Characterization of the aminolytic product of poly(ethylene terephthalate)

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(Received 15 May 1986; revised 31 July 1986)

Various analytical methods were used in addition to weight loss to characterize the products resulting from the aminolysis of both conventional (regular laboratory) poly(ethylene terephthalate) fibre and commercial, basic-dyeable Dacron T92. The results obtained from infra-red spectroscopy and scanning electron microscopy together with elemental analysis of products resulting from progressive degradation of the polymer showed that the corresponding amide of the polyester was ultimately formed on complete degradation. Whilst the weight-loss curves showed considerable variation with varying pretreatment, the result obtained showed little selectivity on the part of the aminolysis and thus was not suitable for estimating crystallinity because low molecular weight crystalline products are deposited and actual weight loss passed through a maximum with time.

(Keywords: aminolysis; methylamine; nitrobenzene; chromatography; Dacron T92; dimethylterephthalamide)

INTRODUCTION

The use of degrading reagents to remove amorphous material rapidly from crystallized polymers has been practised by a number of workers as a means of isolating the crystallized material for more detailed study. Miyagi and Wunderlich[1], for example, used an etching technique followed by electron microscopy to show the existence of lamellar structures in poly(ethylene terephthalate) (PET) after hydrolysis by water under pressure. Aminolysis, using reasonably concentrated aqueous solutions of primary aliphatic amines, was first investigated by Farrow, Ravens and Ward[2], who concluded that a rapid degradation of amorphous material was followed by a much slower attack of crystalline regions. Kurita[3] has suggested that aminolysis is highly selective so that amorphous material is removed rapidly, leaving residues which are highly crystalline. He reached the important conclusion that the initial degradation of amorphous material results in a rapid weight loss which is followed by a much slower loss in weight as the residual crystalline material was attacked. Following this work, similar results and conclusions have been put forward by Overton and Haynes[4] who pointed out the particular suitability of methylamine in separating crystalline and amorphous regions in PET and similar conclusions have been reached by Mehta and Bell[5] and by Mocherla and Bell[6].

Duong and Bell[7] have carried out a careful investigation of the aminolysis of partly crystalline PET film prepared by annealing amorphous film under dry nitrogen. They were particularly concerned to compare the weight-loss curve with initial crystallinity in order to establish the selectivity of the methylamine reaction and whether such weight-loss curves could be used as a means of assessing the extent of the crystallinity of PET samples. Their weight-loss curve is reproduced in *Figure 1*, extrapolation of the slower limb giving an intercept of 35% weight loss at zero time. On the assumption that methylamine is selective, this value should equal the amorphous content, giving a value of crystallinity of 65%. This was, in fact, equal to the value derived from density measurements of the undegraded film. Duong and Bell noted that the ratio of methylamine to polymer must be high and that with less than 100 ml of 40% methylamine for a 3 g PET sample some products crystallized out of the solution. Examination of the residues obtained from degradations carried out with twice this volume of methylamine solution showed that the recovered material was highly crystalline PET having molecular weight of 1800 and $\bar{M}_w/\bar{M}_n$ equal to unity. However, gel permeation chromatography of this material showed not only a sharp peak corresponding to this molecular weight but also a peak at a higher elution volume corresponding to *N,N'*-dimethylterephthalamide, i.e. the final product of the aminolysis.

We have used the aminolysis technique of Duong and Bell to examine filaments of regular PET and of PET containing sulphur groups (Dacron T92) which had been subjected to annealing treatments and also to treatment with dimethylformamide (DMF) solutions. Whilst the weight-loss curves obtained showed considerable variation with varying pretreatment, our results cast considerable doubt on the selectivity of aminolysis and on the feasibility of extrapolating weight-loss curves to obtain a measure of crystallinity.

