Influence of an aqueous acetone medium on the thermal behaviour of solvent treated poly(ethylene terephthalate)

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When amorphous PET filaments are treated in acetone–water mixtures under controlled conditions, they retain amorphous properties. The T_g's and T_c's are lowered well below the usual values and at the same time the structure becomes swollen. Ageing the treated polymer freed from acetone results in a reversible process that gives transition values close to the values for the untreated sample; but the polymeric phase remains swollen. A combined action of primary and secondary plasticizers is proposed in this paper.

INTRODUCTION

The diffusion of solvent molecules into polymeric materials induces large scale concomitant rearrangements. Volume swelling and crystallization are among the most studied phenomena. It has been shown that a good number of solvents can induce a certain degree of crystallinity in the amorphous poly(ethylene-terephthalate) (PET) at room temperature[1,2]. Other solvents produce the same effect at temperatures between 25° and 80°C[3].

In the presence of sorbed solvents the segmental mobility of amorphous polymer chains is greatly enhanced when compared to the amorphous dry polymer. This produces a lower temperature of glass transition. As a consequence, crystallization appears at temperatures well below those required for crystallization of dry PET.

In this paper we will examine the interactions between PET filaments and acetone in the presence of water.

METHODS AND MATERIALS

The PET used was a commercial material used for the production of yarn (viscosity average molecular weight $M_w = 10\,500$). The unoriented amorphous filaments were obtained by extrusion at 280°C and quenched in a cold air stream.

Acetone–water treatments were carried out by soaking PET filaments in various acetone–water mixtures for differing periods of time at 25°C under unrestrained conditions and gentle stirring. The treated samples were then washed with distilled water and allowed to dry at room temperature. The acetone content of the washed and dried samples, as determined by gas-chromatographic quantitative measurements, was always under 0.1%.

First and second order transitions were investigated with a differential scanning calorimeter (Perkin Elmer DSC 4—Thermal Analyzer Data Station).

The infra-red spectra of the filaments were obtained on

a double beam spectrophotometer (Perkin Elmer 983 Infrared Data Station) using a frustrated multiple internal reflection accessory (FMIR) with a KRS-5 crystal[4]. For the study of the *trans–gauche* transformation the bands near 1337 and 1370 cm^{-1} were considered. These two bands are assigned to the *trans* and *gauche* conformations of the glycol moiety of the polymer structural unit, respectively[5].

Specific volume (v_s) measurements were carried out at 20°C in an aqueous potassium iodide solution[6].

RESULTS AND DISCUSSION

PET crystallization can be induced by a large number of solvents, among them is acetone even if its effect is considered as mild[7]. The simultaneous presence of water during the treatment with acetone drastically changes the action of the solvent on the PET filament.

Table 1 shows the effect of increasing percentage of water on some parameters obtained by d.s.c. The glass transition (T_g) and cold crystallization (T_c) temperatures are close to the values of the untreated sample as the percentage of water increases.

The sample soaked for 5 min in the 65/35 acetone–water mixture (PET 5-65/35) shows a remarkable decrease in T_g and T_c after a convenient period of treatment. It was selected to investigate the interactions between PET filaments and acetone in the presence of water.

Wide angle X-ray scattering analysis of this sample gives the typical pattern of amorphous unoriented PET (*Figure 1*).

Figure 2 shows surface modifications induced by the selected acetone–water treatment. At each magnification it is possible to observe the development of surface roughness in the treated sample when compared to the untreated one. This surface roughness is responsible for the lack of homogeneous focusing of the higher magnified picture.

The d.s.c. comparison with the untreated and the

acetone–treated samples is reported in *Figure 3*. The enthalpy of crystallization, which is close to zero after the pure acetone treatment, is always lower in the PET 5-65/35 than in the untreated filaments.

The ratio of *trans–gauche* conformations was also determined. The results of i.r. spectrophotometric analysis are in *Figure 4*. The two bands near 1337 and 1370 cm^{-1} show higher intensity in the PET 5-65/35, but the ratio of their areas remains unchanged. The increase of the intensities suggests enhanced molecular mobility while the unchanged *trans–gauche* ratio excludes the molecular disorientation previously found by Khan and Venkatesch in their studies with strong interacting solvents[5].

