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DIFFERENTIAL SOLUBILITY OF POLY(ETHYLENE-TEREPHTHALATE) FIBRE *vs.* TEMPERATURE

2. Calorimetric study of the non-dissolved fractions

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Abstract

The differential solubility of two poly(ethyleneterephthalate) (PET) fibres was determined in one thermally treated substrate and in another thermally untreated. In both cases, mixtures of phenol/tetrachloroethane with the appropriate composition were used.

The non-dissolved fractions of the untreated PET fibre display a molecular mass and a crystallinity which increase on increase of the temperature of the differential solubility test. In the case of the thermally treated substrate, both the molecular mass and the crystallinity of the residual fraction remain constant on increase of the test temperature.

Keywords: crystallinity, differential solubility, microstructure, molecular mass, poly(ethyleneterephthalate) fibre

Introduction

Anomalous behaviour in the solubilization of PET fibres suggested [1] the existence of a relation between the fine structure of the fibre and its solubility in conventional solvent mixtures. On the basis of this hypothesis, the authors studied the solubility of PET fibres in phenol/tetrachloroethane (Ph/TCE) mixtures in terms of the mixture composition and of the time and temperature of the solubilization treatment. As a result, they developed the differential solubility method for the characterization of PET fibres. The differential solubility of a PET fibre at a determined temperature is the percentage of the fibre that has dissolved in a given Ph/TCE mixture after remaining in contact with it for 30 min.

The differential solubility has become a very useful test of characterization of the microstructure of PET fibres as it is not only very sensitive to the variations that may occur between similar substrates, but also simple, accurate and fast. It can be applied to any type of substrate, in whatever way it is presented (flock, tow, spun yarn or continuous yarn), and also to dyed material. Because of its versatility, it can be applied to solve conflictive situations, even when PET/wool and PET/cellulosic-fibre blends are involved.

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The differential solubility of PET fibres in a Ph/TCE mixture with a given composition increases with the test temperature. This can be attributed to the penetration of the solvent mixture into more compact regions, less accessible at lower temperatures. On the other hand, the differential solubility of PET fibres is very sensitive to their thermal history. A decrease in solubility is produced when a heat treatment is applied to a given original substrate, as a consequence of the global structure becoming more compact, leading to a decrease in the penetration capacity of the solvent at a determined temperature. From the above-mentioned considerations, it is deduced that the higher the intensity of heat treatment applied to a substrate, the lower will be its solubility in Ph/TCE mixtures. The solubility differences can be so important that substrates with important thermal history differences need a different composition mixture in order to achieve good levels of solubility at reasonable temperatures (30–80°C). In the case of the PET supplied by producers to the textile industry, a mixture of 5 Ph/95 TCE is appropriate. For high-temperature dyed, textured or heatset yarns, mixtures richer in phenol (15–25%) are needed [1, 2].

For a better understanding of the significance of the PET solubility curve *vs.* temperature, the authors decided to study the non-dissolved fractions and determine their molecular mass (viscosimetry) and crystallinity (differential scanning calorimetry). The substrates to be used are a thermally untreated original PET and a substrate resulting from the application of thermal treatment similar to that used in dyeing PET fibres at high temperature.

The study of the molecular mass of the non-dissolved fractions by viscosimetry and the determination of the molecular mass of the dissolved fractions (indirectly calculated) were carried out previously [3].

Experimental

Material

Multifilament PET yarn (150 dtex/30 filaments).

Treatments

The yarn was washed with Sandozina NIA at 40°C during 30 min. It was then rinsed with warm water (35°C), then three times with cold water, and finally dried at room temperature.

The resulting material was next subjected to thermal treatment similar to that of a high-temperature dyeing. Treatment was carried out in a Linitest apparatus, in the presence of Sandozina NIA (1 g l^{-1}) at a bath ratio of 1/30. Treatment was started at 60°C, and the temperature was then raised to 130°C in 45 min and maintained during 20 min. Afterwards, the material was washed several times with distilled water to achieve total elimination of the surfactant.

