Effect of Various Morphology and Testing Conditions on Fiber Infrared Spectrum

Weidong Yu, Lei Xiong

College of Textiles, Donghua University, 1882 West Yan-an Rd, Shanghai, 200051 People's Republic of China

Received 30 January 2004; accepted 12 July 2004
DOI 10.1002/app.21187
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of measurements verify that the accuracy, reproducibility, and quality of fiber infrared spectra strongly rely on fiber thickness and morphology, the aperture size and direction, and instrument parameters, despite the use of high resolution in microscopy by using the Continuμm microscope. The effect of fiber cross section and testing parameters on the characteristics of the FTIR microscope spectra is discussed systematically. Meanwhile, the reproducibility of the spectra has also been tested using the transmission and mapping methods. The experimental results show that the size selection of the aperture, fiber flattening, and proper contact between attenuated total reflection crystal and fiber are vitally important for high quality and accuracy of FTIR microscope spectra. Through reasonable parameter setting and sample preparation, in fact, the IR spectra of single fibers can be obtained quickly and reproducibly. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1003–1010, 2005

Key words: FT-IR; microscopy; fibers; infrared spectroscopy; morphology; mapping

INTRODUCTION

KBr disks have commonly been used in measuring fiber IR spectroscopy. In this method, the fiber sample is finely minced and then ground with pure and dry KBr. The mixture is pressed at high pressure to form a transparent KBr disc, and then the spectrum of the slice can be measured.[1] However, single fiber IR spectra can be measured directly by FTIR (Fourier transform infrared) microscopy.[2,3] Not only the transmission and reflection spectra, but also the polarized IR spectra and attenuated total reflection (ATR) spectra by using a FTIR microscope, can be measured conveniently.[4,5] The characteristics of fiber structure and component can also be measured with little damage to fibers and high accuracy by means of this method,[6,7] especially for the measurements influenced due to fiber morphology. Therefore, the application of infrared microscopy, including IR mapping technology, is increasingly popular in fiber science with the development of infrared spectrum instruments.[8,9] Although there are many advantages to infrared microscopy, it is necessary to discuss the fundamental issues in the use of this technique which can easily result in measuring errors, to achieve high quality IR spectra by using the Nicolet spectrometer attached to a Continuμm microscope.

Correspondence to: W. Yu (weidongy@online.sh.cn).

Journal of Applied Polymer Science, Vol. 96, 1003–1010 (2005)

EXPERIMENTAL

Materials and sample preparation

Poly(*p*-phenylene terephthalamide) fibers (PPTA), polyamide fibers (PA), and soy bean-protein fibers (SP) were collected for our measurement. These fiber samples were cleaned with alcohol and ether and then dried at room temperature to remove the contaminant and oil agents on the fiber surface.

Instrument and testing conditions

A Nicolet Continuμm FTIR spectrometer with microscope[10] was used, which was equipped with a Polarizer and an ATR attachment and a narrow-band mercury– cadmium–telluride detector (MCT-A, with the range of the IR spectrum from 4,000 to 650 cm^{-1}) cooled with liquid nitrogen, and the IR resource coming from a Nexus-670 IR spectrometer. The main components of the Continuμm microscope include: a ×10 eyepiece; a ×15 objective condenser; a motorized stage; a single Reflex™ aperture; a visible illumination system, and a CCD camera system, etc. For data and image processing, the OMNIC® and OMNIC Atlμs™ software are installed; the OMNIC Atlμs™ is particularly designed for mapping analysis. Thus, various tests can be performed by the Continuμm microscope, such as transmission, reflection, polarized, and ATR IR measurements, the linear scan and mapping techniques in terms of software, and optic video technology for true video analysis. In addition, spatial-resolution FTIR spectra and functional group imaging can also be acquired and analyzed.

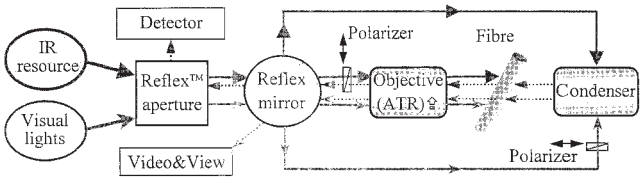


Figure 1 Continuμm FTIR Microscope components and light path.

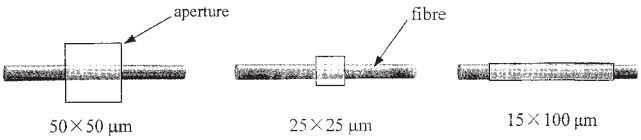


Figure 2 Three types of the aperture size used in transmission.