Specific volume measurements gave 0.748 and 0.745 cm^3/g for the PET, 5-65/35 and the untreated sample respectively. The higher value observed for the PET 5-65/35 is regarded as an indication of the presence of a swollen phase. This in turn could explain the enhanced molecular mobility observed by infra-red spectrophotometry and the lower intensity of the equa-

torial scan of the wide angle X-ray diffraction pattern (see *Figure 1*).

A quantitative evaluation of the swollen phase from the v_s values cannot be done because of the possible presence of extensive voids in the structure of the material as supposed by Lawton and Cates[1].

The morphological characterization so far carried out has allowed us to establish that the PET 5-65/35 retains its amorphous structure, but it is swollen and its T_g is lowered to $\times 12°C$.

This T_g value was found scanning the filaments 30 min after the acetone–water treatment. When we tried to reduce this gap, by cutting down the rinsing and drying times, we observed various T_g values below 0°C. However, the transition appeared as a broadened event disturbed by the concomitant melting of water. A detailed description of these events was made impossible by lack of reproducibility.

These low values of T_g appear to contradict the presence of an amorphous structure. Normally strong interacting solvents lower the T_g value but crystallization concomitantly occurs.

The usual approach to the study of polymer–solvent interactions is based on the comparison of their 'total solubility parameters' (δ_s)[8]. This enables us to plot the T_g depression values *versus* δ_s values of the solvents. For PET fibres two maxima are observed at $\delta_s = 9.85$ and $\delta_s = 12.1$ and the nature of the interactions is considered to be bimodal.

We cannot follow this approach because the acetone/-water mixture is not an ideal solution, therefore it is erroneous to try the calculation of its δ_s value from the additivity rule[10].

The experimental evaluation of δ_s is useless because the

Table 1 Thermal behaviour of PET filaments soaked in various acetone–water mixtures for different periods of time

Samples*	T_g (°C)	T_c (°C)	ΔH_c (J/g)
PET, 3–80/20	10	50	9.1
PET, 5–65/35	12	52	10.0
PET, 15–30/70	75	133	25.5
PET, 120–20/80	76	135	26.6
PET (untreated)	77	135	26.5

* The first number in the annotation refers to the period of treatment (min) the following ratio is the volume ratio of the acetone/water mixture where the filaments were soaked.
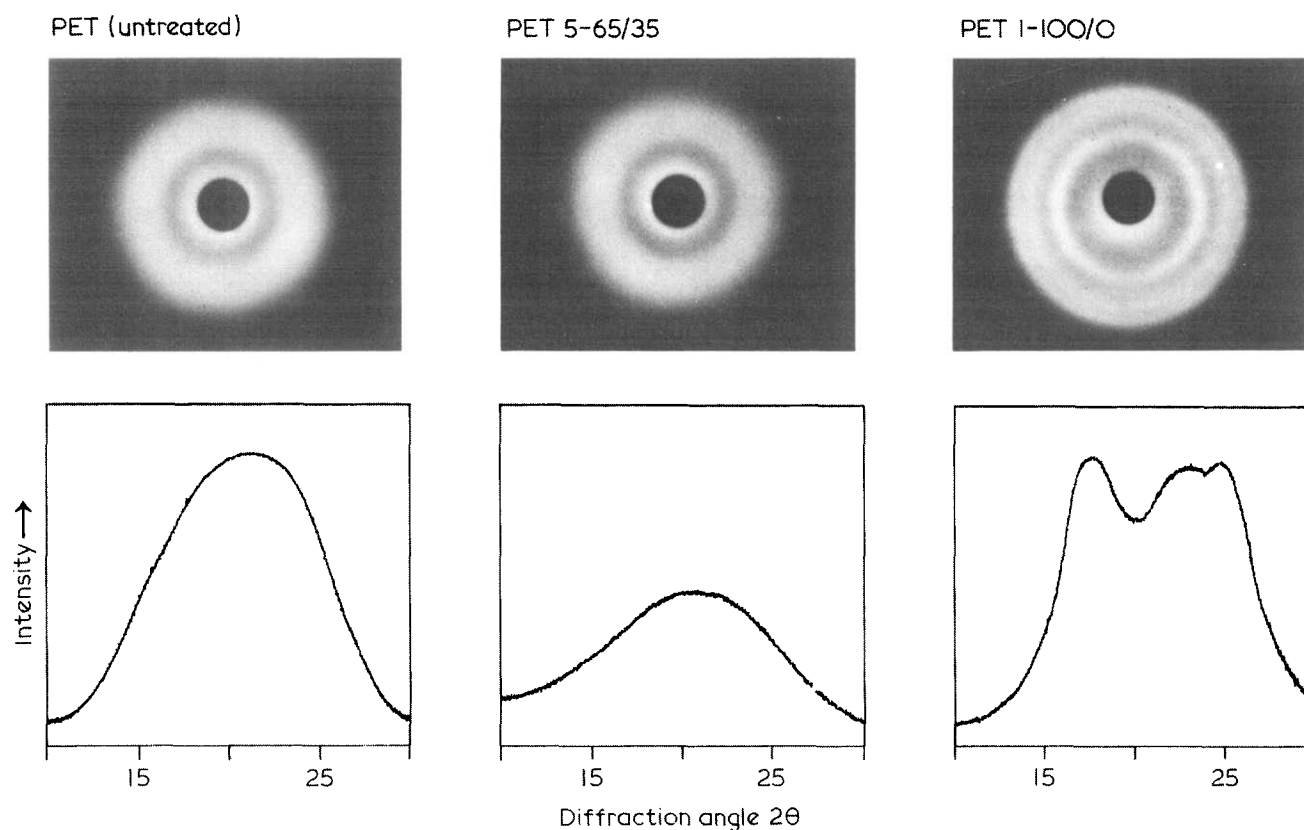
PET (untreated) PET 5-65/35 PET I-IOO/O

