

A Comparison of Specular Reflection and PA-FTIR Techniques in the Analysis of Annealed Injection-Molded Polyamide 6,6

T. JAWHARI, L. QUINTANILLA, and J. M. PASTOR*

Departamento Física de la Materia Condensada, Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain

SYNOPSIS

A comparative study between the specular reflectance and photoacoustic FTIR techniques is presented in this work. The potential and limitations of these two methods are investigated by following and analyzing structural variations that take place at the surface in annealed injection-molded polyamide 6,6. Both spectroscopic techniques appear to be quite sensitive in detecting small structural changes that occur in polyamide 6,6 when submitted to different annealing temperatures. However, the presence of distorted bands in the specular reflection spectra makes the photoacoustic FTIR method more attractive for the IR vibrational analysis of difficult materials (e.g., composites, black-filled polymers, paints, etc.) that cannot be easily characterized by conventional transmission FTIR. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In the last decade new FTIR methods have appeared and been developed such as diffuse reflection (DRIFT), photoacoustic (PA-FTIR), microscopy, or emission Fourier transform spectroscopies, especially as a result of the advantages of Fourier transform techniques and improvements in accessories. Several excellent reviews¹⁻³ of these different techniques have been published. Although these methods yield spectra of much lower quality (i.e., lower signal-to-noise ratio) than that obtained with the conventional infrared transmission experiment, they allow the analysis of specimens with minimum sample preparation without solvent casting, grinding, or pressing as is the case in the transmission experiment. Therefore, these methods are of considerable value when studying physical properties that may be altered by the preparative procedures or when analyzing sample surfaces. Further, the spectroscopic analysis of materials known as difficult samples such as fiber-reinforced plastics, coals, paints, carbon black-filled polymers, etc., is difficult to carry out with the traditional transmission

method and requires the use of more recent techniques such as DRIFT,¹⁻⁸ PA-FTIR,^{1-3,9} or specular reflection spectroscopy.¹⁰⁻¹²

In this work, two of these techniques, PA-FTIR and specular reflection FTIR, are used and compared in their ability to detect structural changes that may occur at the surface of annealed injection-molded polyamide 6,6 samples. A brief description of both techniques is presented.

Specular Reflection-FTIR Spectroscopy

Although specular reflection spectroscopy, sometimes referred to as external reflection spectroscopy, involves a relatively simple experimental setup, it has not been widely used as a method for analyzing polymer surfaces. This is mainly due to the fact that the recorded spectra usually present distorted bands that differ from those of the conventional transmission experiment in the position, shape, and intensity. Furthermore, for low refractive index materials these reflectance spectra are weak. However, in some specific cases, such as characterization of carbon-filled polymers,^{13,14} polymer surfaces,¹⁵⁻¹⁷ painted polymer molding,^{10,13} and fibers,¹³ the method was found to give rapid and valuable information.

* To whom correspondence should be addressed.

The method consists basically of collecting the IR radiation after reflection at the air-sample interface, with incident angles typically of about 45° , and analyzing the component reflected from the front surface. However, the main problem with this method is that other types of reflections occur (see Fig. 1), which tend to distort the spectrum and complicate the interpretation.

The other component that is most often encountered during the specular reflection experiment is the diffuse reflection. This diffuse radiation comes from discontinuities in the refractive index of the polymer that might be due to voids, crystallites, additives, or other inhomogeneities. This produces light scattering and as this scattered light passes through the material it is absorbed and eventually may leave the front surface of the material where it will be detected by the instrument.

Thus, the collection of the specular reflection component alone will essentially depend on the nature of the sample to analyze. The ideal sample for the specular reflection measurement is a material that is homogeneous, optically flat, and infinitely thick.

The vibrational bands of an FTIR specular reflection spectrum have a distorted shape mainly due to the fact that the reflection intensity is greatly affected by the dispersion in refractive index about the resonance frequency.¹⁸ This unconventional shape may be corrected to a more usual FTIR bandshape by applying a mathematical transformation (Kramers-Kronig transformation).¹⁹

Photoacoustic-FTIR Spectroscopy

In the last years PA spectroscopy has been increasingly used mainly because of its ease of use and ability to characterize difficult (often optically opaque) industrial samples²⁰⁻²¹ such as composites,²² liquid crystalline polymers,²³ or polymer fibers.²⁴ Basically, in the PA-FTIR experiment, the incident radiation modulated in the audiofrequency range by the Michelson interferometer impinges onto the sample that is sealed in a small volume containing an IR transparent gas. Some of the IR radiation is absorbed at the vibrational frequencies characteristic of the material to be analyzed. This absorbed energy is transformed into heat in the form of modulated thermal waves that produce pressure variations in the gas. These modulated pressure variations are finally detected by a sensitive microphone and then Fourier transformed in order to obtain the typical IR absorption spectrum.

One of the capacities of the PA technique is its ability to get a depth profile of the sample surface

by varying the modulation frequency of the IR radiation, which has been applied in the analysis of multilayer polymer systems.²⁵⁻²⁶ Also, as the specular reflection spectroscopy, the technique offers the advantage of being relatively simple, nondestructive, and no sample preparation is required.

However, the principal drawback of such a technique is its low inherent sensitivity so that relatively high scanning times are needed. Another limitation is the PA saturation that can sometimes be observed in some specific regions of the spectrum when samples of high optical absorption coefficient are analyzed.

