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Determination of crystallinity of an aliphatic polyester by FTIR spectroscopy

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Summary

In this work, FTIR spectroscopy was applied to the determination of crystalline content in an aliphatic polyester. To this goal, a range of wavelengths (from 560cm^{-1} to 680cm^{-1}), non conventional for this kind of polymers, was selected by analyzing spectra collected during isothermal crystallization tests. A deconvolution of the IR spectrum in that range showed the presence of three peaks sensitive to the amorphous content and one sensitive to the crystal content. An analysis of the time evolution of the absorbances allowed to determine the parameters needed to determine the absolute crystallinity degree. The time evolution of crystallinity during isothermal tests at different temperatures was successfully compared with results obtained by DSC. The procedure was also favorably compared with the result obtained by WAXD on a solid sample at room temperature.

Introduction

IR spectroscopy is a powerful technique for the analysis of morphological characteristics of polymers, like crystallinity [1][2][3]. Compared to DSC it has the obvious advantage of being non destructive; compared to WAXD it allows a quick determination of crystallinity, since an IR spectrum can be collected in a few seconds as opposed to the several minutes taken to collect a WAXD diffractogram. IR spectroscopy is therefore a suitable technique when a rapid determination of crystallinity is required, or when a time evolving phenomenon needs to be followed.

The main difficulties for the application of the technique are two: firstly, the identification of the bands sensitive to the amorphous and to the crystalline content; secondly, the determination of the absorption coefficient ratio between amorphous and crystal.

The main objective of this work is to identify a procedure to determine the absolute crystallinity degree of relatively thick (about 50-100μm) films of an aliphatic polyester. The procedure can be applied to determine the distribution of crystallinity inside injection molded samples (by cutting slices at different distances from the skin) or on extruded films. Because of the thickness of the samples, some of the commonly adopted bands result to be unusable because the absorbances go beyond the instrument sensitivity. Thus, a new region was identified, and the absorption coefficient ratio between amorphous and crystal was determined in order to evaluate the absolute crystallinity degree.

Material

The polymer adopted in this work is a Poly(tetramethylene dodecanedioate) whose characteristics are reported in table 1.

Table 1. Properties of the polyester adopted in this work

M_n	M_w	M_z	M_w/M_n	M_z/M_w	T_m[a]	T_g[b]
g/mol	g/mol	g/mol			°C	°C
20'000	45'000	90'000	2.3	2.0	66	-23

[a] Peak value of a DSC thermogram at 10°C/min
[b] From a DSC thermogram at 10°C/min

A Wide-angle X-ray diffractogram on a 50μm thick sample kept at 120°C (well higher than melting temperature) for 10min (to erase the crystalline memory) and then solidified under slow cooling rate (about 5°C/min) is reported in Figure 1. The WAXD trasmission pattern was analyzed by a deconvolution procedure performed according to a scheme reported by Murthy and Minor [4]. In particular, the full spectrum is considered as a superposition of the a number of reflections, due to each phase present (3 reflections were considered: 2 for the crystalline phase, corresponding to $2\theta=21.2°$ and 24.3°, and 1 for the amorphous halo); each reflection being described by a combination of Lorentzian and Gaussian functions. The crystalline degree, x, calculated by dividing the areas of the crystalline peaks times the areas of all the peaks (amorphous+crystal), resulted to be equal to 61%. The melting enthalpy of the same sample was measured by DSC and resulted to be 82J/g. A combination of the two results allowed to determine the latent heat of crystallization as $\lambda=134$J/g.

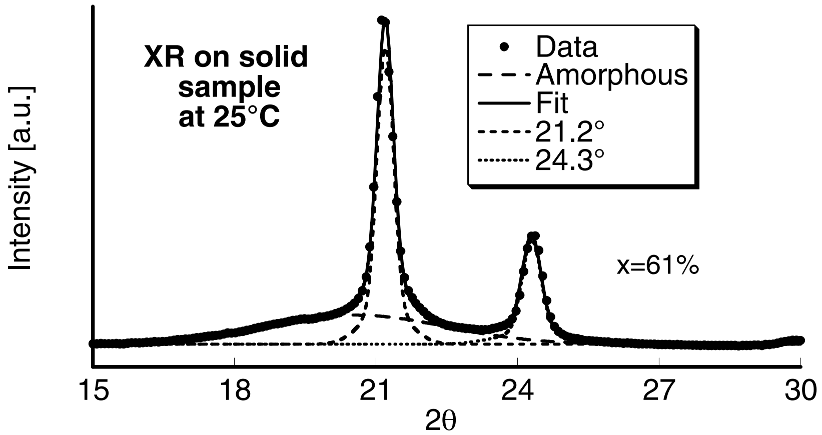

Figure 1. WAXD diffractogram of a solidified sample. The deconvolution is also shown.

