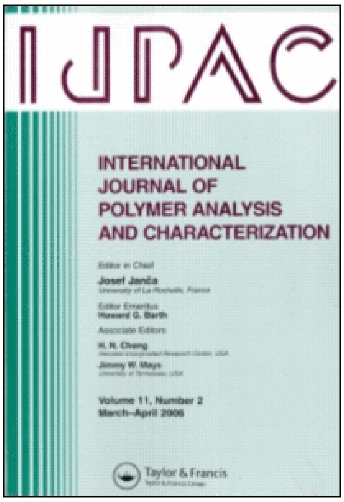

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Characterization of Poly(Ethylene Terephthalate) Using Near and Far FTIR Spectroscopy

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The use of near infrared and far infrared spectroscopy for characterization of poly(ethylene terphtalate) films is discussed. After a brief review of previous work, some examples of transmission spectra of annealed PET, showing complex changes in the absorption bands, are presented. NIR spectra was used to follow the crystallinity (or conformation) of thick PET films without any sample preparation.

Keywords: Spectroscop, poly(ethylene terephtalate), crystallinity, near infrared, far infrared spectroscopy, microspectroscopy

INTRODUCTION

Poly(ethylene terephtalate) (PET) is one of the most important polymers for industrial applications. For example, PET can be used as thin films for video cassettes or as an extrusion blow moldable polymer, and used as a possible substitute of PVC or polyolefins for bottles. The mechanical properties depend on the morphological structure (crystallinity, orientation, etc.). Extensive investigations have been carried out to study the influence of mechanical or heat treatment on the properties of polymers and to establish relationships between morphology and properties [1,2]. To reduce the amount of waste manufactured out of specification, the polymer quality parameters have to be monitored from the molten polymer to the end prod-

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uct. Vibrational spectroscopy is ideally suited for the analysis and characterization of PET [3,4]. Mid infrared studies are numerous and well documented. Absorption bands have been assigned and some of them associated with conformational state of ethylene glycol segments. Lin and Koenig [5] studied, in detail, the trans and gauche conformations in the disordered phase of PET with mid infrared spectroscopy. Raman and FT-Raman spectroscopies have been used to monitoring structural changes of annealed PET samples. For example, the Raman band situated at 1412 cm^{-1} shifts to 1425 cm^{-1} after a thermal treatment and changes of bandwidth of the 1725 cm^{-1} band can be observed [6]. One of the major problems of conventional Raman spectroscopy is due to the strong fluorescence of some samples irradiated with visible light. For the FT-Raman spectroscopy, the problem of the fluorescence is reduced by the use of the NIR diode laser operating at 1.06 nm [7].

Near, far IR, and low frequency Raman investigations constitute only a small part of papers published in the area of molecular spectroscopy of polymers, but exhibit a large potential for practical and theoretical polymer studies. Although there is a great deal of information concerning the interpretation of Raman and mid IR spectra, the fundamental studies of NIR and far IR spectra is lacking. The aim of this work is to show that the high sensitivity of NIR and far IR spectroscopy can be used to follow the changes in the conformation (or the crystallinity) of the PET films.

Near FT-IR Spectroscopy

Near infrared (NIR) analysis has been extensively and successfully used in food industries, but not widely used in the chemical industry. For process and quality control measurements, NIR spectroscopy opens the possibility of rapid, nondestructive multicomponent analysis. In addition NIR spectra of polymers also contain information on structure, and intermolecular and intramolecular interactions. Some absorbance bands can be used directly to monitor chemical reactions, water content or crystallinity. NIR spectroscopy, requires little or no sample preparation, can use path lengths of more than 1 mm and atmospheric water vapor does not interfer. Qualitative and quantitative NIR infrared spectroscopy presents a great opportunity to improve the processing of polymeric materials.