The schematic representation of the optical layout and the functions of the Continuμm microscope are illustrated in Figure 1.

For measuring single-fiber IR spectra by FTIR microscopy accurately, several primary parameters in the operation need to be selected and set first, which include aperture sizes, number of scans, resolution, velocity of motional mirror, and sampling background. The parameters and their ordinary values in measurement are listed in Table I.

RESULTS AND DISCUSSION

Testing parameters

In transmission experiments, the aperture dimension and the number of scans are usually adjusted. The effect of these two testing parameters on the quality of IR spectra was investigated and discussed as follows.

Aperture dimension

An adjustable rectangular Reflex™ aperture is used in the Continuμm microscope. The aperture can be rotated from 0 ~ 360° manually or automatically, and its dimension ranges from 5 μm × 5 μm to 100 μm × 100 μm in the motorized mode, thus the size, shape, and orientation of the aperture can be selected according to the radial and axial direction of a fiber.

The larger the aperture dimension is, generally, the stronger the transmitted IR signal is, but the smaller the interested area on a fiber is detected, so that the absorbance spectrum of the fiber may be concealed in the background signal. On the contrary, small aperture size may result directly in the weak IR signal and low signal-to-noise ratio (SNR). Consequently, the aperture size should be adjusted to fit the sample size to obtain effective and sufficient signal intensity, i.e., the axis of a single fiber should pass the central point of the aperture and the aperture width should be matched to the fiber diameter.

As the fiber diameter used in textiles commonly ranges from 10 to 25 μm, for a comparison, three types of aperture sizes, namely 50 μm × 50 μm; 25 μm × 25 μm; 15 μm × 100 μm, were tested, as shown in Figure 2.

It is obvious that the transmittance of IR signal intensity (I) for these three sets is $I_{25\times\ 25}<I_{15\times100}<I_{50\times50}$ because of the nominal aperture size, but the absorbance of them follows $A_{15\times100}>A_{25\times25}>A_{50\times50}$ due to the actual fiber area. The results are shown in Figure 3. The primary reason is the difference in the effective area to infrared absorption. As a result, the absorbencies at 15 μm × 100 μm and 25 μm × 25 μm are larger and their spectra are better than those of 50 μm × 50 μm though its aperture size is the largest of them.

For the theoretical investigation of the effect of aperture size on IR spectra, the aperture size was adjusted in series along the two directions, i.e. x axis (parallel to fiber axis) and y axis (perpendicular to fiber axis), as shown in Figure 4. Five different sizes were selected to detect the IR spectra of PA fibers in the two directions, respectively. The results are shown in Figure 4 and Table II.

The IR spectra measured by the Continuμm microscope are illustrated in Figure 5. The absorbances of the N–H stretch band (3,302 cm^{-1}) and the C–H stretch band (2,935 cm^{-1}) were used for a quantitative analysis and the results are shown in Figure 6. It shows that the aperture size should match with the fiber diameter. As the PA fiber diameter is about 25 μm, when the aperture size on the y axis (perpendicular to the fiber axis) is less than the fiber diameter, the absorbance for the longer than 40 μm length has no obvious variation though its size increases along x axis. The measured results are illustrated in Figure 5(a) and curve A of Figure 6. The aperture size, however, is larger than the fiber diameter, the IR absorbance obviously decreases as shown in the B curve of

TABLE I
The Testing Parameters (Transmission) and General Setting

Item	Aperture size (μm)	Resolution cm^{-1}	Scans	Velocity cm/s	Background
Setting	25 × 25	8 cm^{-1}	200	1.8988	Air

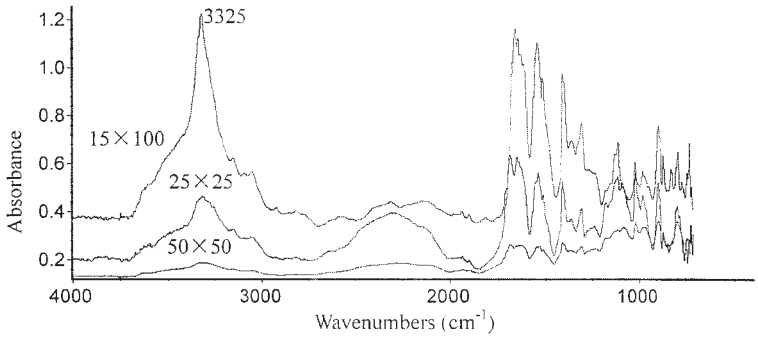


Figure 3 The FTIR microscope spectra of PPTA fibers measured under different apertures.

