surface using reflection technique (8,9). Thus the relative intensity changes in figure 2, indicates that the dipolemoment of C=O stretching vibration tends to be parpendicular to the fiber axis. This is coincident with the results reported by C.J. Brown et al. that the C=O bond makes an angle of 76 degrees with the fiber axis while the C-O bond makes an angle of 47 degrees (10).

When the fiber axes were arranged perpendicular to the plane of incidence in the experiment, the incident angles were variable from 0 to 90 degrees. Little orientation information could be observed. Actually spectrum V in figure 2 is similar to the diffuse spectrum D.

Conclution

We have shown that external reflection spectra of fibers could be obtained using a diffuse reflectance attachment. The relative intensity changes of bands indicate molecular orientation for the drawn polyester fibers, but not for the undrawn fibers. The sample handling technique developed in this experiment has advantage over attenuated total internal reflection (ATR) that there is no optical contact problems in the study of fiberic or brittle samples.

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