EXPERIMENTAL

Materials

The sample used in this work was furnished by the SNPE (France) as a 3-mm thick plate obtained by injection molding of commercial polyamide 6,6 (tradename PA 6,6 Technyl A218); formic acid viscosity ≈ 140 ; $M_w \approx 33000$ and $M_n \approx 16500$. The polymer resin was injected in the mold at a temperature of 269°C with a pressure of 100 bars. The temperature of the mold was fixed at 70°C and the injected sample was maintained in it for 5 s at a pressure of 95 bars.

A DSC measurement made on the as-received polyamide 6,6 sample using a Mettler TA 4000 (DSC/30) instrument gives a value for the heat of fusion of 76.2 J g^{-1} that corresponds to a crystallinity of about 40% using a heat of fusion of 188 J g^{-1} as determined by Starkweather et al.²⁷ for molding pellets.

For the specular reflection and PA-FTIR measurements the specimens were analyzed as received without any sample preparation. The quality of the surface of the plates was examined with an optical microscope and it was found that the surface was quite flat; therefore, relatively good specular reflection spectra could be obtained from these samples.

The thermal treatment was produced by annealing at different temperatures (i.e., 90, 120, 150, 180, 210, 220, and 230°C) the samples for 1 h in an oven and then cooled at room temperature in the open laboratory.

FTIR Measurements

All the IR spectra presented in this study were run with a Mattson FTIR instrument (model Cygnus 100) equipped with a liquid nitrogen cooled MCT detector.

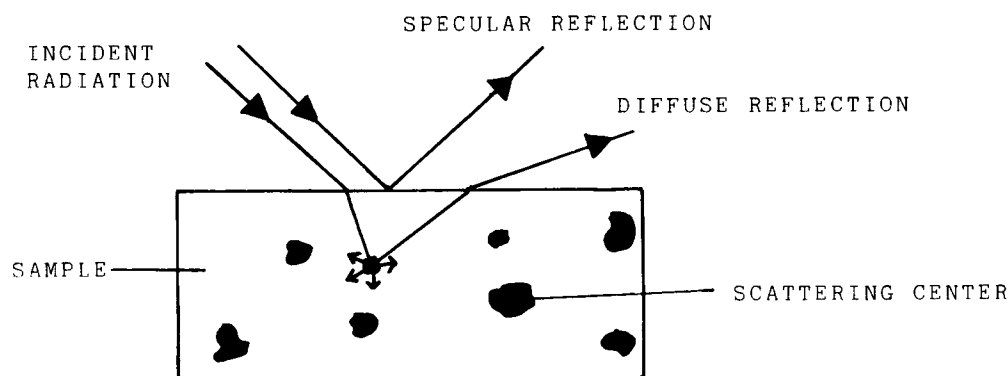


Figure 1 Schematic diagram illustrating the different types of reflection that can take place during the reflectance experiment.

In the case of the specular reflection experiment, the plate samples (3×3 cm) were simply posed on the sampling stage. The incident radiation arrives onto the sample with an angle of 45° to the normal of the sample plane and the reflected beam was collected by a mirror that focuses the reflected radiation onto the detector. The approximate penetration depth of radiation in the sample is about a few hundred nanometers. The corresponding spectrum was recorded and ratioed against a reflection background taken from a mirror. The Kramers–Kronig transformation was not available in our study. As a result the spectra were left uncorrected. Because the purpose of this work is to follow the evolution of identical IR bands of polyamide 6,6 as a function of the annealing temperature, the correction of the reflectance spectra was not considered necessary.

The PA-FTIR signal from samples loaded in a 10-mm diameter cup was recorded with a MTEC 200 PA cell. The best signal-to-noise ratio was observed for a mirror speed of 0.12 cm s^{-1} . The PA reference spectrum was obtained using powdered black carbon that acts as a photoacoustically saturated material. The PA signal provides information from a sample thickness that depends on thermal material properties, the mirror speed, and the specific spectral region. As the spectral ranges that will be considered below appear at about 700, 1000, 1200, and 1300 cm^{-1} and with a mirror speed of 0.12 cm s^{-1} , the structural information provided by the PA signal ranges from 10 to $14 \mu\text{m}$.

Transmission FTIR spectra were also recorded by microtoming thin films of different thicknesses varying between 4 and $20 \mu\text{m}$ from the thermal treated plate samples.

All the spectra presented and analyzed here were recorded at room temperature. In the case of the specular reflection and transmission experiments, the spectra were recorded at 4 cm^{-1} resolution with

accumulation of 150 scans, whereas for the PA-FTIR spectra, the resolution was fixed to 8 cm^{-1} and averaged over 312 scans principally due to the relatively low signal-to-noise ratio.

RESULTS AND DISCUSSION

Figure 2(a,b) show the IR spectra of the untreated polyamide 6,6 sample recorded by specular reflection and PA-FTIR spectroscopies, respectively.

A conventional transmission spectrum of the bulk is also added in Figure 2(c) in order to compare it to the two previous spectra. Due to the strong polar groups present in polyamide 6,6, such a compound is found to absorb the IR radiation strongly. Therefore, in order to obtain a transmission spectrum with a correct level of absorption, it was necessary to microtome very thin films. For example, the spectrum represented in Figure 2(c) was obtained on a polyamide 6,6 film of $4\text{-}\mu\text{m}$ thickness. Such thin films with good optical quality of the surface were difficult to prepare from the molded plate and their corresponding spectra still present a high degree of absorption. It should be also kept in mind that the microtoming procedure may also induce slight crystallization or orientation in the sample under examination.

