Journal of Thermal Analysis, Vol. 41 (1994) 1599-1605

CONTRIBUTION OF THE SECONDARY CRYSTALLIZATION TO THE OVERALL CRYSTALLINITY OF HEATSET POLYESTER

D. Cayuela and J. Gacén

INTEXTER – Universitat Politècnica de Catalunya, C/ Colón n° 15, 08222 Terrassa, Spain

Abstract

The crystallinity of poly(ethyleneterephthalate) has been determined by differential scanning calorimetry and by density. The results obtained by calorimetry show that the increment in the crystallinity due to the heatsetting treatment is produced by the increase of the crystallinity corresponding to the premelting endothermic peak.

Keywords: crystallinity, heatsetting, poly(ethyleneterephthalate), premelting endothermic peak

Introduction

Heat setting of the products made with synthetic fibres is given to stabilize their form and dimensions. An increase of the crystalline material percentage occurs during this operation and the pertinent crystallites are more perfect [1]. The secondary crystallization also contributes to this increase of crystallinity which affects some material that was not crystalline before.

This secondary crystallization is reflected in the thermal curves as a premelting endothermic peak (PEP) and is known as the effective temperature of the thermal treatment. While maintaining constant the other conditions, the substrate remains stable as long as the melting temperature of the crystallites, formed during the secondary crystallization is not surpassed.

The crystallinity of polyester substrates heatset at nominal temperatures between 150 and 200°C has been determined in this study. For this purpose, density measurements (density gradient column and differential scanning calorimetry) have been used. The evolution of the total crystallinity as well as that of each component (main endotherm and pre-endotherm) has been considered to know its relative importance on the substrates heatset at different temperatures.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Material

Polyester yarn, 16 dtex, made with microfibre of 0.9 dtex and stabilized in the production plant at 150°C, has been heatset at 150, 160, 170, 180, 190 and 200°C during 30 seconds.

Characterization of crystallinity

DSC

Trial have been performed in a Perkin-Elmer DSC-7 unit. Measurements have been taken four times and the tabulated value is the average of the four values.

Based on the resulting curves, the following has been determined:

– the temperature of the PEP corresponding to the melting of the crystallites formed in the secondary crystallization occurring on heatsetting the fabric. The PEP value is known as the effective temperature of the thermal treatment which in the case of this study is heatsetting,

– the melting enthalpy of PEP and, from it, its crystallinity,

– the melting enthalpy and the crystallinity of the endotherm corresponding to the main melting of poly(ethyleneterephtalate),

– the total crystallinity as the sum of both crystallinities.

The following analytical conditions were used for the polyester fibres [2]:

Initial temperature: 50°C
Final temperature: 300°C
Heating rate: 20 deg· min^{-1}
Purging gas: Nitrogen (2 $kg \cdot cm^{-2}$)

Density

Density was measured in a density gradient column (DGC) (Davenport). The crystalline fraction was calculated by the equation of Dauber, Bunn and Braun [3]:

$$\alpha = \frac{1.455\,(\varphi - 1.335)}{0.120\,\varphi}\,100$$

where α corresponds to the crystalline fraction of the substrate and φ to its density. The 1.455 and 1.335 values are, respectively, the density of totally crystalline polyester and that of the totally amorphous polymer.

Results

DSC

The results are shown in Table 1.

Figure 1 shows that except in the case of the substrates heatset at 170 and 190°C, the PEP values develop linearly with the heatsetting temperature showing an excellent coefficient of linear correlation ($r = 0.999$).

Because the substrates heatset at 170 and 190°C show an anomalous behaviour, there is strong reason to believe that the temperature applied must have been markedly lower from the one programmed. Therefore, in the following comments the data corresponding to the PEP value will be used rather then those of the nominal or programmed heatsetting temperature, since they reflect the intensity of the thermal treatment better.

Figure 2 shows the percentage values of the crystallinity calculated from the PEP, that of the main endotherm and the total one obtained as the sum of both. The crystallinity of the PEP is observed in this figure to increase linearly ($r = 0.968$) with the effective temperature of the thermal treatment while the crystallinity of the main endotherm remains nearly constant (46.9). Thus, the total crystallinity of polyester seems to increase linearly ($r = 0.958$) with the heatsetting temperature thanks to the contribution of the PEP crystallinity on the total one.

To know the relative importance of each component on the total crystallinity of the fibre, the variation of the contribution percentage of each one versus the total crystallinity has been represented in Fig. 3. Here, the crystallinity of the PEP is seen to increase with the heatsetting temperature up to a value which is almost 10% for the substrate heatset at 200°C while the main endotherm decreases almost to 90%. Both develop linearly and the correlation coefficient is 0.965.

Densities

There is an excellent linear correlation ($r = 0.994$) between the crystallinity from the density and the effective heatsetting temperature.