Test of differential solubility

The differential solubility (D.S.) of a PET fibre at a determined temperature is the percentage of fibre that has dissolved after being in contact with a given Ph/TCE mixture during 30 min. It is expressed as

$$\mathrm{D.S.}(\%) = \frac{\text{mass of sample} - \text{mass of non-dissolved material}}{\text{mass of sample}} \times 100$$

The operating procedure was described earlier [1, 2]. Tests with the original multifilament yarn were carried out at 30, 40, 50, 60, 70 and 80°C, using a Ph/TCE (5/95) (w/w) mixture.

The D.S. of the substrate thermally treated under dyeing conditions was determined at temperatures of 47.5, 49.0, 50.5, 52.0 and 53.5°C, using a Ph/TCE (12.5/87.5) (w/w) mixture.

The non-dissolved material in each test was washed abundantly several times, first with ethanol, and then with distilled water to eliminate the remaining Ph/TCE mixture completely. Finally, the material was dried at room temperature and made homogeneous.

Characterization

Number-average molecular mass

This was determined by viscosimetry on a 0.5% solution in a Ph/TCE (1/1) (w/w) mixture, using the following expression [4, 5]:

$$[\eta] = \frac{(1 + 1.4\eta_{\mathrm{sp}})^{1/2} - 1}{0.35}$$

$$\overline{M}_{\mathrm{n}} = \left[\frac{[\eta]}{1.27\times10^{-4}}\right]^{1.16}$$

where $[\eta]$ is the intrinsic viscosity or the limit viscosity index, η_{sp} is the specific viscosity, and $\overline{M}_{\mathrm{n}}$ is the number-average molecular mass.

Crystallinity and melting temperature

Melting enthalpies of substrates were determined by differential scanning calorimetry on a Perkin-Elmer DSC-7 apparatus. Operating conditions were as follows:

Initial temperature: 50°C, end temperature: 300°C, heating rate: 20°C min^{-1} purge gas: nitrogen (30 ml min^{-1}).

A lower heating rate will reduce the overheating effect, but in this case crystallization could be produced during the differential scanning calorimetry test.

This could increase the crystallinity at the PEP (premelting endothermic peak), which corresponds to the melting of the crystallites induced during the secondary crystallization produced during the industrial thermal treatment applied [7].

Crystallinity was determined by means of the following equation from the melting enthalpy:

$$\text{crystallinity}(\%) = \frac{\Delta H_{\text{exp}}}{117.6} \cdot 100$$

where ΔH_{exp} is the melting enthalpy (J g^{-1}) of the sample, and 117.6 [6] is the enthalpy (J g^{-1}) of the 100% crystalline PET.

The crystallinity of the thermally treated PET was calculated as indicated previously [7].

Results and discussion

Figures 1 and 2 display DSC curves of the thermally untreated PET and the thermally treated PET.

Tables 1 and 2 contain the differential solubility, the melting temperature and crystallinity at the PEP, the peak corresponding to the melting of crystallites formed during the thermal treatment applied (only for the thermally treated substrate), the onset temperature of the melting endotherm, the temperature of the peak of the melting endotherm, the crystallinity of the non-dissolved fraction, and the number-average molecular mass of the non-dissolved or residual PET.

For the thermally untreated PET (Table 1), the molecular mass and the crystallinity of the non-dissolved material increase with the temperature of the differential solubility test, and with the percentage of the dissolved material, practically throughout the whole interval of temperatures studied.

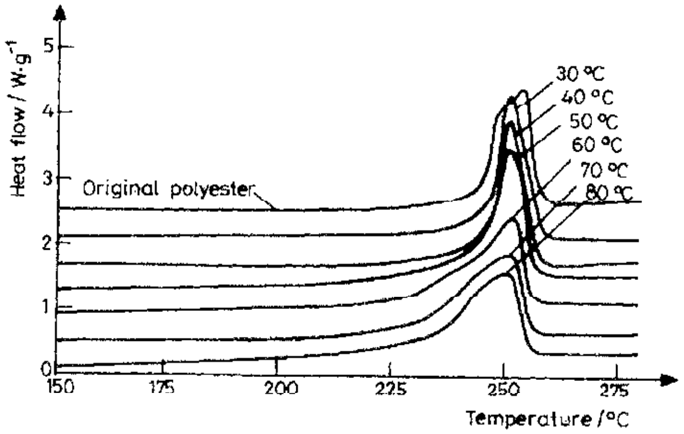

Fig. 1 Melting endothermic peaks obtained by DSC of the thermally untreated polyester and of the residual fractions from the differential solubility test