FTIR spectroscopy during isothermal crystallization

All the experiments were carried out by using a FT-IR Midac M2000 spectrometer and a Specac P/N 21525 cell for temperature control. The cell thermal control is based on a temperature reading performed on the sample bearing, which is not equal to the sample temperature. To overcome this limit, a thermocouple was placed close to the sample. In the following, the thermocouple reading, which correspond to sample temperature, was used to identify each experiment.

As stated above, the polymer samples analyzed are films about 50μm thick (the thickness was measured on the solid samples at the end of each experiment). The temperature program was defined as follows: heating to 120°C (well higher than melting temperature), isothermal step at 120°C for 10min (to erase the crystalline memory), cooling to the test temperature at a rate for about 3°C/min (the maximum rate allowed by the instrument), isothermal step at the test temperature for a time long enough to allow complete crystallization. During crystallization, IR spectra were collected at a rate of about 20s per spectrum and with a resolution of 2cm^{-1}. The isothermal crystallization was followed at 7 temperatures: 53°C, 55°C, 56°C, 58°C, 58.5°C, 59.5°C, 60°C. At higher temperatures the crystallization was too slow to be followed without any risk of degradation, whereas for temperatures lower than 53°C the sample started to crystallize during cooling.

The analysis of the collected spectra allowed the identification of some bands sensitive to the crystalline content (i.e. peaks growing with time): 963cm^{-1}, 856cm^{-1}, 544cm^{-1}, 466cm^{-1}. The region at 1750-1700cm^{-1}, identified in the literature as suitable to determine the crystallinity of polyesters [5][6], was not exploitable in our case because the absorbances in that region were beyond the instrument saturation point.

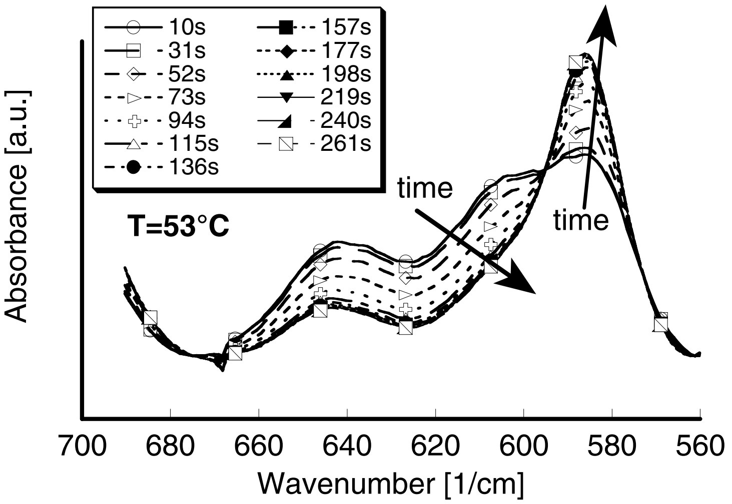

Figure 2. Time evolution of the IR spectrum in the selected region during an isothermal test at 53°C.

The region from 560cm^{-1} to 680cm^{-1} showed some peaks decreasing and one peak increasing with time, as reported in Figure 2 for the isothermal test carried out at 53°C. The same results were found at all the temperatures analyzed.