NIR applications using chemiometric methods are numerous, for example see ref. [8] for a review the use of NIR spectroscopy for the analysis of synthetic polymers. Fukuda *et al.* [9] studied the nature of water sorbed in PET film from dryness to saturation by NIR. The 7000 cm^{-1} (water) band was resolved into three sub-bands; these three compounds were attributed to three kinds of water species differing in the degree of hydrogen bonding. Siesler, [10] using NIR light-fiber, studied PET film processing. The structural changes, occurring during drawing, were monitored by FT NIR with a polarized beam during elongation. In this case, a mid infrared model, obtained with thinner films, were utilized to calibrate NIR measurements [11].

Over the past few years, in-line NIR analysis has become a rapidly emerging technique for molten polymeric processes [12]. Recently, van Uulm *et al.* [13,14] showed that NIR spectra of PET melt contain a sufficient amount of information to estimate the number of carboxylic end groups and the relative viscosity, suggesting that in-line monotoring of this parameters is feasible by this technique coupled with chemometric methods. In addition, NIR spectra of polymers also contain information on conformation and crystallinity. Bulk polymer, films, and fibers of PET have been studied by NIR analysis. Miller and Eichinger [15] used an NIR grating spectrometer with diffuse reflectance to study heat treatment or mechanical strain of PET, and found, by principal component analysis (PCA), that the spectra are sensitive to crystallinity and to molecular orientation.

Although it is well established that overtone bands are interpreted in terms of the local mode (bond deformation), which is characteristic for the NIR region, generally the full NIR spectra are only interpreted in terms of a small number of factors (three to ten). Data reductions are based on regression (principal component regression, partial least square regression, etc.). The use of NIR spectra with PCA or other statistical pakages is a powerful tool for industrial analysis but the chemical aspect is not fully taken into account; better use of quantitative band analysis (with appropriated treatment) is required if spectra of high quality and band assignments were available in the literature.

Often NIR analysis are done with high speed filters instruments or grating spectrometers having a high signal-to-noise ratio but low resolution (20–50 cm^{-1}). They are ideally suited for quality control laboratories or process control. Presently, commercial "low cost" FT-NIR spectrometers with good resolution (better than 4 cm^{-1}) and "extended" KBr beamsplitters are available for mid FT IR spectromers which can record NIR spectra to 10 000 cm^{-1} with a fairly good signal-to-noise ratio. NIR spectroscopy with the development of new, rugged, reliable techniques [16] and fiber-optic probes, opens the possibility of rapid analysis without sample preparation.

Far FT-IR Spectroscopy

Low frequency, far infrared vibrations take into account intermolecular coupling and can be valuable for a better understanding of α, β and γ-transitions [17]. Difficulties of the theoretical approach and the lack of convenient spectrometers can explain the limited number of papers dealing with the study of polymers by FIR spectroscopy.

Conformational analysis, barriers to internal rotation, and vibrational assignment of torsional modes of organic molecules has been investigated by Durig *et al.* [18] using far infrared (FIR) and low frequency Raman. Recently, Klaeboe [19] reviewed various vibrational methods employed for conformational studies of small molecules and a monograph dealing with the investigation of the structure, phase transitions and reorientational motion of molecules in organic crystals was presented by Zhizhin and Mukhtarov [20]. Low frequency spectroscopy of single crystals to study phonon absorption has been reported [21]. The spectroscopy of polymers in the low frequency infrared region suffers lacks a solid theoretical approach. However, due to the high level of water vapor absorption and low level of polymer absorption, purging (vaccum) of the spectrometer is required, limiting FIR to the laboratory rather than for plant use. Information concerning Raman and far infrared spectroscopy have appeared in reviews [17,20–23]. Information concerning a low-temperature cell, IR cryostats and high-pressure far infrared cell are given in ref. [24,25]. Spectral artifacts arising in the 15–120 cm^{-1} region at low temperature are discussed in ref. [25].