When the crystallinities obtained by both methods (DSC and DGC) (Fig. 4) are compared, the total crystallinity deduced by differential scanning cal-

Table 1

Heatsetting temperature °C	PEP			Main peak		Total	
	PEP / °C	ΔH / J·g^{-1}	Crystallinity / %	ΔH / J·g^{-1}	Crystallity / %	Crystallinity DSC / %	Crystallinity DGC / %
150	137.3	2.08	1.86	54.41	46.27	48.13	41.5
160	145.4	2.60	2.21	55.08	46.84	49.05	43.5
170	153.6	2.97	2.53	55.32	47.04	49.57	44.3
180	167.3	5.11	4.34	55.79	47.44	51.78	46.6
190	169.4	5.21	4.43	55.08	46.84	51.27	47.4
200	188.9	6.05	5.14	55.39	47.10	52.24	49.5

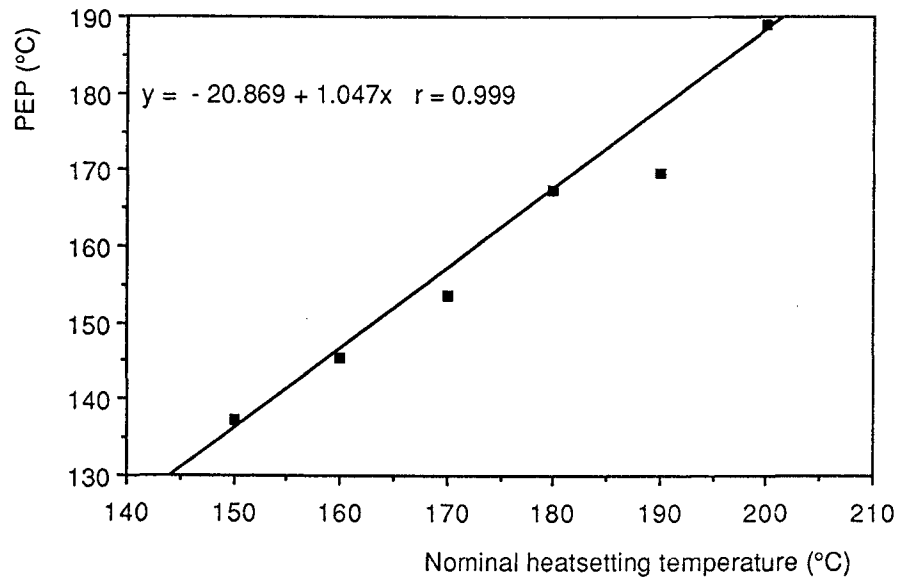

Fig. 1 Relation between the effective and nominal heatsetting temperatures

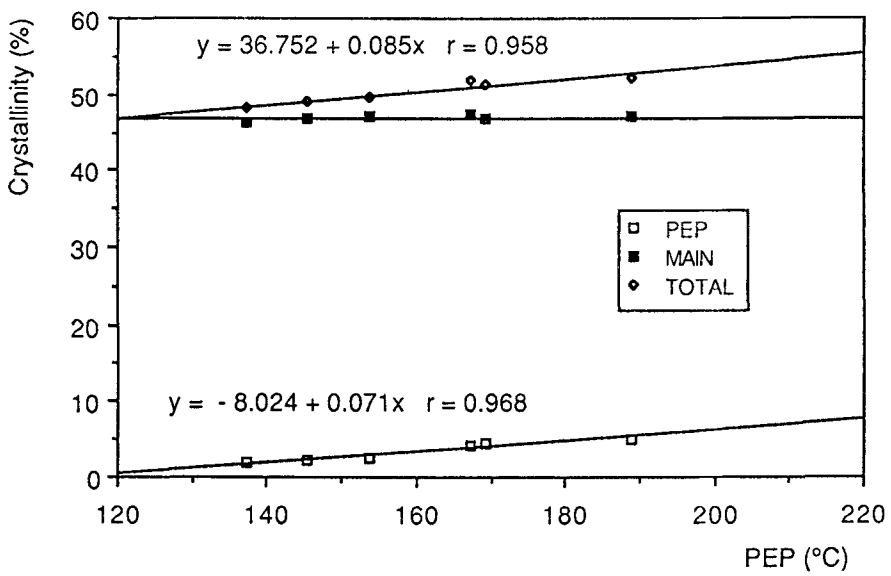

Fig. 2 Variation of the crystallinities of PEP, main and total endotherm with the effective heatsetting temperature