Diffraction angle 2θ

Figure 1 Wide angle X-ray scattering and related equatorial scans (Siemens Diffractometer mod. 500-D). (For an explanation of the samples, see *Table 1*)

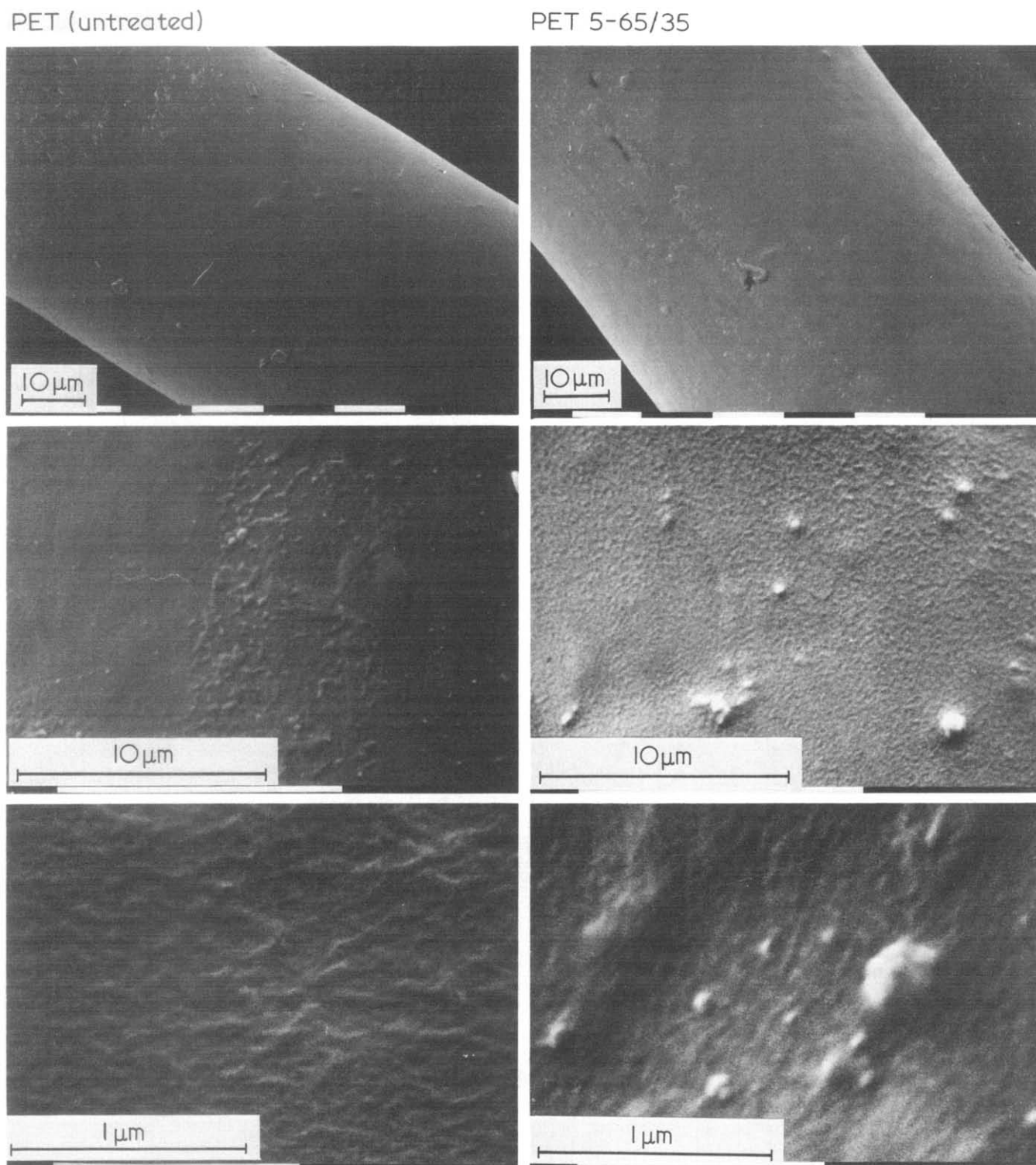PET (untreated)   PET 5-65/35

Figure 2 Surface electron micrographs of PET samples at increasing magnifications (see *Table 1*). (Courtesy of Dr. R. Brebner, Philips Analitica, Milan)

high polar interactions and the hydrogen-bondings of water would invalidate the prevision of the polymer-solvent compatibility.

Table 2 shows the time-dependency of the PET/acetone–water interactions. By soaking the filaments for increasing periods of time we obtained the same d.s.c. profile as for the PET, 1–100/0 sample.

Knox[11-13] stated that PET, whose δ_s value is 10.7[14,15], may be represented as composed of an aromatic and an aliphatic ester residue having δ_s values of 9.85 and 12.1, respectively.

A Lewis acid such as acetone can only interact with the aliphatic ester residue but its δ_s value, 9.77, is far from the δ_s value of the PET aliphatic residue. The resulting action can only be a mild one. However, acetone can lower the T_g of PET and allow crystallization to occur.