EXPERIMENTAL

NIR spectra were recorded with a Perkin Elmer FTIR 1760X (Beaconfield, UK) with a ceramic source, a KBr beamsplitter, and DTGS (deuterated triglycine sulfate pyroelectric crystal) detector fitted with a KBr window. Micro spectra and mapping were recorded with a Nicolet FTIR 550 Magna spectrometer (Madison, WI) with a tungstene/halogen source, a CaF_2

beamsplitter coupled with a Nic-Plan microscope, and a MCT (mercury-cadmium-telluride) detector. FIR measurements were carried out, at room temperature, using a Bruker IFS66V spectrometer (Karlsruhe, Germany) with a Globar/Hg source, a Mylar beamsplitter (6-μm or 23-μm thick depending on the wavelength) and a DTGS/polyethylene window detector.

Infrared spectra of PET samples (from 300-μm to 800-μm thick) have been observed in the range 7000 to 4000 cm^{-1} and 700 to 20 cm^{-1} at 4 cm–1 resolution, using the transmission mode and averaged over 100 scans. Three PET batches (M_W between 22 000 and 45 000) were studied. The density of the initial films ranged between 1.345 and 1.355. The PET films have been annealed at 60°, 95°, 125°, 150° and 180°C for 5 min to 1 week in an air oven.

RESULTS AND DISCUSSION

Near FT-IR Spectroscopy

After the annealing process, the NIR spectra of PET films have been recorded at room temperature. The spectra of PET film (M_W 22 000) annealed in air oven at 95° and 125°C are presented in Figure 1. The PET

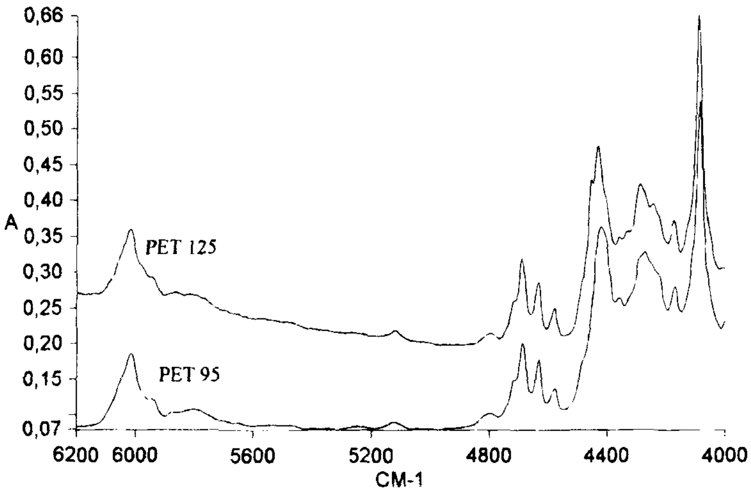

FIGURE 1 NIR transmission spectra of PET films crystallized at 95° and 125°C.

band assignments are presented in Table I and the peak positions from the spectra obtained are in Table II.

The changes in PET film spectra are numerous and are complicated by the shrinkage of the film near its glass-transition temperature and with increased scattered light related to the PET crystallinity which causes baseline shifts. Although the band widths of NIR spectra are comparatively wide and 4 or 8 cm^{-1} resolution is generally used to acquire NIR spectra with Fourier-transform spectrometers, improved resolution (2 cm^{-1}) can be

TABLE I Tentative band assignments in the NIR region for PET (13,15).

Observed bands, cm-^{1}	*Assignments*
6015–6025	aromatic C-H stretch (1st overtone) + methylene stretching
5800	overtones of CH, CH_2
5200–5250	combination bands of H_2O
5115–5125	2nd overtone C = O stretch
4680-4580	combination C-H aromatic stretch + ring
4420–4450	combination methylene strech and bend
4350	combination band of CH_2
4290-4170	bands involving CH_2, aromatic CH and COO groups
4080	aromatic combination bands

TABLE II NIR peak positions (cm^{-1}) of crystallized PET films.