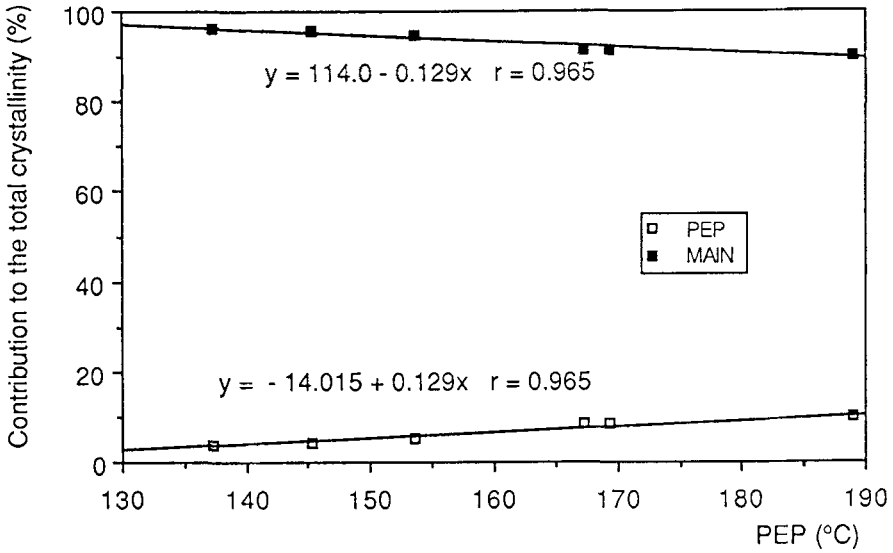

Fig. 3 Variation of the contribution to the total crystallinity from the PEP and total crystallinities with the effective heatsetting temperature

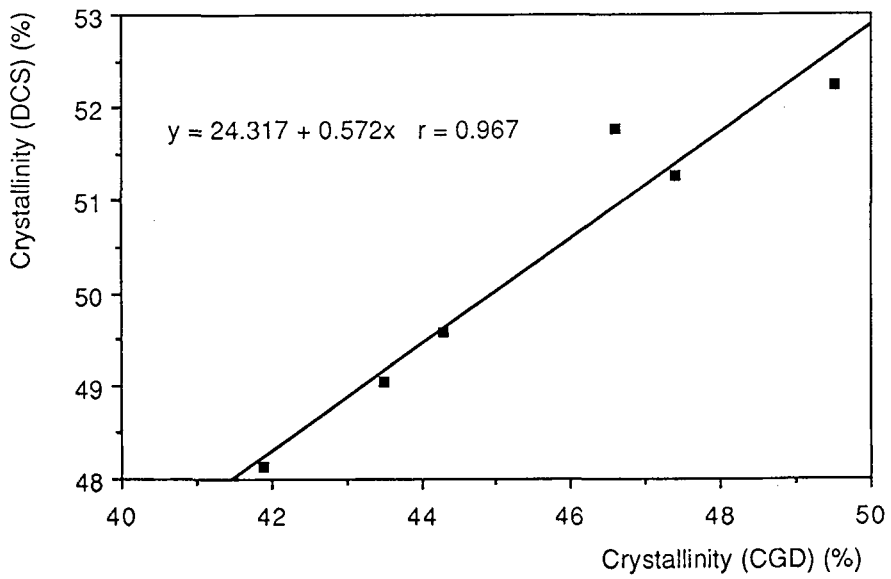

Fig. 4 Relation between the total crystallinity obtained in a DSC and that calculated from the densities

orimetry is observed to develop linearly with the crystallinity of the fibre obtained from the density measured in a density gradient column.

Conclusions

1 The crystallinity deduced from the main melting remains nearly constant on increasing the heatsetting temperature.

2 The crystallinity deduced from PEP increases with the heatsetting temperature.

3 The increase that occurs of the total crystallinity, deduced by DSC, on increasing the heatsetting temperature is mostly due to the crystalline component generated during the secondary crystallization.

* * *

The authors thank Mrs. M. Garcia for her cooperation in the experimental work and La Seda de Barcelona, S. A. for the generous contribution of the substrates used in the experimental part of this work.

This paper corresponds to tasks developed under the support of BRITE-II Project Programme: BREU-CT90-0267 (European Community).

References

1 G. Heiderman and H. Berndt, Chemiefasern, Textilindustrie, 24/76 (1974) 46.
2 J. Gacén and D. Cayuela, Melliand Textilberichte, September 1990, 654.
3 R. P. Daubeny, C. W. Bunn and C. J. Brown, Proc. Roy. Soc., A226 (1954)

Zusammenfassung — Mittels DSC und mit Hilfe der Dichte wurde die Kristallinität von Poly-(ethylenterephthalat) bestimmt. Die mittels Kalorimetrie erhaltenen Resultate zeigen, daß die Zunahme der Kristallinität im Zusammenhang mit der Heißhärtungsbehandlung durch die Zunahme der dem endothermen Vorschmelz-Peak entsprechenden Kristallinität verursacht wird.