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A COMPARATIVE STUDY OF THE CRYSTALLINITY DEGREE OF PET BY DTA, X-RAY DIFFRACTION AND IODINE SORPTION TECHNIQUES

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ABSTRACT

PET fibres, with different degrees of crystallinity induced by different thermal treatments have been investigated by DTA, X-ray diffraction and iodine sorption techniques and the results have been compared with the mechanical properties of the yarns spun from these fibres. Values for the degree of crystallinity have been plotted vs. temperature at which thermal treatment was carried out and the curves obtained have been compared with graphs of mechanical properties vs. temperature. Good agreement of the results from the three different methods was obtained.

INTRODUCTION

Natural as well as synthetic fibres exhibit a complex structure with regular and irregular regions. The regular regions, called "crystallites" are of particular interest in yarn processing since their extent (measured as a percentage and called "degree of crystallinity" [1]) has a strong influence on the mechanical and physical properties [2]. The extent of the regular region is generally influenced by the temperature at which the fibres are treated and thus the heat-setting operation is that which gives the fibre its mechanical properties. Consequently many methods to determine the degree of crystallinity of the fibres have been proposed but all exhibit a major disadvantage, namely the absolute values obtained from each method differ in an irregular pattern. Moreover computation of the absolute values re-

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quires two standards: one each of 100% amorphous character and 100% crystalline character, or at least, a reference sample with a known degree of crystallinity [3]. These are not easily obtained and preserved in an ordinary industrial laboratory. This paper aims to show that even if the absolute values are different, the relative values (using the value for untreated fibre as reference) are able to predict the changes in the mechanical properties closely enough to be useful as indexes for treatment.

The X-ray diffraction methods for determination of the crystallinity degree are the most used. From them we have chosen Fernov-Preston's method [4] which gives an apparent percentage of degree of crystallinity using eqn. (1)

$$c_a = \text{crystalline fraction area/crystalline + amorphous fraction areas} \quad (1)$$

Another method for the degree of crystallinity is by the use of DTA techniques. It is based on the assumption that crystalline and amorphous regions make different contributions to the melting enthalpy of the fibre and therefore the surface of the melting effect peak should be directly proportional to the extent of the crystalline region [5].

The third method we have used is iodine sorption. It is based on the assumption that iodine is absorbed only in the amorphous regions of the fibre and the amount of absorbed iodine is linearly correlated to the extent of the amorphous region [6].

EXPERIMENTAL

Materials

PET yarns, 150 den, supplied by I.Ch. Săvineşti were subjected to different temperatures ranging from 100°C to 240°C in 20 K steps for 10 min.

In order to perform the DTA experiments and X-ray diffraction, the yarns were cut very fine, and 0.1200 g samples were pressed at 350 kgf mm^{-2} for 2 min, to obtain round pills.

The reagents iodine, potassium iodide, acetic acid, phenol, sodium thiosulphate and starch of analytical grade have been obtained from "Reactivul", Bucharest.

Equipment

A derivatograph (MOM, Budapest 12 1500, Paulik–Paulik–Erdey type) for DTA curves, a diffractometer (DRON 3) for X-ray investigations and an Instron apparatus for the mechanical tests were used.

Procedure

DTA A sensitivity setting of 100 μV for DTA, a heating rate of 20 K min^{-1}, an air atmosphere, alumina as reference and platinum crucibles were used. Temperature range was from 20 to 500°C. The areas of the melting endothermal peak at 260–280°C were measured and compared by weighing.

X-ray diffractometry The working conditions were: Cu K radiation, 34 kV, 28 mA and GYR goniometer. Angles ranged from 10 to 20° and eqn. (1) was used for the calculation.

Iodine sorption Determination of this parameter was performed at 50°C in the usual way. The formula used was

$$I_s = \frac{1.2691Vb}{m} \tag{2}$$

where V is the used volume, b is the concentration of the solution and m is the mass of the fibre.

Mechanical tests The elongation, tenacity and Young's modulus for PET yarns of 10 m have been obtained using a weight of 450 g. Equations (3), (4), (5) and (6) were used for the parameters

$$\Delta l = \frac{l - l_0}{l} 100 \tag{3}$$

$$T = \frac{0.450}{F_c} \tag{4}$$

$$F_c = F + \frac{F - J}{100} \tag{5}$$

$$E = \frac{T}{\Delta l} 100 \tag{6}$$

where Δl is the elongation, l and l_0 are the final and initial lengths respectively, T is the tenacity, F and F_c are the fineness and the corrected fineness respectively, S is the shrinkage percentage and E is the Young's modulus.