PET Air	*PET Dried at 60°C*	*PET Cryst. at 95°C*	*PET Cryst. at 125°C*	*PET Cryst. at 150°C*	*PET Cryst. at 180°C*
6015	6015	6016	6019	6021	6024
5799	5798	5804			
5247					
5123	5125	5122	5120	5118	5118
4684	4688	4689	4690	4690	4690
4632	4631	4632	4634	4635	4637
4576	4576	4577	4578	4579	4579
			4456	4456	4457
4422	4424	4421	4430	4431	4433
4358	4359	4361	4360	4360	4360
				4335	4335
4271	4273	4273	4290	4290	4290
4173	4172	4175	4175	4176	4177
4084	4084	4086	4090	4091	4092

useful to monitor crystallinity changes; very small variations in the morphology can be detected using derivative curves. Figure 2 shows the second-derivative spectra of Figure 1. The second-derivative treatment compensates for the shift of baseline and the small differences between spectra can be seen more easily.

Substantial changes can be observed during annealing: peak shifts, changes in the number of observed peaks, and in the bandwidth. From room temperature until 90–100°C we observe two broad peaks near 4422 and 4272 cm^{-1} but the position of the maximum is not well defined. Above 100°C, striking modifications begin to appear in this area, a small shoulder appears at 4455 cm^{-1}, the peak maximum near 4422 shifts to 4430 cm^{-1} and the shape of the band near 4272 cm^{-1} changes slowly. This temperature is in good agreement with the temperature where changes have been observed with mid IR and Raman spectroscopy.4,5 Above 125°C two overlapped peaks are observed at 4456 and 4430 cm^{-1} (the peak at 4556 cm^{-1} is smaller than the peak at 4430 cm^{-1}) and two new peaks are observed near 4335 and 4250 cm^{-1}. Between 150° and 180°C, the intensity of the 4456 cm^{-1} band increases. After 170°C, the 4456 cm^{-1} band absorbes more than the 4432 cm^{-1} band. These changes in the methylene combination (stretch and bend) region agree with changes in the conformational structure of PET chains observed with mid IR and Raman.

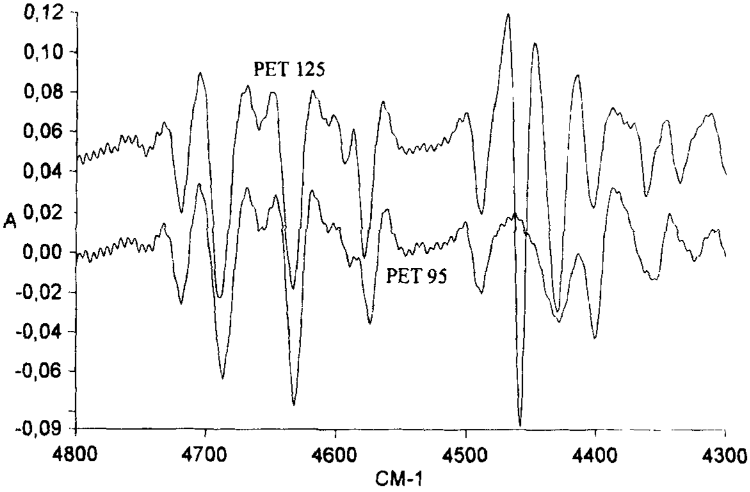

FIGURE 2 2nd-derivative NIR curves of PET films shown in Figure 1.

Spectral changes also concern the 4080 cm^{-1} aromatic combination band: the peak maximum shifts to the height wavenumber, its intensity increases and its bandwidth decreases when the temperature of thermal treatment rises, again the main changes are observed around 100°C. Changes in vibration of the benzene ring were also observed in the mid IR and FT-raman spectra and related to the packing change in the crystalline region [4]. The 4000–4400 cm^{-1} region is out of the range of the low-OH silica light-fibers, and many NIR analyzers are operable only after 4300 cm^{-1}, therefore little information was available for this region.