We have been able to show more convincingly in addition that the main product of the amine degradation

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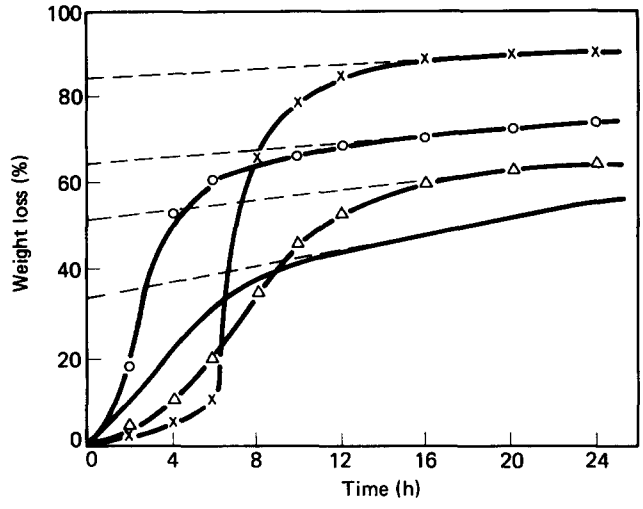

Figure 1 Weight loss *versus* time of aminolysis for laboratory PET: ———, result of Duong and Bell[7]; ×, lab. PET, control; △, lab. PET, heat set, 200°C, 3 h; ○, lab. PET, DMF-treated, 95°C, 1 h

is the theoretically expected amide, i.e. *N,N'*-dimethylterephthalamide, of both aminolysis and ammonolysis reactions of the polymer.

EXPERIMENTAL

Materials

Laboratory PET. The fibres (43 denier, nine multifilaments, no twist) were prepared from bright polymer chips (Courtauld UK Ltd) which were dried under vacuum at 120°C for 24 h before spinning. They were spun in a laboratory unit under nitrogen at 270°C and subsequently drawn five-fold at 80°C on a laboratory draw frame.

Dacron T92. This is a basic-dyeable polyester containing some residues of 5-sulphoisophthalic acid. Commercial filaments supplied by E. I. Dupont de Nemours and Co. Inc. (Leicester, UK Division) were used. The total sulphur content was found to be 0.64% by weight, corresponding to 3.76% of phthalic acid residues being sulphonated.

Both fibres were purified by extraction with petroleum ether at 60°C for 1 h, drying at 60°C under vacuum for 24 h followed by scouring at 60°C for 1 h in a 0.1% aqueous solution of Lissapol N (ICI), rinsing in distilled water at room temperature and finally drying in vacuum at 60°C for 48 h.

Treatments

Heat treatments. The fibres were heat set at 200°C in the relaxed condition. A stoppered tube containing a thermometer was inserted into the extended neck of a flask containing boiling nitrobenzene. The temperature in the tube stabilized at 200°C and at this stage the stopper was quickly removed, the fibres suspended on a length of stainless-steel wire were introduced and the stopper reinserted. For laboratory PET the heat setting time was 3 h; for Dacron T92 the time was 3 min or 1 h.

DMF treatments. The fibres were treated in the relaxed condition. They were simply suspended on a stainless-steel wire in a flask of DMF maintained at 95°C by immersion in a heated water bath. After 1 h they were removed, surface liquid removed by blotting and finally dried at 65°C *in vacuo* for 24 h, after which time there was no further loss in weight.

Aminolysis. About 50 mg of vacuum-dried fibre was accurately weighed and placed in 5 ml of 40% w/v aqueous methylamine solution, contained in a tightly stoppered tube at room temperature and maintained with occasional shaking for various periods of time. In the first experiments the samples were filtered, carefully washed with distilled water and then vacuum dried overnight at 30°C. The residues were then carefully reweighed. This is essentially the procedure of Duong and Bell[7]. In some later experiments, the residues after aminolysis were separated by centrifugation rather than by filtration. In this case, clear supernatant liquors were obtained (as against turbid filtrates). The residues were washed, dried and weighed as for filtration. They were also examined on a hot-stage microscope.

Density measurements

The densities of the various fibre samples were measured in a density gradient tube established with carbon tetrachloride and n-heptane so as to give a working range of 1.45 g cm^{-3} to 1.30 g cm^{-3} (ref. 7). The tube was maintained at 23°C by means of a water jacket and calibrated using standard floats.