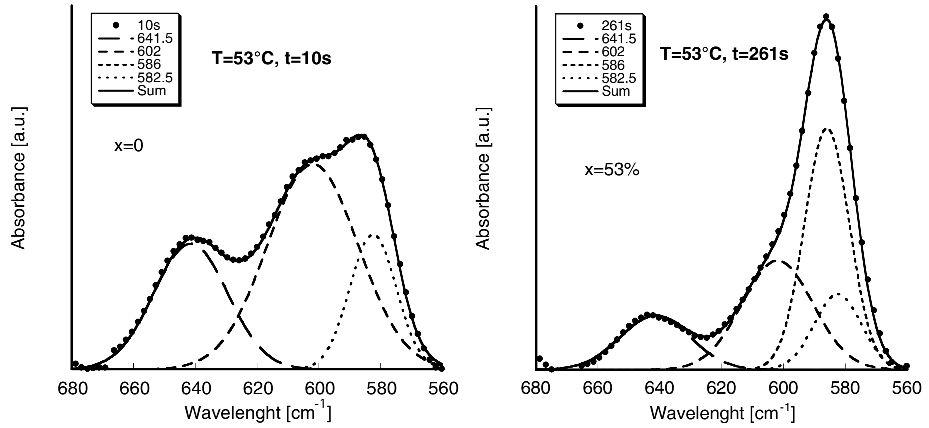

Figure 3. Deconvolution of the IR spectrum at the beginning (left) and at the end (right) of an isothermal test at 53°C. The peak assigned to the crystalline phase (586cm^{-1}) is not present at the beginning, when the sample is amorphous. The crystallinity degree reported was calculated by eq. 4 (see below).

A deconvolution of the spectra [7] in that region, at all the temperatures and times analyzed, allowed to identify four peaks (Figure 3). Three of them (centered at 641 cm^{-1}, 602.5cm^{-1} and 582.5cm^{-1}) were decreasing on time, and were thus assigned to the amorphous phase. The one centered at 586cm^{-1} was instead increasing on time and was absent in the spectrum of the molten polymer; it was therefore assigned to the crystalline phase.

Analysis of results

According to the Lambert-Beer law

$$A = Kcl \qquad (1)$$

in which A is the absorbance, l is the thickness of the sample, K is the absorption coefficient, c is the concentration of absorbing units.

Once a characteristic band of the amorphous phase is identified, the following equation can be written (c_p is the concentration of polymer and x the crystalline degree)

$$A_{\nu=am} = K_{\nu=am}\, l\, c_p\, (1-x) \qquad (2)$$

Similarly, for a characteristic band of the crystalline phase

$$A_{\nu=cr} = K_{\nu=cr}\, l\, c_p\, x \qquad (3)$$

The crystalline degree of the sample can be found by coupling equations 2 and 3:

$$x = A_{\nu=cr} / (A_{\nu=am} + \kappa A_{\nu=cr}) \qquad (4)$$

in which

$$\kappa = K_{\nu=cr} / K_{\nu=am} \qquad (5)$$

A measurement of the crystalline degree can be thus performed by FTIR analysis once the ratio κ between the absorbivities is known. This ratio can be determined by

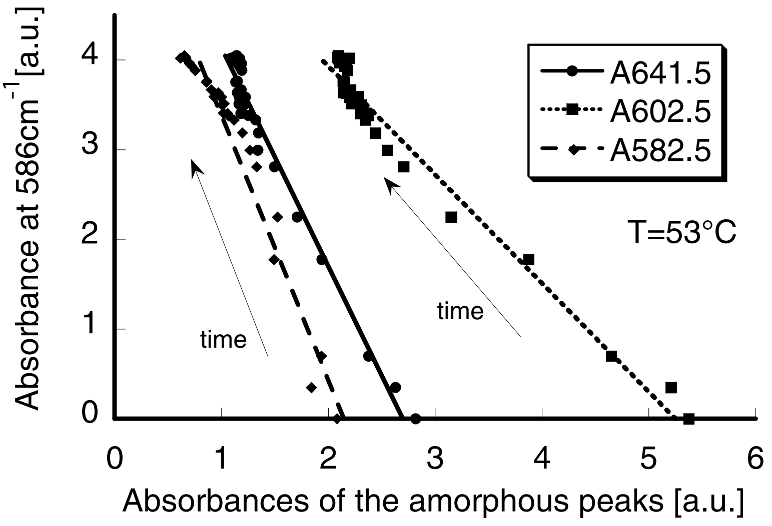

Figure 4. Areas of the peaks centered at 641cm^{-1}, 602.5cm^{-1} and 582cm^{-1} (assigned to the amorphous phase) plotted against the area of the peak centered at 586cm^{-1} (assigned to the crystal phase). The value of κ for each of the couple amorphous-crystal is given by the slopes.