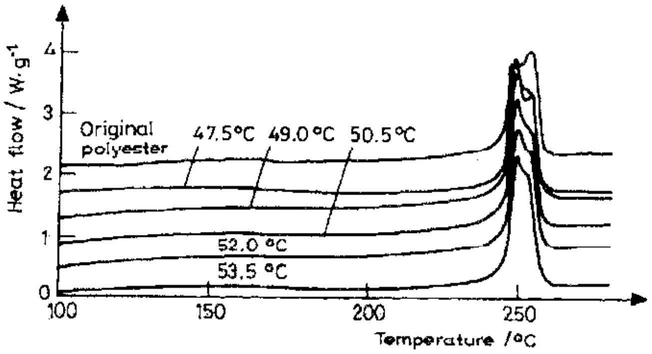

Fig. 2 Melting endothermic peaks obtained by DSC of the thermally treated polyester and of the residual fractions from the differential solubility test

A higher molecular mass indicates a fractionation in increasing molecular masses on increase of the temperature of the differential solubility test. It is unlikely that the totality of the material can be separated only in terms of its molecular mass: PET is a semicrystalline polymer and (in accordance with the two- or three-phase model [8–10] a given macromolecule can go through (or form part of) a succession of arranged regions (crystallites) and disarranged or amorphous regions. This means that, on increase of the temperature, part of the material in the most compact zones in which the solvent is less accessible at low temperatures, becomes dissolved.

In DSC curves of the non-dissolved material (Fig. 1), the melting enthalpy (crystallinity) increases, while the melting endotherms become flatter and wider as the temperature of the D.S. test is increased. In particular, the onset temperature of the melting endotherm decreases, from 246.4°C for the residue/substrate attained at 30 to 233.9°C for the residue/substrate attained at 80°C. This could in-

Table 1 Melting temperature, crystallinity and number-average molecular mass of non-dissolved fractions (untreated substrate)

T_{Test}/°C	Differential solubility/%	T_m onset/	T_m peak/	Crystallinity/%	M_m/ kg mol^{-1}
		°C			
Original		244.1	252.9	46.8	20.99
30.0	6.5	246.4	250.0	45.0	22.06
40.0	16.8	246.1	250.3	47.7	22.97
50.0	27.2	245.2	250.0	49.0	23.75
60.0	50.0	239.4	251.1	52.5	26.24
70.0	68.1	239.9	250.9	53.8	28.04
80.0	79.7	233.9	250.2	56.2	26.89

Table 2 Melting temperature and crystallinity relating to the mean endotherm and the premelting endothermic peak, and the number-average molecular mass of non-dissolved fractions (thermally treated substrate)

T_{Test}/ °C	Differential solubility/ %	Premelting endothermic peak		Mean peak			Overall crystallinity/ %	M_m/ kg mol^{-1}
		Temperature/ °C	Crystallinity/ %	T_m onset/ °C	T_m peak/ °C	Crystallinity/ %		
Original		161.9	5.4	57.9	247.6	46.1	51.4	20.74
47.5	5.5	161.5	4.0	56.7	248.6	46.6	50.6	20.88
49.0	31.9	161.1	4.0	56.6	248.9	46.4	50.4	20.59
50.5	52.9	161.7	4.3	57.0	249.4	46.3	50.6	20.60
52.0	71.9	161.8	4.2	57.0	249.4	46.0	50.2	20.53
53.5	97.2	161.2	3.5	56.2	249.0	46.3	49.7	20.84

dicate that the size distribution of the crystallites in the non-dissolved material of the thermally untreated substrate becomes less narrow as the temperature of the D.S. test is increased.

The broad endotherm observed at the highest solution temperatures (60, 70 and 80°C), with a wider distribution of crystallite sizes, does not seem to be due to a plastifying effect of the medium, because in this case a secondary crystallization detectable via the corresponding PEP would be produced.