Infra-red measurements

Samples were ground to a fine powder at the temperature of solid carbon dioxide and then incorporated in KBr discs in the usual way. Spectra were recorded using a Perkin–Elmer 710B i.r. spectrophotometer.

Scanning electron micrographs

Samples of fibres and of the residues following aminolysis were examined using an ISI-100A scanning electron microscope at magnifications ranging from 350× to 720×. The samples were gold-plated.

RESULTS AND DISCUSSION

Weight-loss curves

The weight-loss curves obtained following the procedure of Duong and Bell[7] are given in *Figures 1* and *2*. They differ significantly from the results of Duong and Bell in that they are sigmoidal, i.e. there is either some initial inhibition of attack by methylamine or, more likely, the molecular fragments resulting from initial cleavage of the ester bends are too large to be extracted. Nevertheless, in all cases the rate of loss of weight eventually slowed down resulting, after 24 h, in curves which could be extrapolated back to zero time to give intercepts on the weight-loss axis which should correspond to the percentage of amorphous, or more accessible, material. The corresponding values of percentage crystallinity are given in *Table 1*, together with the crystallinity values calculated from density measurements.

Compared with the result of Duong and Bell—who obtained exactly the same values of percentage crystallinity by the two methods—the agreement is not good, although for the laboratory PET a linear relationship exists between the two sets of values. The Dacron T92 was a commercial sample of unknown

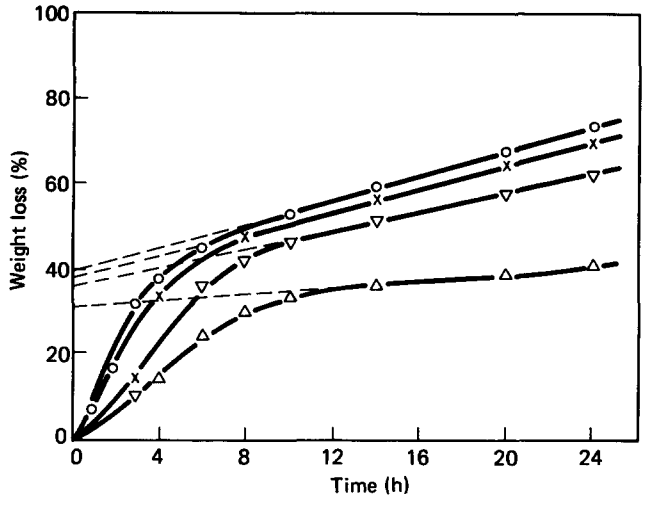

Figure 2 Weight loss *versus* time of aminolysis for Dacron T92: ×, control; △, heat set, 200°C, 3 min; ▽, heat set, 200°C, 1 h; ○, DMF-treated, 95°C, 1 h

Table 1 Crystallinity values from aminolysis and from density measurements

Material	Crystallinity (%)	
	From wt loss	From density[a]
Lab. PET, control	15	7.9 (1.345)
Lab. PET, heat set (200°C, 3 h)	50	61.0 (1.408)
Lab. PET, DMF-treated (95°C, 1 h)	38	45.8 (1.390)
Dacron T92, control	62	42.0 (1.385)
Dacron T92, heat set (200°C, 3 min)	64	54.0 (1.400)
Dacron T92, heat set (200°C, 1 h)	70	55.8 (1.402)
Dacron T92, DMF-treated (95°C, 1 h)	60	53.3 (1.399)

[a] Assumed densities of fully crystalline and fully amorphous regions are 1.455 g cm^{-3} and 1.335 g cm^{-3} respectively[8]. Measured densities in parentheses

history and is therefore unlikely to be comparable with the control sample of laboratory PET. For both polymers, however, the heat set samples have higher crystallinities than those treated with DMF by both methods. It is worth noting that for Dacron T92, which contains sulphonated residues, sulphur was completely removed when between 35 and 45% of the initial weight had been lost, i.e. the sulphonated residues are located in the more accessible (non-crystalline) regions.