Comparing these three spectra, it can be observed that the PA-FTIR spectrum is quite similar to that recorded by transmission whereas the IR bands of the specular spectrum appear to be distorted. In good agreement with the literature,^{28,29} the frequency position of the bands in the specular reflection spectrum appears shifted to the higher frequencies, varying from 1 to 2 cm^{-1} up to 30 cm^{-1} depending on the mode considered, when compared to the frequency of the bands present in the transmission spectrum of polyamide 6,6.

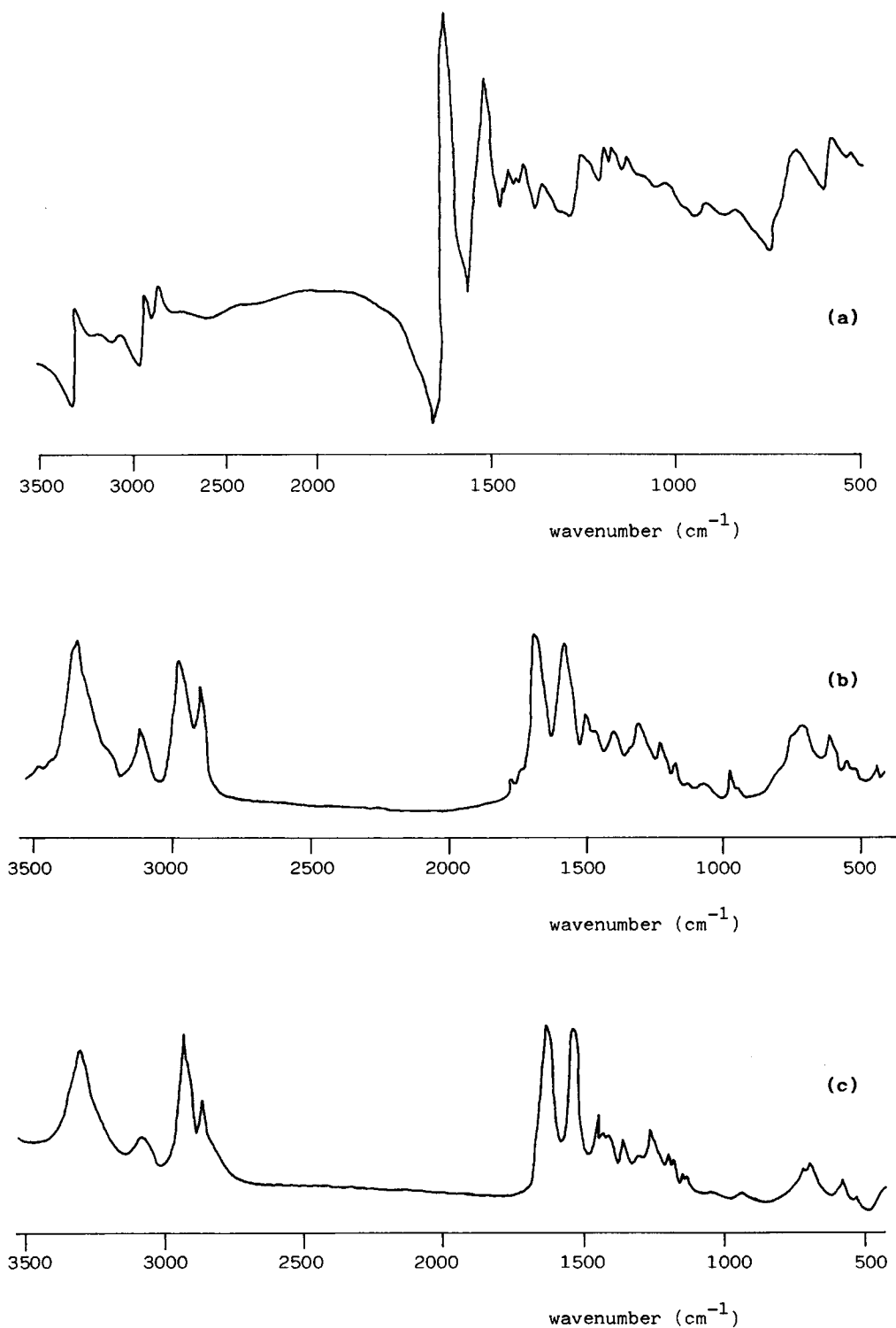


Figure 2 FTIR spectrum of an untreated injection-molded polyamide 6,6 sample recorded with the (a) specular reflection, (b) photoacoustic, and (c) conventional transmission methods.

In Figures 3–5 discussed at continuation, four spectra were chosen and plotted, corresponding to the annealing temperatures (i.e., 120, 180, and

230°C, as well as the nontreated sample) that clearly show the evolution of spectral features that take place with the thermal treatment.