analyzing the time evolution of the absorbivities during isothermal tests [6]. In fact, by combining equations 2 and 3 the following relationship is easily obtained

$$A_{\nu=cr} = K_{\nu=cr}\, l\, c_p - \kappa A_{\nu=am} \qquad (6)$$

and thus the slope of plot of $A_{\nu=cr}$ vs. $A_{\nu=am}$ provides the value of κ.

This procedure was carried out at all the temperatures analyzed: during the time, the absorbance of the peak centered at 586cm^{-1} (assigned to the crystal phase) was plotted against absorbances of the peaks centered at 641cm^{-1}, 602.5cm^{-1} and 582cm^{-1}. The resulting plot obtained for the isotherm at 53°C is reported in Figure 4; similar results were obtained at all the temperatures analyzed. It can be noticed that the three plots are indeed linear (within the experimental uncertainties), having different slopes and converging toward the same intercept, in agreement with equation 6.

The values found for κ (the slope) for each of the couples amorphous-crystal, and for the product $K_{\nu=cr}\, c_p\, lo$ (the intercept, normalized to a sample thickness lo=50μm), are reported in figure 5 for all the temperatures analyzed. The values of the ratios between the absorption coefficients of crystalline and amorphous phases are nearly constant with temperature. A slight decrease on increasing temperature is only found when the peak of the amorphous at 582.5cm^{-1} is considered. It must be considered to this regard that the peak at 582.5cm^{-1} is the smallest one and at high crystallinity levels is overcome by the peak of the crystal. Thus, it is affetcted by the largest errors. The average values of 2.75 ($K_{c,586}$/ $K_{a,582.5}$), of 1.2 ($K_{c,586}$/ $K_{a,602.5}$) and of 2.32 ($K_{c,586}$/ $K_{a,641.5}$), taken constant with temperature, were adopted for all the following analyses. The value of the product $K_{c,586}\, c_p$ is nearly the same for all the amorphous bands, thus confirming the validity of eq. 6. Some deviation is again found for the peak at 582.5cm^{-1}.

The values of κ identified above were adopted to calculate for each spectrum the value of the crystallinity degree x, according to eq. 4. The evolution of calculated crystallinity degree during an isothermal test at 53°C is reported in figure 6, considering all the amorphous peaks selected in this work.

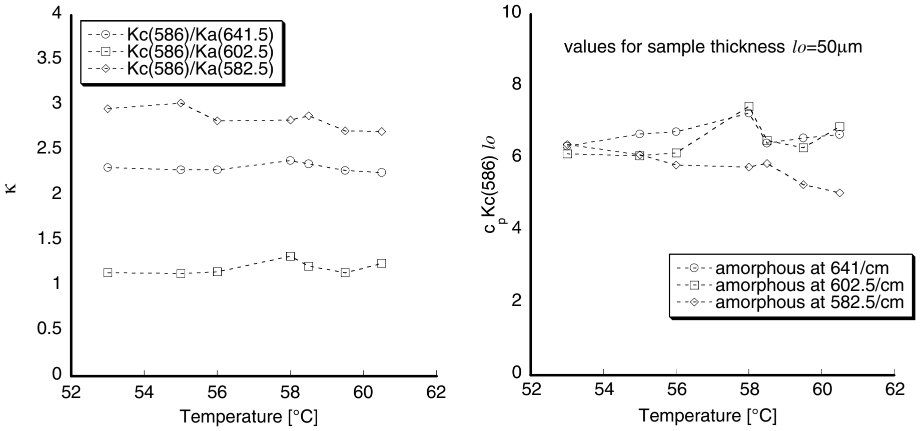

Figure 5. Left: values found for κ (defined by eq. 5) for each of the couples amorphous-crystal, and for the product $K_{\nu=cr}\, c_p\, lo$ (*lo*=50μm) for all the temperatures analyzed.