For both polymers it was observed that filtration was not fully effective, the filtrates being milky in appearance, so that the measured values of weight loss are all slightly high and some experiments were therefore repeated using centrifugation rather than filtration. These results are given later.

I.r. and s.e.m. results

It is implicit for the success of the method that aminolysed material remains completely dissolved in the amine solution used. The general conclusion is that 40% methylamine solution is adequate for this purpose, although less concentrated solutions may not be, provided the ratio of methylamine solution to PET is sufficiently high[4,5,7]. Duong and Bell[7] used 200 ml of solution for 3.0 g of PET film; they reported that if less than 100 ml of solution were used some crystallization of the degradation products occurred. We used 5 ml of 40% methylamine solution for 50 mg of fibre, which should have retained all degradation products in solution, but we nevertheless felt it desirable to check the i.r. spectra of the filtered solid samples to ensure that they were entirely PET. Some spectra are given in *Figure 3* for undegraded samples and for samples degraded for 6 h and for 24 h. It is clear that the chemical composition of the residues changes with aminolysis, and in particular the C=O stretching band at 1720 cm^{-1}, which is characteristic of an ester group, moves to 1630 cm^{-1} where it may be assigned to the C=O stretching frequency of the secondary amide group. At the same time appear bands at 1545 cm^{-1} assignable to >NH deformation and at 3350 cm^{-1} assignable to NH stretching. The spectra after 96 h of aminolysis show no further change from the 24 h samples and so it must be assumed that the residues collected after 24 h are virtually fully degraded and contain amide rather than ester bonds.

Support for this contention comes from a scanning electron microscope investigation of the residues. After up to 6 h of aminolysis the residues still consist of essentially fibrous material, although strongly etched. After 24 h no fibrous material is present and the residues consist of flat crystals often stacked together (*Figure 4*), these residues being identical for laboratory PET and for Dacron T92. The final product of aminolysis of PET is *N,N'*-dimethylterephthalamide, $C_{10}H_{12}N_2O_2$, and the crystals recovered after 24 h of aminolysis were confirmed as this by elementary analysis—found C 63.8%, N 14.6%, H 6.4%; $C_{10}H_{12}N_2O_2$ requires C 63.5%, N 14.6%, H 6.3%. The crystals had m.p. 325°C. Farrow[2] obtained similar values in elementary analysis and Duong and Bell[7] have reported a peak for *N,N'*-dimethylterephthalamide in g.p.c. analysis of the residues obtained after 24 h aminolysis of PET film. The latter workers, however, also obtained a peak for crystalline PET of $MW \simeq 1800$, which they regarded as the major product.

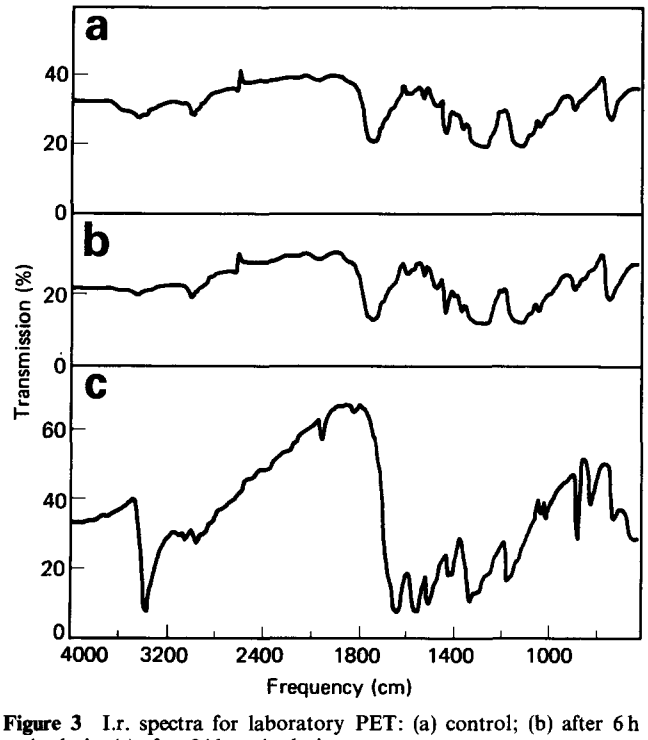

Figure 3 I.r. spectra for laboratory PET: (a) control; (b) after 6 h aminolysis; (c) after 24 h aminolysis