The two bands at 936 and 1146 cm^{-1} have long been used for studying the crystalline variation in polyamide 6,6.³⁰ The former has been assigned to the C—CO stretching mode in the crystalline phase whereas the latter corresponds to a CO twisting vibration characteristic of the amorphous region.³¹ These two bands were observed in the specular reflection spectrum at 943 and 1151 cm^{-1} , whereas in the PA-FTIR spectrum these two bands appear at about 936 and 1146 cm^{-1} . Although the shape of these two bands is found to be quite distorted in the reflectance spectra, therefore complicating their analysis, a change in the intensity of these two bands can be observed to take place between 120 to 180°C [see Fig. 4(a)]. Increasing the annealing temperature up to 230°C produces a much greater variation (the intensity of the 943 cm^{-1} increases whereas that of the one at 1151 cm^{-1} is found to decrease). Similarly, the PA-FTIR spectra presented in Figure 4(b) show a clear increase in intensity of the band at 936 cm^{-1} and a decrease of that at 1146 cm^{-1} when the annealing temperature is over 180°C. Therefore, these results indicate that a significant structural reorganization occurs when the annealing temperature gets over 180°C. Such restructuring is probably due to an increase in the degree of more regular polymer chains in polyamide 6,6.

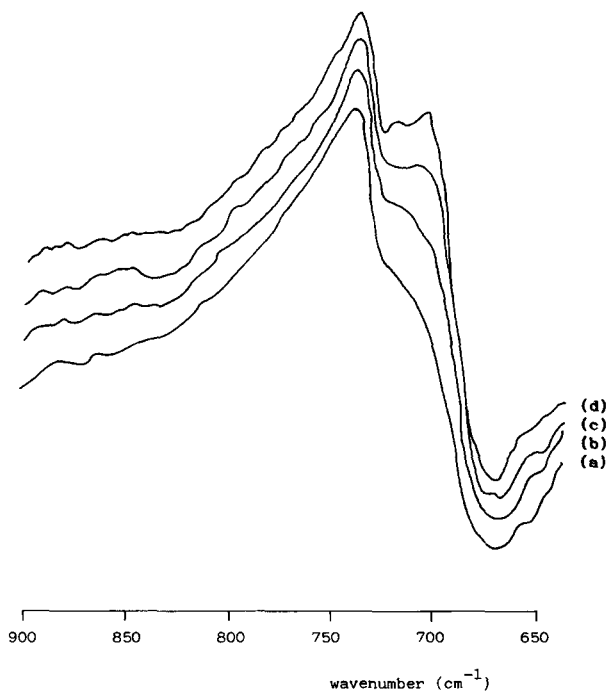


Figure 3 (a) Specular-FTIR spectra in the amide V region of (a) untreated sample and samples annealed at (b) 120, (c) 180, and (d) 230°C, respectively.

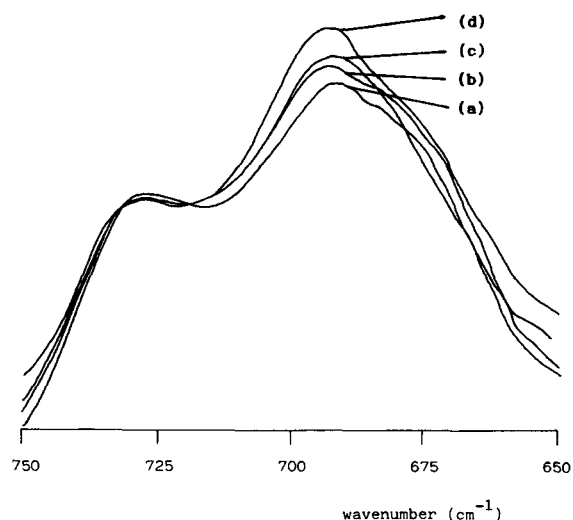


Figure 3 (b) PA-FTIR spectra in the amide V region of (a) untreated sample and samples annealed at (b) 120, (c) 180, and (d) 230°C, respectively.

Another interesting feature of our results is the clear increase in intensity of the IR band about 700 cm^{-1} , which appears as a shoulder in the reflection spectrum, when compared to the band at 738 cm^{-1} for annealing temperature greater than approximately 180°C [see Fig. 3(a)]. These two bands are present at 693 and 727 cm^{-1} in both the conventional transmission and PA-FTIR spectra of polyamide 6,6. The PA-FTIR spectra as shown in Figure 3(b) corroborate the specular results. It can be effectively observed that the intensity of the low wavenumber band, that is, at 693 cm^{-1} , increases significantly as the annealing temperature is raised over 180°C. This band known as the amide V was assigned to the NH out-of-plane deformation vibration³²⁻³³ in polyamides and was also attributed³⁴ to the crystalline part of polyamide 6,6 (the amide band of the amorphous region appears apparently below 680 cm^{-1}). According to this assignment, our results would suggest that above the annealing temperature of approximately 180°C, there is enough molecular motion to permit some segments along the polymer chain to be reorganized in a more regular manner, which is in agreement with the previous result obtained from the analysis of the bands at 936 and 1146 cm^{-1} .

Two other bands, at 1224 and 1329 cm^{-1} , of low intensity have been reported³⁵⁻³⁷ to increase with the annealing treatment. These two bands were assigned³⁵⁻³⁷ to chain-folded conformations in polyamide 6,6 and were found to give valuable information on the regularity of the folds. In the present study, similar features have been detected in both the specular and PA-FTIR spectra of the annealed

samples. For example, the specular reflection spectra shown in Figure 5(a) indicate that a new shoulder appears at about 1227 cm^{-1} for the sample annealed at 180°C and increases in intensity as the annealing temperature varies from 180 up to 230°C . No clear changes could be observed in the specular-FTIR spectra near the frequency of the second fold band, that is, about 1329 cm^{-1} . This result may be due to the wide spectral feature between 1280 and 1340 cm^{-1} in the specular spectrum that would mask the weak shoulder near 1329 cm^{-1} . In the case of the PA-FTIR spectra, a shoulder near 1335 cm^{-1} can be detected when the annealing temperature reaches approximately 180°C and increases further in intensity as the annealing temperature is raised to 230°C [see Fig. 5(b)]. The other fold band near 1224 cm^{-1} in the PA-FTIR could not be as clearly