RESULTS AND DISCUSSION

Table 1 gives results for the degree of crystallinity of PET. The decreases between 160 and 180°C have been also reported by other investigators [7]. Table 2 gives the relative areas of DTA peaks, the results of iodine sorption and the results of mechanical tests. The obtained data are represented in Fig. 1 in arbitrary units, each mechanical property being compared with the crystallinity.

It can be readily seen that DTA and X-ray diffraction results are close.

TABLE 1

The degree of crystallinity of the heat-treated yarns

Treatment		Sample number	Crystallinity degree (i_c) (%)
Temperature	Time (min)		
Untreated		0	1.40
100°C	10	1	5.40
120°C	10	2	25.26
140°C	10	3	27.00
160°C	10	4	30.22
180°C	10	5	29.45
200°C	10	6	29.33
220°C	10	7	37.25
240°C	10	8	38.80

Also it has to be pointed out that elongation curve results, measuring a mechanical property are close to those obtained from DTA and X-ray diffraction curves which shows a strong influence of degree of crystallinity on this property. It can be assumed, according to the recorded data, that there is a proportional change of elongation with the degree of crystallinity so that this mechanical property may be used as another index for this property.

Since the tenacity is a regular decreasing function according to eqn. (6), Young's modulus will exhibit an inverse proportionality to the degree of crystallinity, as shown in Fig. 1.

The influence of crystallites is well shown by the curves for the mechanical properties as well as by those of the physical properties. The sensitivities

TABLE 2

The relative values of physical and mechanical tests

Sample number	Relative iodine sorption	Relative DTA peak areas	Relative elongation	Relative tenacities	Relative Young's modulus
0		1.000	1.00	1.00	1.00
1		1.047	2.63	0.95	0.36
2		1.219	2.73	0.93	0.34
3		1.297	2.85	0.90	0.32
4		1.312	2.85	0.88	0.31
5	1.000	1.219	2.68	0.87	0.32
6	1.429	1.172	2.63	0.85	0.33
7	0.857	1.203	3.10	0.84	0.27
8	0.785	1.250	3.60	0.83	0.23

of each of the techniques used are similar and are close enough to the changes in mechanical properties for any to be used to predict the behaviour of the thermally-treated yarns. For a mill laboratory which has either DTA or X-ray diffraction equipment and no standard material, the investigations can be conducted efficiently with the untreated material as reference.