Figures 6 and 5(b). According to the analysis of aperture-size effect on the absorbance of N–H and C–H stretch bands, the optimal aperture size should be 16 $\times$ 40 μm^2 for fibers.

As a result, it is verified in theory and experiment that the aperture must match with the interested area of the observed fiber to acquire the characteristic signal and to avoid disturbance from the uninteresting area.

Number of scans

Increasing the number of scans can reduce the noise level of IR spectra, i.e., raise SNR and sensitivity, so that the small peaks representing fiber characteristics can be distinguished from the background noise. However, this increasing of scan number requires a long time.

The number of scans is generally about 200 scans.[6,8] For comparison, four infrared microscope spectra from 100, 200, 400, and 800 scans have been measured for PPTA fibers (nonflattened). It can be found from Figure 7 that the small number of scans results in high noise and low absorbance at characteristic absorption bands, such as N–H stretch at 3,325 cm^{-1}, especially for the spectrum of 100 scans, as shown in the bottom curve in Figure 7. Theoretically, according to the measurement principle of the Continuμm, the more scans taken, the lowerer the noise level and the higher is the quality of the spectrum. However, the large number of scans requires more time and may increase the disturbance from the sample and outer environment. Since the spectra from 200, 400, and 800 scans are better, and have little difference between each other, the reasonable selection is 200 $\sim$ 400 scans at the interesting area of a single fiber.

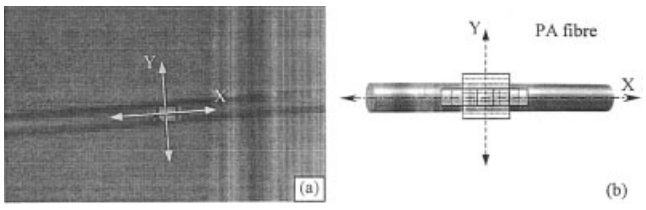


Figure 4 The orientation of aperture adjustment. (a) video image, (b) schematic diagram.

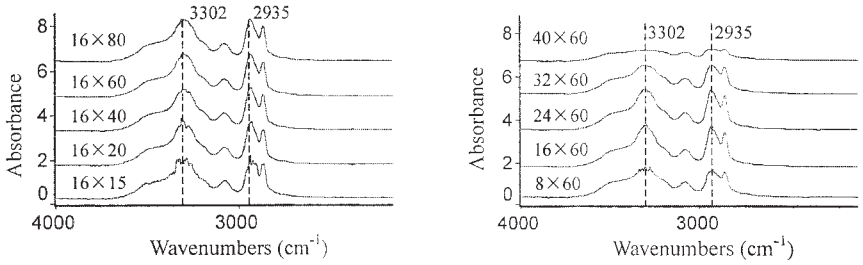
Effect of fiber morphology

Flattening effect

For transmission testing, the sample thickness should be from 5 to 15 μm.[10] If the sample thickness is more than 15 μm, the transmittance would be too low to acquire a better resolution spectrum. On the contrary, the high transmittance due to thin fibers will also cause bad resolution because of the low absorbance.

TABLE II
The Absorbance of N-H and C-H Stretch Band

Expansion along fiber axis (x axis)			Expansion along radial direction (y axis)		
Aperture sizes (μm)	Absorbance		Aperture sizes (μm)	Absorbance	
	N-H (3302 cm^{-1})	C-H (2935 cm^{-1})		N-H (3302 cm^{-1})	C-H (2935 cm^{-1})
16 × 80	1.645	1.142	40 × 60	0.305	0.165
16 × 60	1.521	1.121	32 × 60	0.979	0.630
16 × 40	1.652	1.158	24 × 60	1.504	1.069
16 × 20	1.215	1.115	16 × 60	1.538	1.117
16 × 15	0.955	0.933	8 × 60	1.066	0.515



(a) Expansion along fiber axis (X-axis) (b) Expansion along radial direction (Y-axis)

Figure 5 The IR microscope spectra of Polyamide fibers obtained from the different settings of aperture sizes.

For example, the PA fiber with about 25 μm in diameter was flattened to about 10 μm and the quality of its IR spectrum was improved. The IR microscope spectra of flattened and nonflattened PA fibers are shown in Figure 8. It can be seen easily that the flattened fiber has a better spectrum than the non-flattened.