identified as the one at 1335 cm^{-1} . Thus, the temperature range where an increase in the bands assigned to the folded chain conformations is observed in both specular and PA-FTIR spectra is consistent with the temperature where previous structural changes were detected. This result shows that the temperature around 180°C corresponds to the onset of large enough molecular motions in polyamide 6,6 that permit a better packing of the polymer chains. Further, the structural reorganization observed here appears to affect the interphase between crystalline and amorphous regions with a probable increase in the regularity of the folds as the annealing temperature is increased above 180°C .

Other spectral features were also observed to change with the annealing temperature in both the specular and PA-FTIR spectra of polyamide 6,6 such

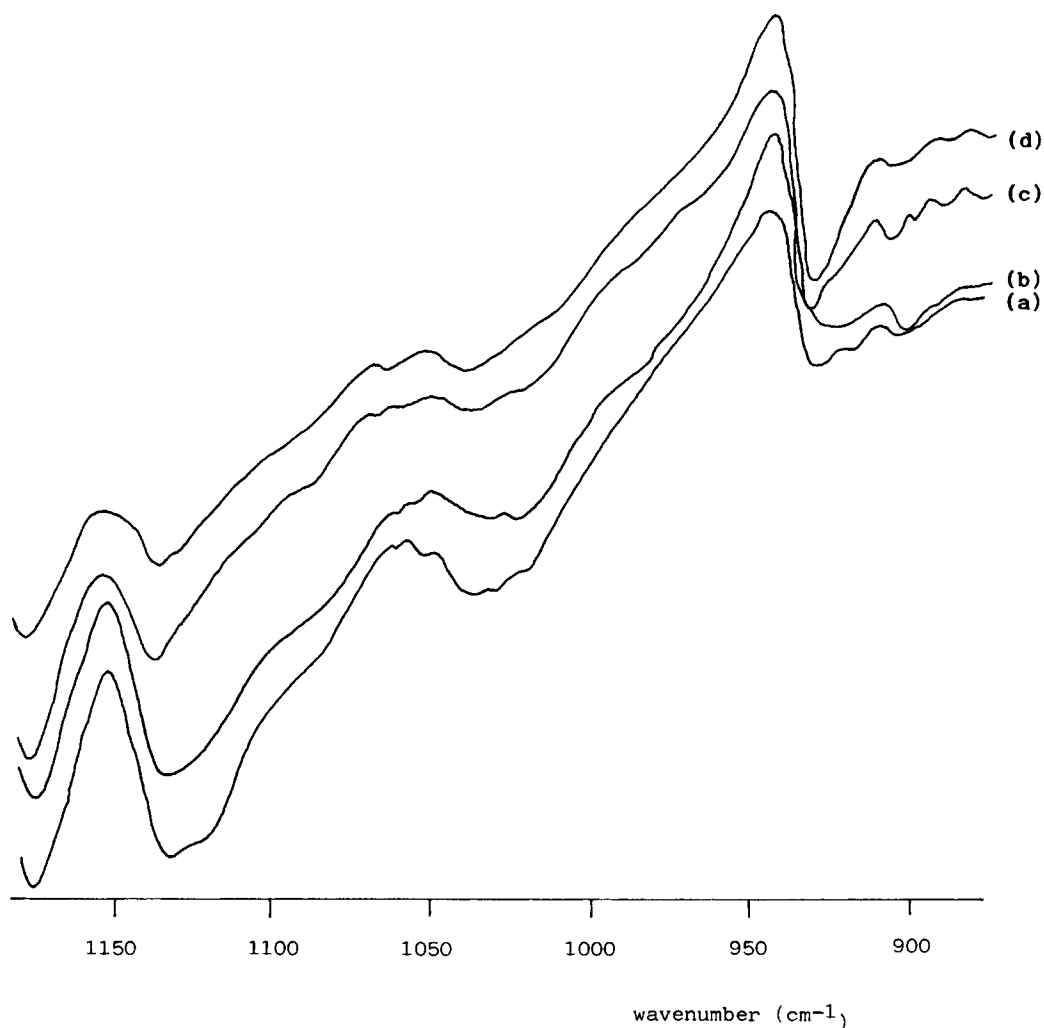


Figure 4 (a) Specular-FTIR spectra between 875 – 1180 cm^{-1} of (a) untreated sample, and samples annealed at (b) 120 , (c) 180 , and (d) 230°C , respectively.

as variation in intensity and band shape. For example, the bandwidth of those at 739, 1374, 1467, and 1478 cm^{-1} , appears to decrease when the annealing temperature increases above approximately 180°C. This may reflect the gain of coupling in the crystalline phase as a result of the annealing process.

Further, both reflectance and PA-FTIR spectra do not reveal the presence of an absorption band above 3400 cm^{-1} characteristic of the N—H stretching mode of nonbonded amide groups. This result is thus in good agreement with previous works³⁸⁻⁴² that consider that at room temperature essentially all amide groups are hydrogen bonded.