It can be seen that the crystallinity soon increases with time until a plateau of about 55% is reached after about 5min. All the amorphous peaks give rise to the same value of crystallinity at each time; only the curve calculated by using the amorphous peak at 582.5cm^{-1} gives rise to a large scatter, especially at high crystallinity values, as already noticed above. The other two bands, 641cm^{-1} and 602.5cm^{-1}, when coupled with the crystalline band at 586cm^{-1} provide quite reproducible results. The same features were noticed at all the temperatures analyzed.

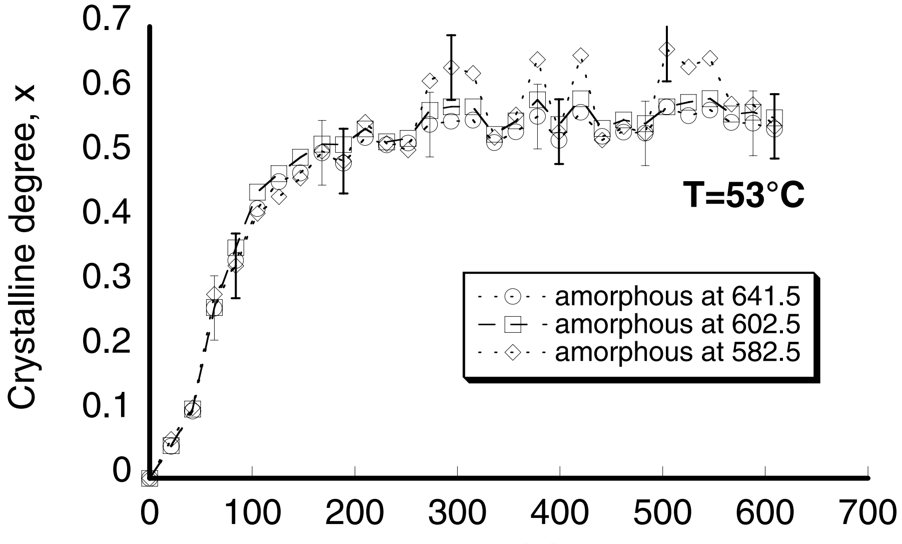

Figure 6. Time evolution of calculated crystallinity degree during an isothermal test at 53°C, considering all the amorphous peaks selected in this work. The crystalline band is centered at 586cm^{-1}.

Evolution of crystallinity during isothermal tests

The evolution of crystallinity degree measured by the procedure identified in this work during all the isothermal tests is reported in figure 7 as symbols. Only the crystalline degree calculated by using the peak at 641cm^{-1} are shown. As expected, on increasing temperature the crystallization evolution becomes slower. The final value of crystallinity, however, is always between 50% and 60%.

Some DSC tests were conducted by reproducing the same thermal history followed by the samples during the analysis by IR spectroscopy. The sample cups were always loaded with flat samples about 100μm thick. The evolution of crystallinity during the calorimetric isothermal tests was calculated as [8]

$$x(t) = \frac{\int_{s=0}^{t} w(s)dt}{\lambda} \qquad (7)$$

where *w(t)* is the thermal flux measured by the instrument in W/g and λ=134J/g.

The results of DSC analysis are compared in figure 7 with the time evolution of crystallinity measured by FTIR. The comparison is satisfactorily: not only the final values of crystallinity measured by both techniques are about the same, but also the whole evolution of crystallinity at each temperature is quite similar. This is a clear