Fibers usually have a round cross section and a diameter (or width) of 10 $\sim$ 25 μm. The scale is almost the same as the wavelength, from 2.5 to 25 μm, of middle IR radiation. When the IR radiation passes through a fiber, diffractions at different wavelength will occur and may influence the absorbance and SNR of the spectrum. But the flattening makes fiber thickness more even, and effective area larger, thereby reducing the effect of various diffractions and enhancing the SNR. The diffraction effect is shown in Figure 9, and the improvement of the spectrum of flattened PPTA fiber is evident. The test indicates that it is necessary to flatten fibers with a small metal roller on a glass slide before the IR measurement.

Effect of the uniformity of thickness

Besides the effect of fiber thickness, the fiber morphology, namely the uniformity of fiber thickness, also influences the characteristics of the spectra at the same time.

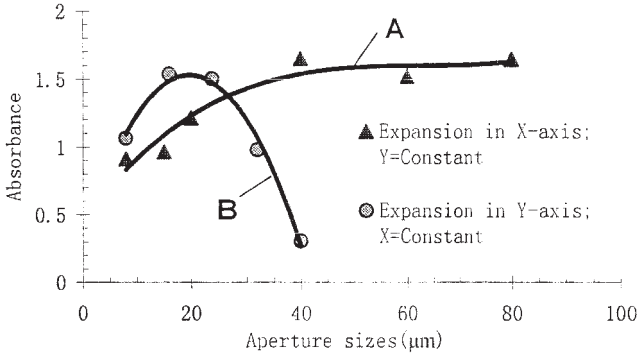


Figure 6 The effect of aperture sizes on N-H stretch band absorbance of polyamide fibers.

Let A be the absorbance of fibers and b represent the thickness. Beer's law[11] shows

$$A = \lg(I_0/I) = ab \tag{1}$$

Where a is the specific absorptivity (cm^{-1}) of fibers, I_0 is the intensity of incidence, and I is the intensity of transmission.

If the specimen thickness is nonuniform and cannot be measured, deviations from Beer's law will occur and influence the characteristic constant, a. For example, as shown in Figure 10, one specimen is uniform, which has the thickness of 20 μm. The other is nonuniform, but the average thickness is 20 μm, in that half of the specimen is 5 μm in thickness, while the other half has a thickness of 35 μm. Referring to eq. (1), for the uniform specimen, $I = I_0 10^{-20a}$; for the nonuniform spectrum, the thin part of the specimen transmits $I_1 = I_0 10^{-5a}$, while the thick part transmits $I_2 = I_0 10^{-35a}$, and the average transmittance $\tilde{I} = 12(10^{15a} + 10^{-15a}) \times (10^{-20a} I_0)$. The value of $(10^{15a} + 10^{-15a})$ is more than 1, so the following relationship is evident: $\tilde{I} > I$, $\tilde{A} < A$.

If one considers the cross section of a fiber as round, as shown in Figure 11(a), the transmittance can be derived from the following equations. Since $b = 2R\sin\alpha$,

$$I_i = \frac{1}{10^{ab}} I_0 = I_0 10^{-2aR\sin\alpha} \tag{2}$$

$$I_C = \int_R^R I_i dx = \int_0^\pi I_0 10^{-2aR\sin\alpha} d(R\sin\alpha) \tag{3}$$

$$\bar{I}_C = \frac{1}{2R}\int_0^\pi I_0 10^{-2aR\sin\alpha} R\sin\alpha d\alpha = \frac{1}{n}\sum_{i=1}^{n} I_i \tag{4}$$

If the same cross-sectional area, as shown in the fiber in Figure 11(a), is adopted, but in uniform thickness and the same width, $2R$, as shown in Figure 11(b), the

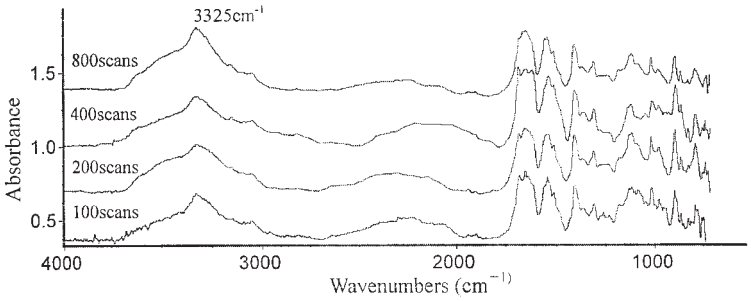


Figure 7 Transmission spectra of PPTA fiber from different scans.