CONCLUSIONS

Both the specular reflection and PA-FTIR analysis of thermal treated polyamide 6,6 molded plate were able to detect structural variations that are in agreement with previous studies of annealed polyamide

6,6 samples carried out by conventional transmission FTIR spectroscopy. From this study, it was observed that structural variations appear to take place at about the same temperature range (around 180°C) indicating that above this value there is enough thermal energy to permit a better packing of the polymer segments.

It must also be precised that the information obtained here is characteristic of the surface of the sample and the great advantage of using the specular reflectance and the PA-FTIR techniques is that no sample preparation was required.

The distortion of the IR bands in the reflectance spectra makes this method less attractive than its PA-FTIR counterpart. In the case of our study, where no mathematical transformation was used to correct the distorted bands, the specular reflectance method was found to be useful only for qualitative determination. However, it can be noted that the recent developments made in FTIR reflection spectroscopy as well as the application of exact theory^{17,43}

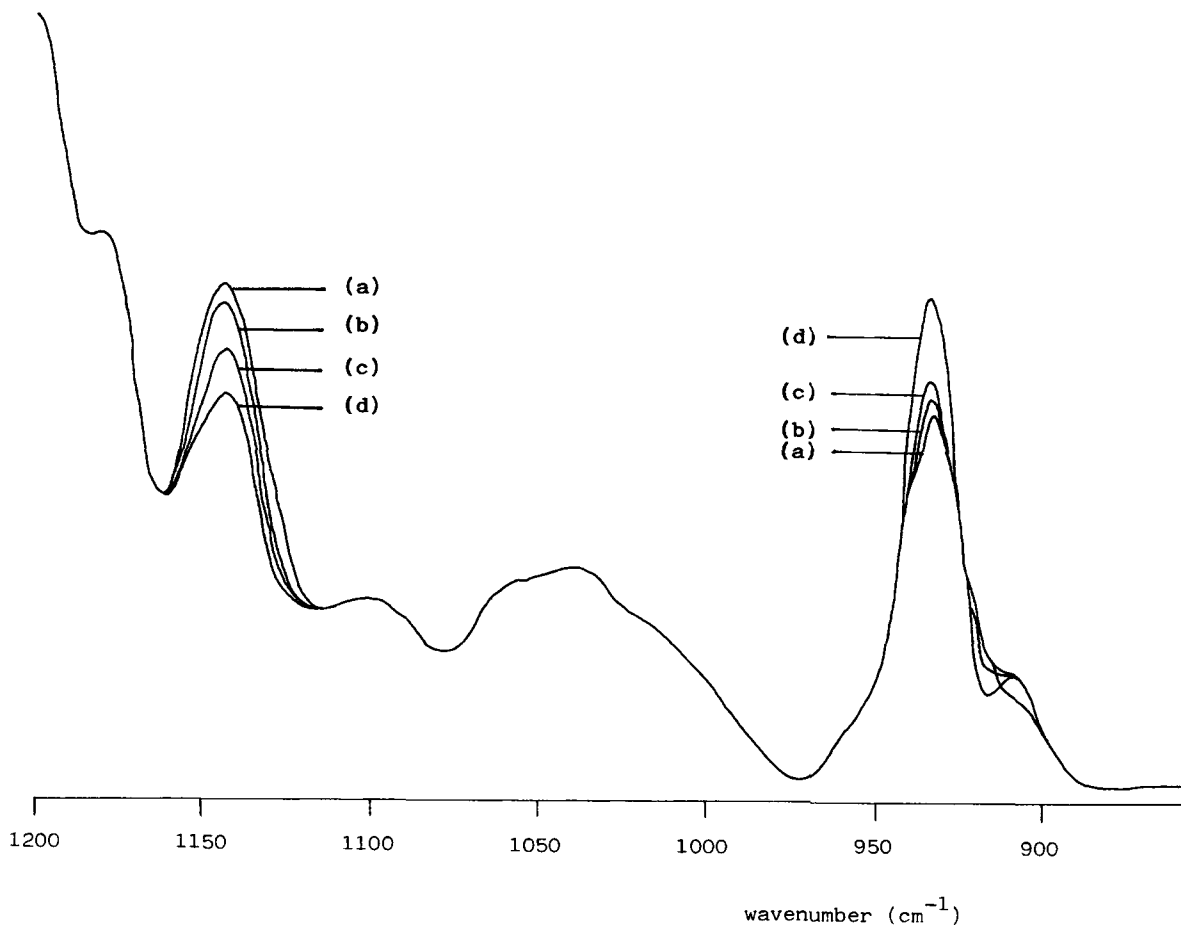


Figure 4 (b) PA-FTIR spectra between 855–1200 cm^{-1} of (a) untreated sample and samples annealed at (b) 120, (c) 180, and (d) 230°C, respectively.