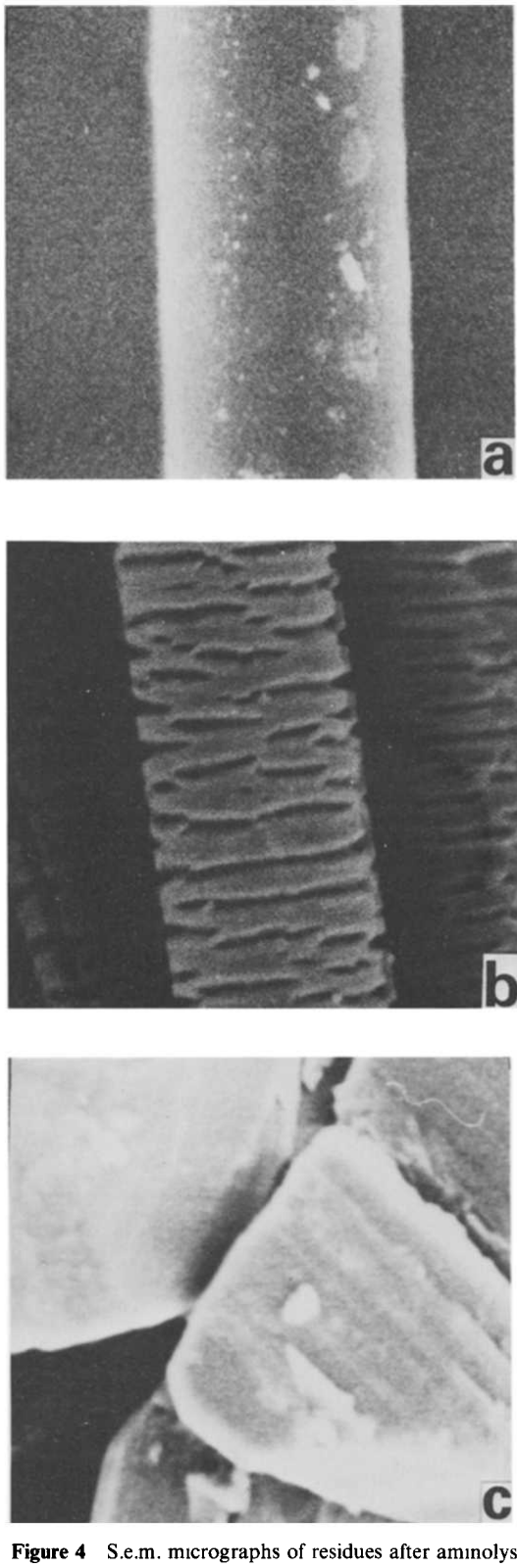

Figure 4 S.e.m. micrographs of residues after aminolysis

Centrifugation experiments

The results described above show that the insoluble residues obtained after aminolysis of both unmodified PET fibres and of sulphonated PET fibres may contain *N,N'*-dimethylterephthalamide in addition to crystalline PET especially after extended times of reaction, e.g. 24 h. The dimensions of these crystals are greater than the diameters of the original fibres (see *Figure 4*) and the crystals must have grown from solution. In other words treatment of PET with aqueous methylamine leads not only to degradation and dissolution of PET but also to the deposition of crystals of *N,N'*-dimethyl terephthalamide, so that the composition of crystals of *N,N'*-dimethylterephthalamide, so that the composition of the solid residues will be continuously changing. If this is so, the weight-loss curve is not simply a representation of the degradation of PET and extrapolation will not yield a value of percentage crystallinity.