Smaller variations in the intensity, frequency and bandshape of the bands situated in the 4750–4550 cm^{-1} region have been observed. The crystallinity of the PET film has been estimated from the the density measurements (1.335 for amorphous PET, 1.455 for crystalline PET [26], and 1.468 for oriented, highly crystalline PET [13]). However, no linear correlation between the density and the intensity of the 4085 cm^{-1} band, using the band at 4685 or at 4576 cm^{-1} as internal reference, has been observed. The overtone band at 5800 cm^{-1} decreases with an increase of annealing temperature and can be correlated with the relative amounts of trans and gauche conformers of the ethylene glycol segments (this band was more intense for the molten polymer).

After 15 min of the annealing treatment, no significant shift of bands have been detected, only the bandwith slowly decreased. For temperatures above 150°C, the scattered light increases with annealing time, so, after 1 week at 180°C, the quality of transmission spectra becomes relatively poor. Similar results were obtained with the two others PET samples having different molecular weight, as expected, only the crystallization rate decreased slowly as the molecular weight increased [27]. However, the orientation, which might be introduced during the polymer processing [28] or the environment [29], can influence the results.

FT-IR microsampling has been extended into routine quality control of samples that are several hundred micrometers in size [30]. Unfortunately this technique requires samples of suitable thickness (5 to 15 μm) to be studied in transmission mode by mid IR spectroscopy. Sample preparation is time consuming, needs skilled personnel [31] and microtomy can modify the polymer structure. Surface samples can be quickly studied by ATR (reflection) but need an expensive ATR objective. NIR microspectroscopy, in contrast, can provide good spectra on relatively thick samples (50 to 500 mm) in the transmission mode [32] .

Figure 3 shows the mapping of heterogeneous PET film, the spectra were recorded for 100-μm apertured regions, 200 scans at 8 cm^{-1} resolution. The low level of absorbance (0.5 U.A.), which is due to the low absorptivity of combination and overtone bands, and the good signal-to-noise ratio of these spectra allow the use of microspectroscopy imaging [33]. For instance, Figure 4 shows the mapping using the 4085 and 4685 cm^{-1} band ratio. The reconstructed image, using ratio of bands, can be used to monitor chemical or structural variation through a polymer, but requires good band assignments. The transmission techniques have the disadvantage of not giving information concerning the surface of the sample, which can be a problem since the PET films have a core-shell structure [34].

NIR spectroscopy has enormous potential for controlling and studying the morphology of polymers and polymer blends. Although the NIR analysis has been used successfully for quantitative analysis, the NIR spectra will need to be interpreted in the same manner as the mid IR spectra. This is because the full applicability of NIR spectroscopy depends upon the fundamental interpretation of spectra during the annealing or curing of polymers. It has been found that two-dimentional (2D) vibration spectroscopy, correlation of mid IR and NIR regions, can improve the spectra interpretation [35,36].

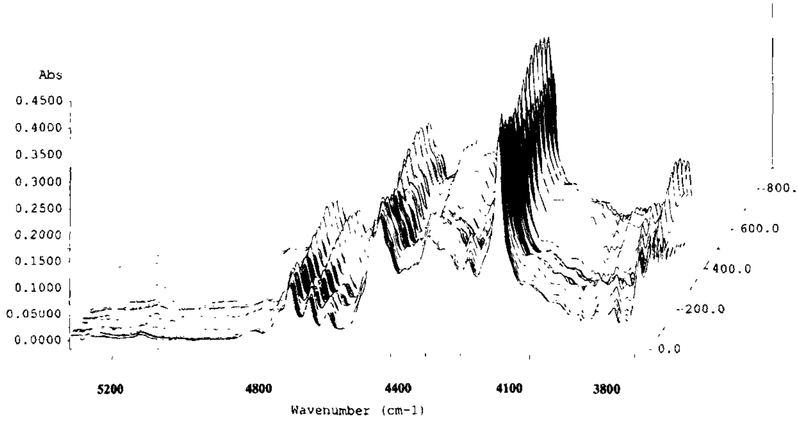

FIGURE 3 Microtransmission spectra of an heteregeneous cystallized PET film (500-mm thick).