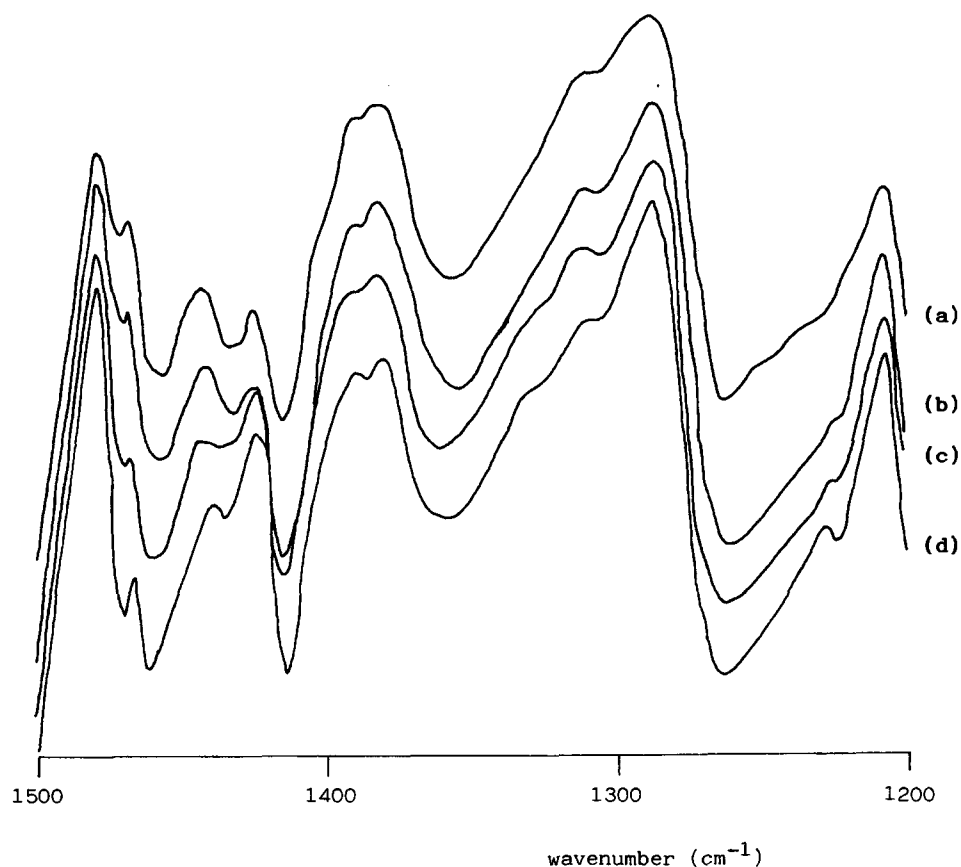


Figure 5 (a) Specular-FTIR spectra between 1200–1500 cm^{-1} of (a) untreated sample and samples annealed at (b) 120, (c) 180, and (d) 230°C, respectively.

allow the minimization of these spectral distortions and the use of external reflection spectroscopy as a method for quantitative analysis. Its main advantage, when compared to the PA-FTIR method, is its

higher signal-to-noise ratio. Longer accumulation time is thus needed when recording PA-FTIR spectra and practical resolution obtained with the PA-FTIR method is often limited to 8 cm^{-1} whereas

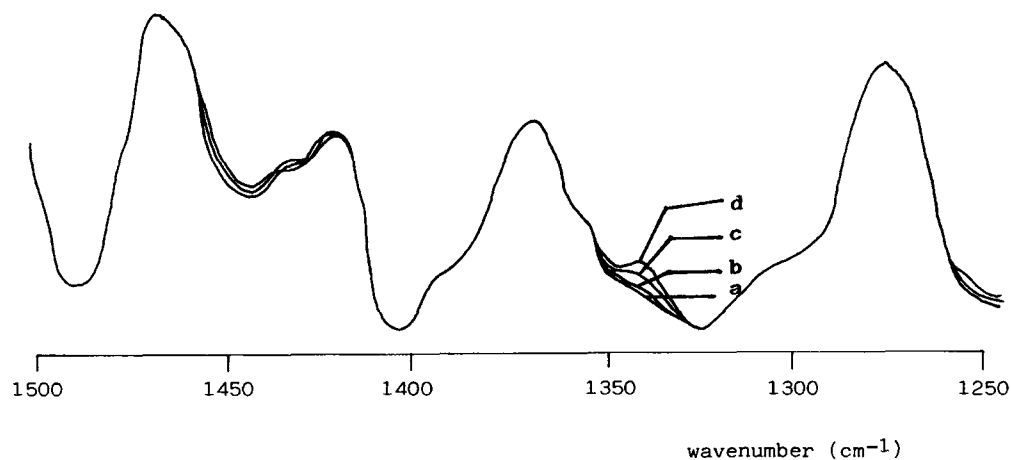


Figure 5 (b) PA-FTIR spectra between 1250–1500 cm^{-1} of (a) untreated sample and samples annealed at (b) 120, (c) 180, and (d) 230°C, respectively.

specular spectra can be obtained with a resolution of 2 or 4 cm^{-1} . However, the significant advantage in using the PA-FTIR method is that its spectral information is very easy to interpret (similar to conventional transmission spectra). Further, as shown recently in a PA-FTIR investigation of the structural changes that take place in thermally treated PET,⁴⁴ this technique can be conveniently used for quantitative analysis.

This work was supported by the CICYT (program MAT90-0914).