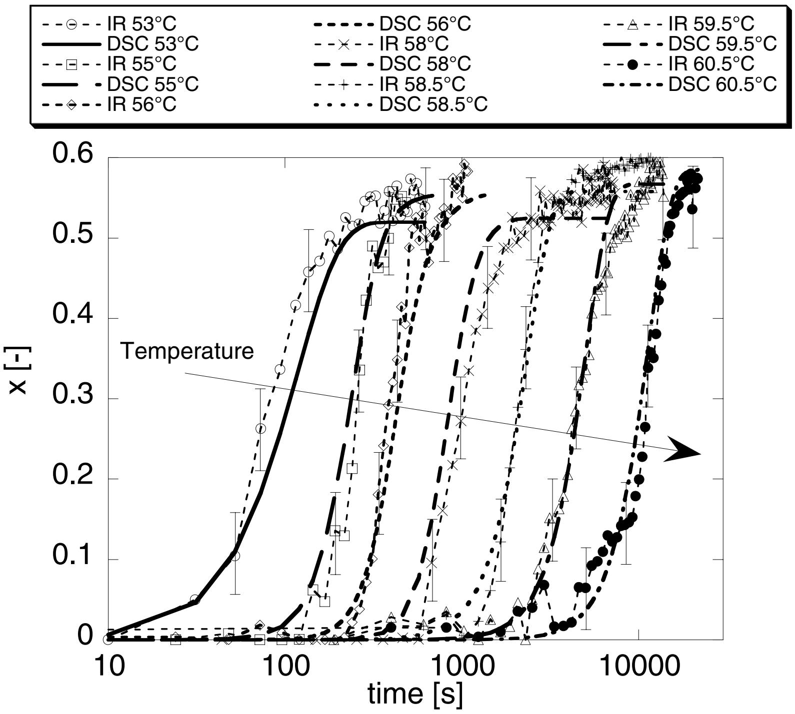

Figure 7. Symbols: time evolution of crystallinity degree measured by FTIR during all the isothermal tests, considering the amorphous peak at 641cm^{-1}. Lines: time evolution of crystallinity degree measured by DSC during isothermal tests at the same temperatures.

indication that the procedure identified in this work provides a reliable method for measuring the crystallinity of polyester films.

Comparison with WAXD

The same film analyzed by WAXD, whose diffractogram is reported in fig. 1, was also analyzed by FTIR, according to the procedure identified in this work. The result of the deconvolution procedure is reported in figure 8.

The crystallinity degree measured by FTIR on that sample was 65%, that is quite similar to that measured by WAXD (61%). This is a further confirmation of the reliability of the procedure.

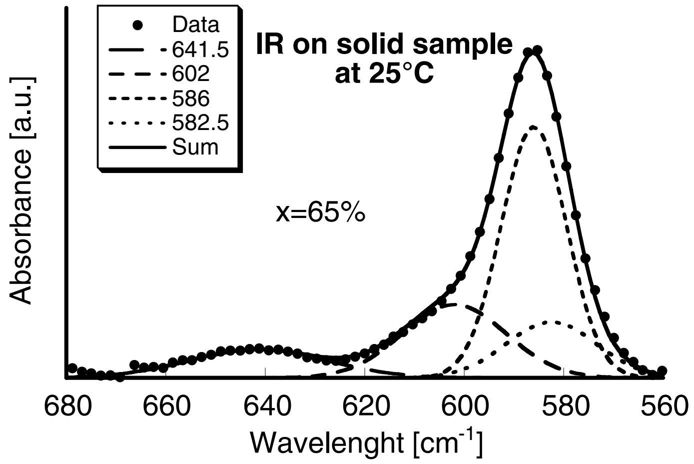

Figure 8. FTIR spectrum of a solidified sample. The deconvolution according to the procedure identified in this work is also shown.

Conclusions

In this work, a new procedure based on FTIR analysis was identified to measure the crystallinity degree of an aliphatic polyester.

In particular, some isothermal crystallization tests were carried out by revealing at selected time intervals the IR spectrum of the samples. The analysis of these spectra allowed to identify a region (from $680cm^{-1}$ to $560cm^{-1}$) which was selected as a good candidate for representing the evolution of amorphous and crystalline content inside the sample. The spectra in that region were analyzed by a deconvolution procedure and three peaks (centered at $641cm^{-1}$, $602.5cm^{-1}$ and $582.5cm^{-1}$) were assigned to the amorphous phase whereas one (centered at $586cm^{-1}$) was assigned to the crystalline phase. The analysis of the absorbances allowed to identify all the parameters needed for a quantitative determination of the absolute crystalline degree.

The procedure was adopted to analyze the evolution of crystallinity during isothermal crystallization tests at several temperatures, and the results favorably compared with DSC analysis conducted in the same conditions.

The results of the procedure were also successfully compared with those obtained by WAXD, thus confirming the suitability of the procedure identified for the quantitative analysis of crystallinity content in aliphatic polyesters.

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