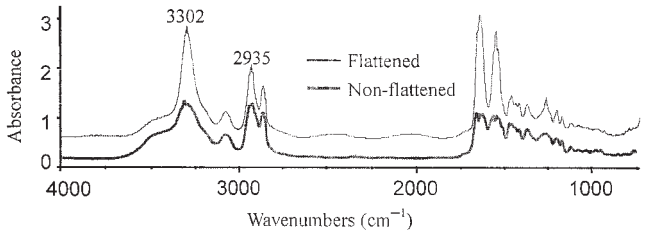


Figure 8 Comparison of the IR transmission spectra of PA fibers.

equivalent average thickness is $\pi R/2$, and the equivalent transmittance (I_E) can be found as:

$$I_E = I_0 10^{-\pi a R/2} \tag{5}$$

Suppose that the specific absorptivity is 100 cm^{-1}, i.e., $a = 100\ cm^{-1}$, the fiber diameter is 20 μm ($R = 10\ \mu$m), from eqs. (2) and (4); the average transmittance (I_C) is 0.7538 I_0, corresponding to an absorbance of 0.1227; the equivalent transmittance (I_E) is 0.6966 I_0, and the absorbance is 0.1570. The distribution curves are shown in Figure 11(c). Therefore, it is verified again that the flattened fiber has a higher absorbance and better resolution spectrum in theory and practice, as shown in Figure 12.

Interference effect

Although the quality of IR spectra can be improved, by flattening fiber morphology, there still exists questions of a light interference. When the IR radiation passes through the flattened fiber with even thickness, interference phenomenon may occure due to multiple internal reflections in the specimen, as shown in Figure 13(a). If the path difference, between the transmitted and the reflected component light, matches a multiple of a wavelength, the result of the light interference will affect the shape of the IR spectrum at that wavelength. Generally, some sinusoidal fluctuation will appear on the baseline, which is shown in Figure 13(b).

According to the peak position of the sine wave, the fiber thickness, b, after being flattened can be estimated:[11]

$$b = 1/2n(\tilde{\nu}_h - \tilde{\nu}_l) \tag{6}$$

where n is the refractive index, in air $n \approx 1$, and $\tilde{\nu}_h$ and $\tilde{\nu}_l$ are adjacent wavenumbers at the maxima of the sine wave. For example, from Figure 13(b), the thickness of flattened SP fiber can be calculated: $b = 1/2(2360 - 1790) = 0.000877\ cm = 8.77\ \mu m$.

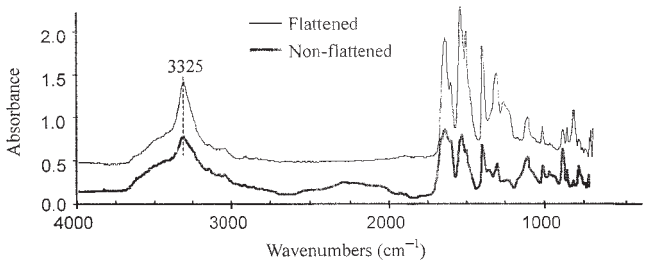


Figure 9 Comparison of IR transmission spectra between non-flattened and flattened PPTA fibers with about 12μm in diameter.

ATR spectra

The slide-on ATR attachment in the Continuμm FTIR microscope can be applied to analyze surface defects and inclusion of fibers with little or no sample preparation. For very fine fiber, to make good contact between ATR crystal and fibers, several fibers were arranged compactly on a glass slide and flattened with a steel roller to make the surface smooth and the thickness even, as shown in Figure 14(a), and then the

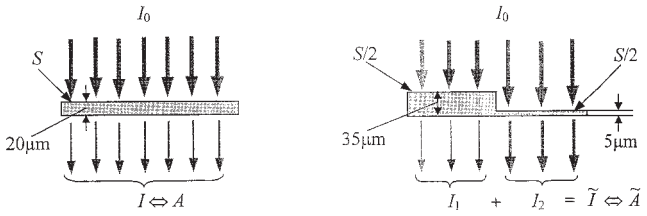


Figure 10 Comparison of absorbance between uniformity and non-uniformity membranes.