The time–dependency of our treatments suggests that water has a hindering effect on the action of pure acetone. The acetone–water mixture lowers the T_g, but crystallization can be avoided by treatment for a short period of time.

This interpretation is in agreement with the ageing

behaviour of PET 5-65/35. In *Table 3* we report the thermal characterization of this sample aged for different periods of time at room temperature. T_g and T_c values regain the transition temperatures of the untreated sample.

Infra-red spectrophotometry of the aged samples shows a gradual regression of the intensity of the two bands previously considered (data not shown). This regression is justified by the increase in T_g value that causes a lower molecular mobility. The specific volume of the aged filaments remains unchanged. A swollen state of PET treated in an aqueous medium has already been observed by Knox et al.[16].

Water (with regard to PET) can be considered as a secondary plasticizer, because of its chemical non-affinity. Its action enlarges the size of the three dimensional internal structure by breaking bonds among the active centres on the macromolecules similar to common non-solvent plasticizers.

In the absence of the primary-plasticizers (acetone was removed by washing), over a period of time, the action of
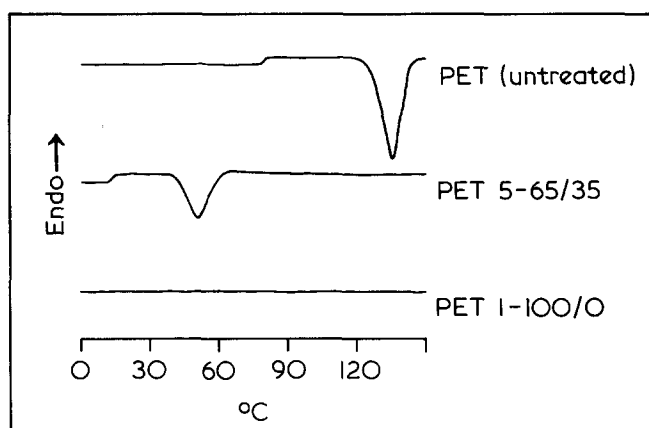