Some experiments with laboratory PET were therefore repeated but the solid residues were separated from the mother liquors by centrifugation rather than by filtration. In this way completely clear mother liquors were obtained. Furthermore, after washing, drying and weighing, the residues were examined by means of a hot-stage microscope which enabled approximate values of melting point to be determined. The weight-loss curves are given in *Figure 5* and the results of the microscopy in *Table 2*.

Compared with *Figure 1*, the values for weight loss in *Figure 5* are slightly lower, as would be expected from the different method of collection. More importantly, the aminolyses were carried out for longer times and the weight-loss curves can now be seen to pass through a maximum after 30 h. Clearly after about 30 h the rate of crystallization from the amine solution begins to exceed the rate of aminolysis and dissolution of PET, but this process must be contributing to the shape of the curve at earlier times.

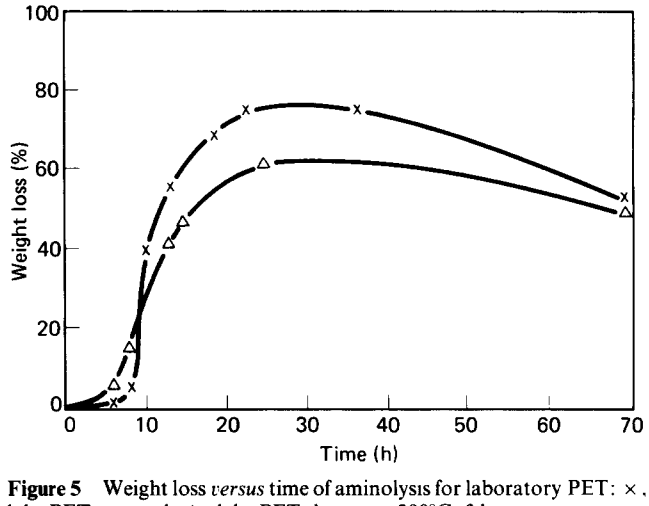

Figure 5 Weight loss *versus* time of aminolysis for laboratory PET: ×, lab. PET, control; △, lab. PET, heat set, 200°C, 3 h

Table 2 Microscopic appearance of aminolysis residues

Time of aminolysis (h)	Appearance and melting point (°C)
0	Fibres, 255–262
4	Fibres, 257–260
6	Fibres, 258–261
10	Fibres, 247–251
12	Fibres, 230–240; Powder, 220
14	Fibres, 235–247; Powder, 228
18	Fibres, 292; Crystals, 292–295; Powder, 205–212
21	Fibres, 297; Crystals, 297–299, Powder, 205
36	Crystals, 309–315
70	Crystals, 313–317

From *Table 2*, it can be seen that for up to 10 h of aminolysis the residues remain fibrous and the melting points are reasonable for PET by this method of measurement with some impurity present at 10 h. At 12 and 14 h of aminolysis the melting points fall markedly (indicating, possibly, impurities) and there appears to be two forms of material. At 18 h there is clear formation of high-melting crystals, which cannot be PET, and after 36 h all of the residue is high-melting point crystals. The final melting point of 313–317°C accords with the value of 325°C found for *N,N'*-dimethylterephthalamide.

CONCLUSIONS

The weight-loss curves (*Figures 1*, *2* and *5*) show clear differences between the differently treated samples, confirming that the rate of aminolysis is affected by variations in physical structure. Thus, in all cases the heat set samples, which from density and from wide-angle X-ray measurements were most crystalline, showed the smallest weight loss. However, it is equally clear from the other evidence that the shapes of the curves are influenced by factors other than simple aminolysis and dissolution of PET, so that in these cases it is not possible to extrapolate a part of the curve to zero time and simply read off the percentage crystallinity from the intercept. Indeed, with complete curves such as in *Figure 5* extrapolation is not possible.

We feel that the method should be used with some caution and should always be combined with some other analysis of aminolysis residues.

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