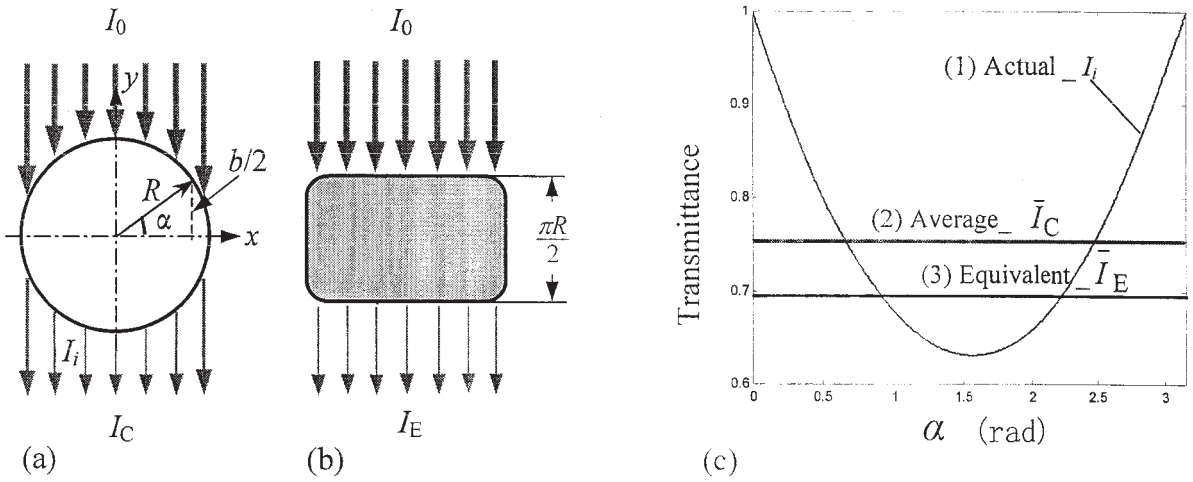


Figure 11 Transmittance of different cross section and their distribution curve. (a) fiber cross-section, (b)equivalent cross-section in rectangle, (c) the distributed curve of transmittance..

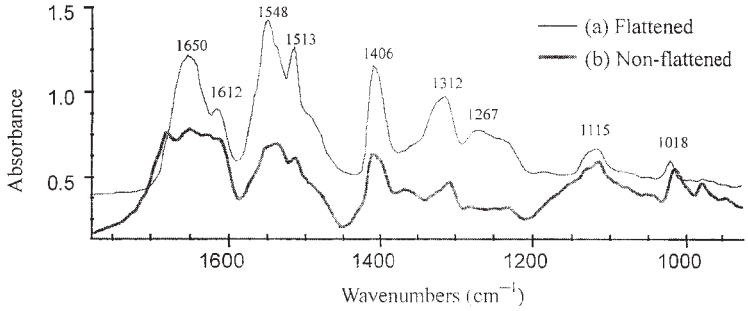


Figure 12 The effect of morphology on transmission spectra of PPTA fiber (a) non-flattened; (b) flattened.

ATR crystal was pressed on the surface of the fibers. The spectra of PPTA fiber were recorded in the reflection mode by 200 scans at 8 cm^{-1} resolution and 100 μm × 100 μm aperture. Proper contact pressure must be kept during the signal collecting, otherwise much noise will occur in the spectra, as shown in Figure 14(b).

Reproducibility of spectra

During measurement, heat radiation, atmosphere variation, and nonuniformity of fiber can all affect the microscope spectra. For the investigation of test reproducibility, soybean protein (SP) fibers sensitive to heat were measured, which were treated by IR radiation for different aging times *in situ*, as illustrated in Figure 15. Obviously, the aging time covers all of the normal measuring time. Meanwhile, the fibers were moved in and out at every measurement to fit an actual situation. The imitation test indicated that no significant differences were found in the spectra of the SP fiber: only minor differences in peak intensity and shape were observed. A similar investigation was performed by the following mapping technique.

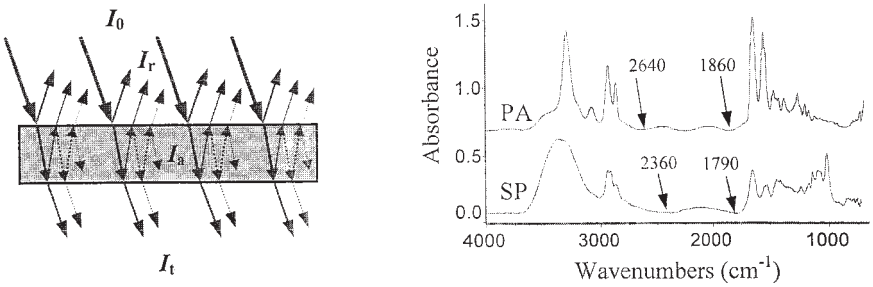


Figure 13 Interference effect on transmission spectra of the top PA fiber in 2640~1860cm^{-1} and the bottom SP fiber in 2360~1790cm^{-1}.