It is also observed that the original substrate is slightly more crystalline than the residue from the D.S. test at 30°C. Cimecioglu *et al.* [11] demonstrated that the PET oligomers were eliminated by chloroform extraction, and also that thermal treatment causes polymerization in the solid state of the oligomers. On the basis of that paper, Sarma and Patel [12] observed that the exothermic curvature in a PET thermogram could be due to the polymerization in the solid state of the oligomers present in the commercial yarn; however, this curvature disappeared after the sample was extracted with a mixture of methanol-chloroform during 20 h.

As explained in an earlier paper [3], the lower molecular mass of the fraction dissolved at 30°C can be easily understood as it logically corresponds to oligomeric material and to low molecular mass material. If the possible polymerization of oligomers in the solid state during the thermal analysis is considered, the melting enthalpy, and therefore the crystallinity of the original substrate can be explained as being higher than that of the substrate from the D.S. test at 30°C.

Table 2 presents data corresponding to the thermally treated PET. Its lower solubility and fast solubilization are related to the formation of large spatial arrangements [13], which therefore have a much more radicalized structure, with a small proportion of amorphous zones.

With respect to the variation in the molecular mass *vs.* the temperature of the solubility test, Table 2 shows that the molecular mass of the residual fractions remains practically constant throughout the whole interval of temperatures. This means that no fractionation of the molecular masses occurs, in complete contrast with what happens with the original substrate.

As concerns the DSC curves of the non-dissolved material (Fig. 2), neither the melting enthalpy (crystallinity) nor the shape of the melting peaks of the residual material varies on increase of the temperature of the D.S. test. This indicates a much more compact structure and the existence of crystallites of more regular size than those of the thermally untreated substrate; it follows that the hydrothermic treatment applied to the substrate results in a uniform crystallite size.

The PEP observed in these curves corresponds to the melting of crystallites induced during the secondary crystallization produced during the thermal treatment applied. Even though they are very small crystallites, they can not be dissolved in the D.S. test, as they are not a separate material from the global structure of the fibre (two- or three-phase model) [8–10].

Differences between the thermally treated substrate and the original one could be attributed to the fact that in this case the material with lower molecular mass is located in zones more easily accessible to the solvent/non-solvent mixture. With regard to the treated substrate, its much higher compactness would prevent the material with lower molecular mass from gradually separating as the fibre progressively dissolves as a consequence of the temperature increase.

Conclusions

Under the experimental conditions applied in this study, the following conclusions can be drawn:

1) As the temperature of the differential solubility test of thermally untreated PET increases, so does the number-average molecular mass of the dissolved and residual fractions and also the crystallinity of the residual fraction.

2) In thermally treated PET, the molecular mass of the non-dissolved and dissolved fractions remains constant on increase of the temperature. The crystallinity of the residual fractions also remains constant; this holds not only overall, but also for that corresponding to the main endotherm and to the endotherm prior to melting.

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References

1 J. Gacén, J. Maillo and J. J. Baixauli, Melliand Textilberichte, 61 (1980) 187.
2 J. Gacén and J. Maillo, J. Text. I., 86 (1995) 527.
3 J. Gacén, D. Cayuela and I. Gacén, J. Text. I., in press
4 H. Frind, Faserforschung und Textiltechnik, 5 (1954) 296.
5 W. Griehl and S. Neue, Faserforschung und Textiltechnik, 5 (1954) 423.
6 D. W. Van Krevelen, 'Properties of Polymers. Their estimation and correlation with chemical structure', Elsevier 1976, p. 91
7 D.Cayuela and J. Gacén, J. Thermal Anal., 41 (1994) 1599.
8 D. C. Prevorsek et al., Text. Res. J., 47 (1977) 107.
9 J. Gacén, 'Aspectos de las fibras químicas', Universitat Politècnica de Catalunya, 1990, p 33.
10 J. Gacén and J. Maillo, 'Fine structure variations in polyester fibres heat treated', COMETT-EUROTEX, 1995, p. 39.
11 A. L. Cimecioglu, S. H. Zeronian, K. W. Alger, M. J. Collins and G. C. East, J. Appl. Polym. Sci., 32 (1986) 4719.
12 T. S. Sarma and N. B. Patel, Text. Res. J., 7 (1988) 429.
13 I. Goodman, 'Synthetic fibre-forming polymers', The Royal Institute of Chemistry, London 1968, p. 17.