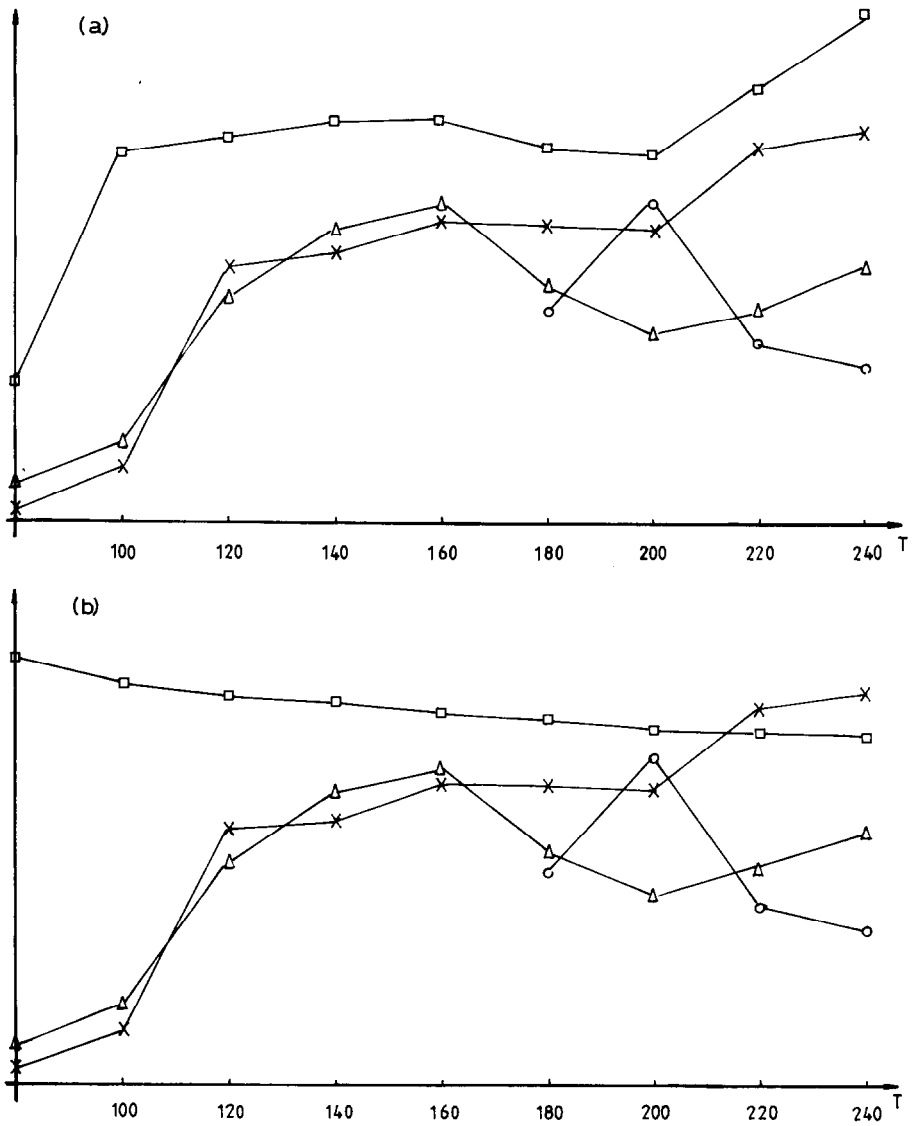

Fig. 1. (a) Elongation and crystallinity vs. temperature; (b) tenacity and crystallinity vs. temperature; (c) Young's modulus and crystallinity vs. temperature. □, Mechanical property, ×, crystallinity index from X-ray diffraction, ○, crystallinity index from iodine sorption, △, crystallinity index from DTA.

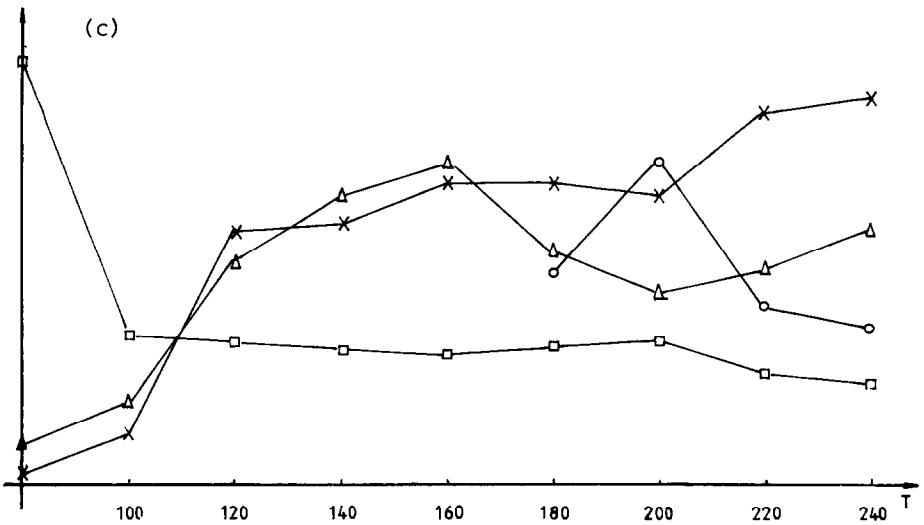

Fig. 1. Continued.

CONCLUSIONS

The experimental data from a comparative study of PET yarns by means of DTA, X-ray diffraction and iodine sorption techniques and mechanical tests shows the similarity of the results from physical tests and those from mechanical tests. They also emphasize the strong influence of degree of crystallinity on the mechanical properties of the yarn.

The curves of the melting endothermal effect vs. temperature of treatment and of degree of crystallinity as given by X-ray diffraction and calculated using eqn. (1) vs. the same temperature are close enough to allow substitution of one method for another.

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