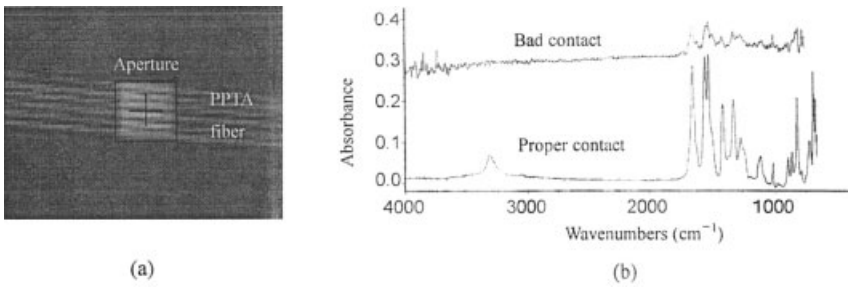


Figure 14 ATR measurements (a) video image of PPTA fiber, (b) Comparison of ATR spectra of PPTA fiber at different contact pressure.

Mapping technology in infrared microscopy was also carried out in further studies for reproducibility tests. It is a powerful analytical technique for the component distribution measurement of fibers. A large number of spectra can be collected quickly and automatically by measuring a series of spectra at each set point in a sample area. The point-of-interest analysis can be performed automatically, and the difference of the chemical composition at different positions can be figured out by using OMNIC Atlμs™ software.[12]

In the automated point-of-interest analysis, two points of interest of a SP fiber (1 and 2) and the same background (B) of air were specified, as shown in Figure 16(a) and then the spectra were collected alternatively at points 1 and 2 compared to B, respectively, with an aperture of 12 μm $\times$ 80 μm and 200 scans at 8 cm^{-1} resolution. Six spectra at each point were acquired. The results are illustrated in Figure 17(a). Analyzing the spectra measured at the same point showed that no significant difference could be found at either point 1 or point 2. This indicates that FTIR microscopy is a reproducible technique for obtaining IR spectra of single fibers.

However, a differences of the spectra between the two points can be distinguished easily due to their different locations in the radial direction and the different effective areas analyzed. The measurements show that the mapping technique for IR microscopy can be used in the component and distribution characterization of microregions with high accuracy and sensitivity.

It seems there is no difference among the spectra in Figure 17(b) because the mapping line is the fiber axis. The mapping conditions used for recording Figure 17(b) were as follows: an aperture of 25 $\times$ 25 μm^2, 200 scans for each single spectra at a resolution of 8 cm^{-1}, 10 μm step-length along the line direction with 110 μm total length, and the air background as a reference

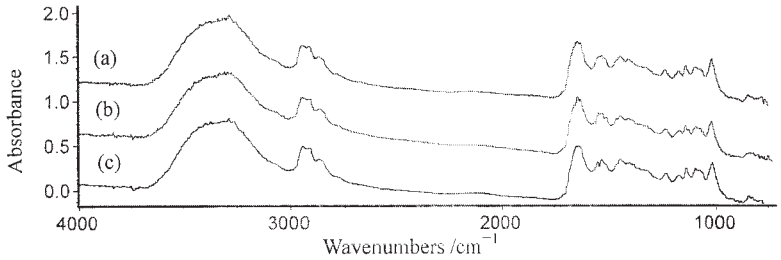


Figure 15 Transmission spectra of SP fibers. (a) untreated; (b) treated for 8 min by IR radiation; (c) treated for 16 min by IR. radiation.

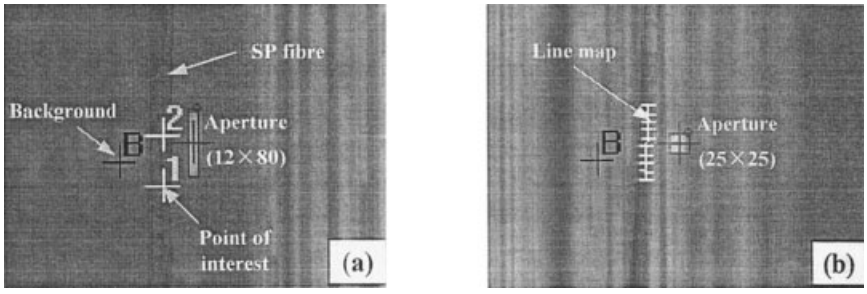


Figure 16 The video images in the Continuμm microscope. (a) automated point-of-interest analysis, (b) line map analysis.