Figure 3 D.s.c. analysis of PET filaments. (See *Table 1*)

Table 2 Thermal behaviour of PET filaments in function of the period of treatment

Samples*	T_g (°C)	T_c (°C)	ΔH_c (J/g)
PET, 1−65/35	66	110	18.6
PET, 3−65/35	15	56	15.0
PET, 5−65/35	12	52	10.0
PET, 10−65/35	n.d.	39	9.1
PET, 30−65/35	n.d.	−	−
PET, 1−100/0	n.d.	−	−

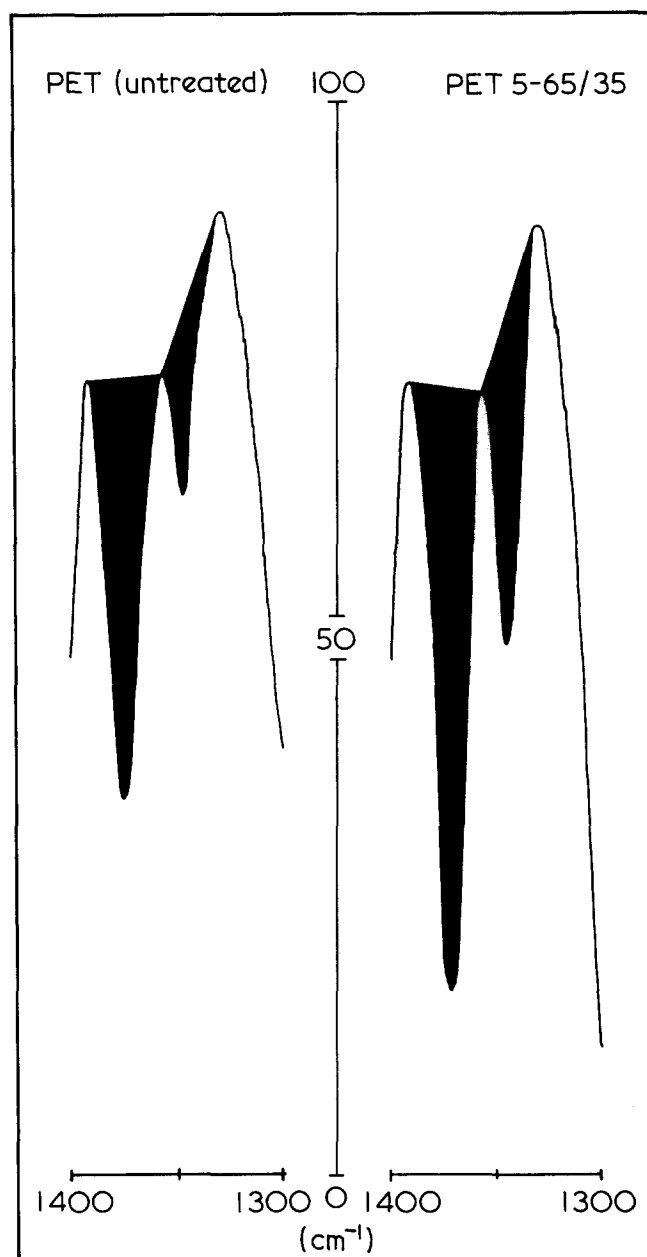* For explanation of notation used see Table 1.

Figure 4 Infra-red absorptions of 1337 and 1370 cm^{-1} bands. (See *Table 1*)

the attractive forces among the macromolecules gradually squeezes out the water and reforms the initial tightly arrayed structure.

ACKNOWLEDGEMENT

Table 3 Characterization of PET, 5−65/35 aged for increasing periods of time

Ageing (h)	v_s (cm³/g)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
0.5	0.748	12	52	10.0	259	39.8
1	0.748	25	65	10.9	260	41.0
1.5	0.748	27	67	11.4	259	40.3
15	0.748	45	88	13.7	261	41.1
55	0.748	60	102	14.4	258	42.1
100	0.748	64	109	16.7	260	40.8
400	0.748	73	116	16.2	259	39.0
PET untreated	0.745	77	135	26.5	258	43.0

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