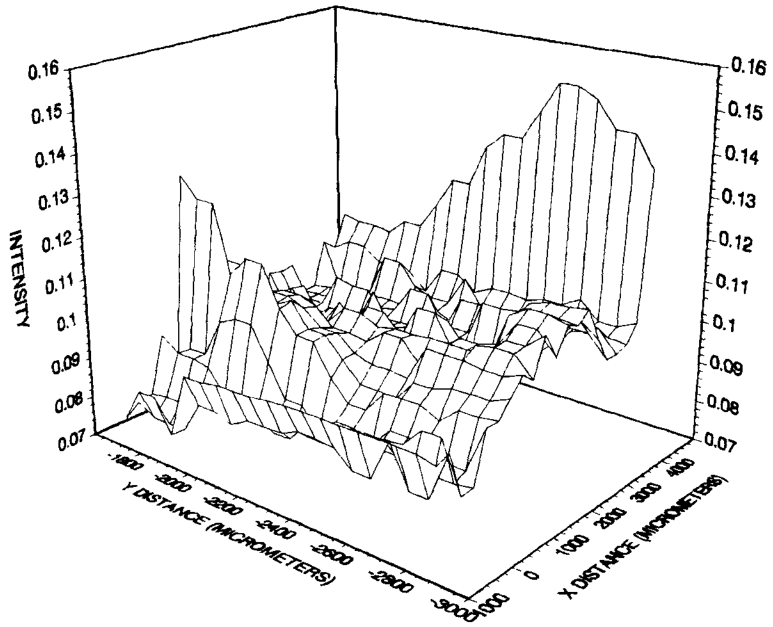

FIGURE 4 Reconstructed image obtained, after mapping of PET film, using band intensity.

Far FT-IR Spectroscopy

Far IR spectra of different crystallinity PET films are presented in Figures 5a and 5b. These spectra were recorded only at room temperature due to the lack of a vacuum cryostat. Some changes in spectra were observed as a function of the annealing temperature in the 125–75 cm^{-1} region. However, band assignments were not easy because some studies of semicrystalline polymers do not give a satisfactory agreement between the observed spectra and the predicted spectra on the basis of the group symmetry. For exemple, 11 bands were identified in the range 400 to 10 cm^{-1}, whereas only eight internal modes are predicted; additional features were assigned to a lattice mode and to the effect of crystal symmetry [37]. Description of low-frequency spectra would be better if we take into account the spectroscopy of skeletal modes of the macromolecules, rather than separate chemical unit monomer. This is because the FIR spectra are mainly due to collective excitations in a more or less disturbed lattice. This intermolecular vibrational coupling can lead to the development of a series of resolvable vibra-