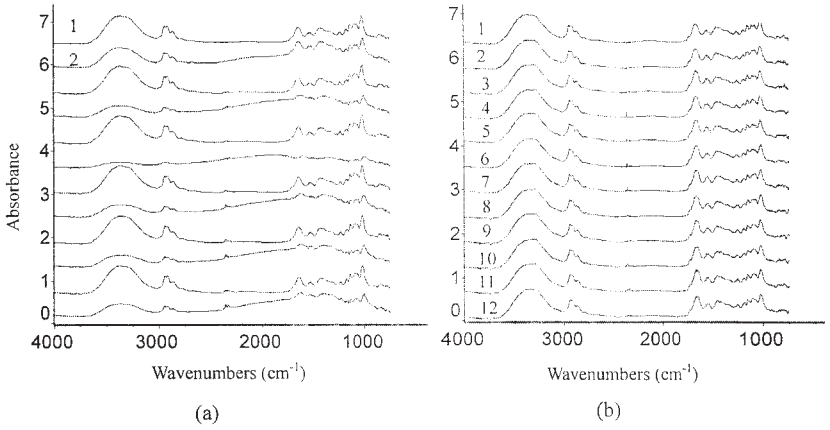


Figure 17 Transmission spectra from two points of SP fibers. (a) Two points: point 1 in the center and point 2 at the edge of the fiber, (b) All the points on the mapping line are along the fiber axis.

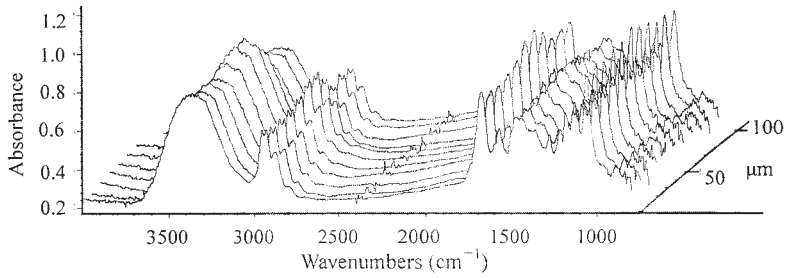


Figure 18 Spatial-resolution FTIR spectra of the SP fiber at 10μm step length.

point. The total collecting time was about 20 min. The spatial-resolution FTIR spectra (waterfall) were made and are shown in Figure 18. Some difference between points 1 and 2 indeed exist because the last three spectra differ from the others at the height of several absorbent peaks. The results imply that there is variation of component or structure in the different regions of the fiber.

CONCLUSION

A study of the application of FTIR microscopy on single fibers was carried out, and the effects of fiber morphology and testing parameters on the IR spectra were analyzed. The accurate and reproducible IR spectra of single fibers can be acquired through appropriate parameter settings of the Continuμm microscope and sample preparation.

Apart from the issues mentioned in the present paper, there still exist some factors influencing the quality of IR spectra, e.g., the contaminant or damage on fiber surface and H_2O or CO_2 in the atmosphere, which should be analyzed in further experiments.

References

1. Moharram, M. A.; EL-Bahy, G. M. S.; Rabie, S. M.; Mahmoud, O. M. *Polym Plast Technol Eng* 1997, 36, 635.
2. Messerschmidt, R. G.; Harthcock, M. A.; Infrared Microspectroscopy. Marcel Dekker: New York, 1988; p 93.
3. Tungol, M. W.; Bartick, E. G.; Montaser, A. *Appl. Spectrosc.* 1990, 44, 543.
4. Krishnan, K. *Polym Preprints,* 1984, 25: 182.
5. Singh, B.; Gupta, M.; Anchal, V.; Tyagi, O. S. *Polym Int* 2000, 49: 1444
6. Vasanthan, N.; Salem, D. R. Structure characterization of heat set and drawn polyamide 66 fibers by FTIR spectroscopy. *Mat Res Innovat,* 2001, 4: 155
7. Chen, R. Y.; Jakes, K. A. Effect of pressing on the infrared spectra of single cotton fibers. *Appl Spectrosc* 2002, 56 646
8. Mavrich, A. M.; Ishida, H.; Koenig, J. L. Infrared mapping of surface-modified Kevlar fiber-reinforced epoxy systems. *Appl Spectrosc* 1995, 49, 149.
9. Koenig, J. L.; Arvanitopoulos, C. D. *Appl Spectrosc* 1996, 50, 1–10.
10. Continuμm User's Guide. Nicolet Instrument Corporation: Madison, 1999; p 1–6.
11. Garton, A. Infrared Spectroscopy of Polymer Blends, Composites and Surfaces. Hanser Publishers: Munich; 1992; p 66.
12. Atlμs User's Guide Nicolet Instrument Corporation: Madison 2001; p 1–23.