REFERENCES

- P. R. Griffiths and M. P. Fuller, *Advances in infrared and raman spectroscopy*, R. J. H. Clark and R. E. Hester, Eds., Vol. 9, Heyden, London, 1982, p. 63.
- J. M. Chalmers and M. W. Mackenzie, *Advances in applied Fourier transform infrared spectroscopy*, John Wiley, Chichester, 1988, p. 105.
- M. W. Urban and J. L. Koenig, in *Vibrational Spectra and Structure*, J. Durig, Ed., Elsevier, Vol. 18, Amsterdam, 1990, p. 127.
- J. M. Chalmers and M. W. Mackenzie, *Appl. Spectrosc.*, **39**, 634 (1985).
- J. L. Koenig, *Pure and Appl. Chem.*, **57**, 971 (1985).
- J. L. Fuller, Jr. and N. R. Smyrl, *Fuel*, **64**, 1143 (1985).
- P. R. Young and A. C. Chang, *SAMPLE J.*, **March–April**, 70 (1986).
- E. G. Ghatzi, H. Ishida, and J. L. Koenig, *Appl. Spectrosc.*, **40**, 847 (1986).
- J. A. Graham, W. M. Grim III, and W. G. Fateley, in *Fourier Transform Infrared Spectroscopy—Application to Chemical Systems*, J. R. Ferraro and L. J. Basile, Eds., Vol. 4, Academic Press, Boston, 1985.
- M. A. Harthcock, L. A. Lentz, B. L. Davis, and K. Krishnan, *Appl. Spectrosc.*, **40**, 210 (1986).
- M. Claybourn, P. Colombel, and J. Chalmers, *International Workshop on FTIR*, E. F. Vansant, Ed., Antwerp, 1990, p. 118.
- J. R. Ferraro and J. M. Williams, in *Practical Fourier Transform Infrared Spectroscopy: Industrial and Laboratory*, J. R. Ferraro and K. Krishnan, Eds., Academic Press, San Diego, 1990, p. 41.
- M. Claybourn and P. Colombel, *Bruker Report*, **1**, 8 (1990).
- M. Claybourn, P. Colombel, and J. Chalmers, *J. Appl. Spectrosc.*, **45**, 279 (1991).
- J. A. Reffner and W. T. Wihlborg, *Internat. Lab.*, **July–August**, 19 (1990).
- G. Boven, R. H. G. Brinkhuis, E. J. Vorenkamp, and A. J. Schouten, *Macromolecules*, **24**, 967 (1991).
- Y. Ishino and H. Ishida, *Appl. Spectrosc.*, **46**, 504 (1992).
- S. G. Lipson and H. Lipson, *Optical physics*, Cambridge University Press, Cambridge, 1981.
- B. Harbecke, *Appl. Phys.*, **A40**, 151 (1986).
- R. O. Carter III and M. C. Paputa Peck, *Appl. Spectrosc.*, **43**, 468 (1989).
- R. O. Carter III, M. C. Paputa Peck, and D. R. Bauer, *Polym. degradation stability*, **23**, 121 (1989).
- E. G. Chatzi, M. W. Urban, and J. L. Koenig, *Die Makromol. Chim. Macromol. Symp.*, **5**, 99 (1986).
- O. Barres, C. Friedrich, B. Jasse, and C. Noël, *Makromol. Chem. Macromol. Symp.*, **52**, 161 (1991).
- M. W. Urban, E. G. Ghatzi, B. C. Perry, and J. L. Koenig, *Appl. Spectrosc.*, **40**, 1103 (1986).
- M. W. Urban and Koenig, *Appl. Spectrosc.*, **40**, 994 (1986).
- P. A. Dolby and R. McIntyre, *Polymer*, **32**, 586 (1991).
- H. W. Starkweather, Jr., P. Zoller, and G. A. Jones, *J. Polym. Sci. Phys. Ed.*, **22**, 1615 (1984).
- R. T. Graf, J. L. Koenig, and H. Ishida, *Appl. Spectrosc.*, **39**, 405 (1985).
- J. L. Koenig, *Spectroscopy of Polymers*, ACS, Washington, DC, 1992, p. 44.
- H. W. Starkweather, Jr. and R. E. Moynihan, *J. Polym. Sci.*, **22**, 363 (1956).
- J. Jakes and S. Krimm, *Spectrochim. Acta, Part A*, **24a**, 19 (1971).
- H. B. Kessler and G. B. B. M. Sutherland, *J. Chem. Phys.*, **21**, 570 (1953).
- T. Mizazawa, T. Shimanouchi, and S. Mizushima, *J. Chem. Phys.*, **24**, 408 (1956).
- A. Miyake, *J. Polym. Sci.*, **44**, 223 (1960).
- J. L. Koenig and M. C. Agboatwalla, *J. Macromol. Sci. Phys.*, **B2**, 391 (1968).
- P. D. Frayer, J. L. Koenig, and J. B. Lando, *J. Macromol. Sci. Phys.*, **B3**, 329 (1969).
- C. G. Cannon and P. H. Harris, *J. Macromol. Sci. Phys.*, **B3**, 357 (1969).
- D. S. Trifan and J. F. Terenzi, *J. Polym. Sci.*, **28**, 443 (1958).
- D. Garcia and H. W. Starkweather, Jr., *J. Polym. Sci. (PP)*, **23**, 537 (1985).
- E. Bessler and G. Bier, *Makromol. Chem.*, **122**, 30 (1969).
- W. J. MacKnight and M. Yang, *J. Polym. Sci., Polym. Symp.*, **42**, 817 (1973).
- L. R. Schroeder and S. L. Cooper, *J. Appl. Phys.*, **47**, 4310 (1976).
- J. A. Mielczarski, M. Milosevic, and S. L. Berets, *Appl. Spectrosc.*, **46**, 1040 (1992).
- L. Quintanilla, J. C. Rodríguez-Cabello, T. Jawhari, and J. M. Pastor, *Polymer*, to appear.

Received March 10, 1993

Accepted June 14, 1993