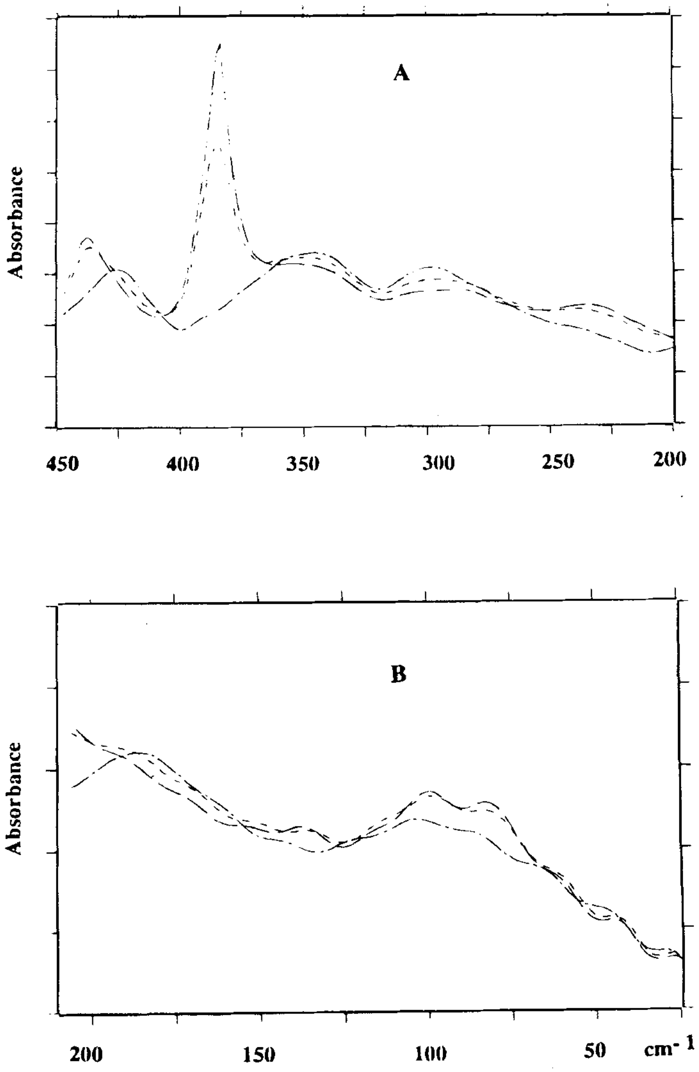

FIGURE 5A and 5B Far 1R spectra of PET films, amorphous initial film (___ _ ___), crystallized at 95°C (_ _ _), and crystallized at 125°C (___ ___).

tional modes characteristic of the length of the coupled units. These calculations are rather difficult mainly because of the absence of simple symmetry and the presence of a large unit cell. The coupling of normal vibrations of successive repeat unit necessitates evaluation of the dispersion of the normal modes in the first Brillouin zone [38]. In addition, the size and defects of crystals and the amorphous part influence band shape and peak position, and additional bands can be observed [17,21].

Generally, far IR studies need to be correlated with Raman spectroscopy to assign all vibrational frequencies [18,20,25]. Using low frequency Raman spectroscopy (LFRS, 2–200 cm^{-1}) one observes acoustical vibration modes, localized in crystallites (e.g., longitudinal acoustical modes in polyethylene), or localized in the amorphous phase because of disorder. LFRS allows one to study the structure of polymers at the nanometric scale, and after mechanical or thermal treatment (orientation, crystallization, etc.), but requires expensive Raman spectrometers to operate near the Rayleigh line [39]. Nevertheless for some polymers, correlations with changes of the FIR spectra versus temperature and the α, β or γ-transitions observed with electrical or mechanical spectroscopy have been made [40].

Conclusions

Conformational changes caused by thermal treatment of PET films can be monitored with FT NIR spectroscopy. The good resolution of FT spectrometers brings information not directly available from grating spectrometers. Main changes can be observed in the 4500–4000 cm^{-1} region : band shifts, novel absorption bands appear, and changes in relative intensity are detected. The 4685 and 4576 cm^{-1} bands show smaller changes during annealing. The main changes are in broad peaks located around 4425 and 4272 cm^{-1} which take place near 100° and 135°C. These temperatures are in good agreement with results obtained from mid IR or Raman spectroscopy. In the same manner, NIR microspectroscopy gives useful information on crystallinity (or conformation) of PET film with minimal sample preparation. A further advantage for NIR spectroscopy is the excellent transmittance of light-fibers for this region. Although similar information has been obtained using mid IR spectrometry, NIR spectroscopy allows the use of thicker samples in the transmission mode and can be successfully used for process or quality control. However, NIR spectra of polymers need to be interpreted, as in the case of the mid IR spectra, for better utilization of this technique.

Presently, far IR is limited to laboratory studies. This technique is sensitive to changes of crystallinity, but the theoretical interpretation of spectra is not easy. Improved communication between statisticians, spectroscopists and polymerchemists will help to overcome these difficulties.

Acknowledgments

FIR spectra were recorded by J. C. Boulou, Bruker (France) and NIR microspectra were recorded by B. Beccard, Nicolet (France).

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