Some Thermal Studies on Poly(ethylene Terephthalate)

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Synopsis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of poly(ethylene terephthalate) has been carried out on samples of amorphous, cold-drawn, heat-crystallized, and acetone-crystallized polymer. From DTA it appears that for amorphous material a prolonged "secondary" crystallization process follows a primary process in the region of 140°C. For cold-drawn polymer, heat treatment does not reflect differences observed in previous x-ray diffraction studies. The TGA gives evidence that a high temperature endothermic peak observed in DTA may not be directly associated with depolymerization. With acetone-crystallized material a high degree of acetone retention is detected.

INTRODUCTION

In recent years there has been a noticeable increase in the application of thermal analysis, particularly differential thermal analysis (DTA), and of thermogravimetric analysis (TGA) to many branches of chemistry including polymer chemistry. In the former technique (DTA), a sample is heated at a constant rate alongside an inert material, and as the temperature rises exothermic or endothermic changes which the sample may undergo are recorded as positive or negative peaks, the area of a peak being a measure of the amount of heat associated with the change. The changes may be physical in origin, e.g., phase changes as in melting, or chemical, as in oxidation. Similarly, in the case of TGA, positive or negative weight changes which occur are again recorded as a function of temperature and time. One of the advantages of these techniques, with the use of the automatic types of commercial apparatus now available, is that a rapid assessment of thermal and gravimetric behavior may be made over a wide temperature range from which not only qualitative but also quantitative evaluation may be made.[1]

Application has been made to all branches of polymers, i.e., to fibers, plastics, and rubbers, but in general this has been limited to one or the other of the techniques and either to physical or chemical changes. This is particularly the case for poly(ethylene terephthalate) (PET) on which there has been a certain amount of DTA work both from the physical and chemical points of view. For example, Ke,[2] using quenched and annealed polymer as well as commercial forms of the material as fiber and film, has presented evidence of a glass temperature at 70°C., with exothermic peaks

in the region of 125 and 220°C. which are attributed to crystallization of the quenched material, and with an endothermic peak around 265°C. which is believed to be due to melting. From the results there is also an indication of reversal to exothermic behavior immediately following melting, particularly with drawn polymer. Schwenker and Beck[3] have carried out similar studies on drawn and undrawn Dacron and have extended the temperature range. Their results indicate a slightly higher value for the glass temperature (77°C.) for the undrawn material, with a single exothermic peak at 136°C. and an endothermic peak at 260°C. in air or 262°C. in nitrogen. The essential difference between these results and those of Ke appears to lie in the absence of the exothermic premelt crystallization peak. At higher temperature the results give evidence of an endothermic reaction at about 447°C. in an atmosphere of nitrogen, suggestive of depolymerization. In air an exothermic reaction is indicated at higher temperatures. Scott[4] has reported a value of 70°C. for the glass temperature, again from DTA studies, with peaks also for crystallization and melting as before but with no strong indication of a secondary premelt crystallization process.

In the present work an attempt has been made to clarify this latter anomaly and to extend the study to include polymer which has been cold-drawn at room temperature. At the same time TGA has been carried out with a view towards complementing the DTA results. A separate experiment on acetone-crystallized polymer has also been carried out, the results of which may be relevant to the above study and also to work on the liquid-induced crystallization of PET.

EXPERIMENTAL

Materials

The PET used in these studies was in the form of film (thickness = 2×10^{-2} cm.) and was essentially amorphous (density = 1.339 g./cc., corresponding to a calculated degree of crystallinity $\cong 3\%$). From this, a sample was crystallized by heating at 140°C. for 30 min. A second sample was cold-drawn at room temperature by stretching on a Hounsfield tensometer (draw ratio $\cong \times 4$). A third sample was crystallized by immersion in acetone for 24 hr. at 25°C., previous work having indicated that this time was sufficient for complete crystallization.[5] One portion of this sample of film was then subjected to a vacuum treatment for 48 hr. to remove loosely held acetone.

Apparatus

TGA studies were carried out on a Stanton thermobalance (Model HT-M). The apparatus employed for DTA was similar to that described by Roberts and co-workers[6] with a Honeywell Brown 1 mv. potentiometric recorder attachment. Sample temperature was measured at intervals with the aid of a Pye potentiometer (Model 7569P).

Technique

TGA. Samples (0.26 g.) were cut into approximately 0.1 in.² pieces and heated in a 10-ml. recrystallized alumina crucible on the thermolance at a controlled rate of heating. This was 2°C./min. in the range 20–100°C. and 6°C./min. in the range 100–500°C., the rate being linear in both cases. The atmosphere surrounding the sample was initially air, although during rapid evaporation of monomers or other breakdown products this may be considerably altered. A buoyancy correction was applied to all results, this being determined in a separate experiment by heating an empty 10 ml. crucible under the same conditions.

DTA. The ceramic cell and arrangement of thermocouples were as described previously.[6] Samples were prepared as for the TGA, two methods of packing being employed. In the first the sample (0.2 g.) was packed undiluted into the second compartment of the cell; in the other a "sandwich" technique was used in which 0.1 g. of sample was placed between two 0.25 g. layers of α-alumina. In both methods the sample was heated at a controlled rate of 8°C./min. and the differential temperature was recorded against the inert sample of α-alumina packed into the first compartment of the cell. It is considered that the atmosphere surrounding the sample in the first technique was comparable to that in the TGA studies. In the second method, however, the sample is heated in a limited supply of air so that, particularly when chemical breakdown occurs, the atmosphere in the vicinity of the polymer must be oxygen limited.

Other experimental techniques, together with relevant data, which were felt to be desirable in connection with elucidation of the primary results of the investigation are described in context later.

RESULTS

DTA results for amorphous PET, including both open and sandwich samples, are shown in Figures 1 and 2, respectively. The curve for the heat-crystallized sample, studied under open conditions is shown in Figure 3. Figures 4 and 5 relate to a cold-drawn sandwiched specimen and one which had been heated at 140°C. for 30 min., respectively. The results for the acetone-crystallized, and subsequently evacuated, sample under open DTA conditions is shown in Figure 6.

Figure 7 shows the TGA results for a sample of amorphous polymer; as the corresponding results for heat-crystallized and cold-drawn samples were identical in every respect to those of the amorphous, these are not presented. The curves for the acetone-crystallized material which are different from those mentioned above are shown in Figure 8. Figure 8a refers to a nonevacuated sample and Figure 8b to the sample which has received a vacuum treatment.

DISCUSSION

Figures 1 and 2 both show evidence of an inflection in the curve in the region of 75–80°C. indicative of a second-order glass transition and so is in

general agreement with the results of previous workers. A crystallization peak is seen to occur in the region of 140°C., but unlike the results of Ke, and more like those of Scott and of Schwenker and Beck, there is little suggestion of a pronounced secondary premelt crystallization. However, the possibility of a secondary but perhaps more continuous crystallization process is not entirely ruled out, as such behavior might conceivably influence the baseline if it is relatively small and drawn out. That this suggestion may have some validity is supported by the fact that if one accepts the observed baseline at its face value it would appear, on the basis of peak areas that the energy associated with melting is substantially greater than that for crystallization. On the other hand it would be necessary to look for some other endothermic process concurrent with melting. Now under isothermal degradative conditions in air, discoloration is observed to accompany melting, and there is also a progressive weight loss.[7]
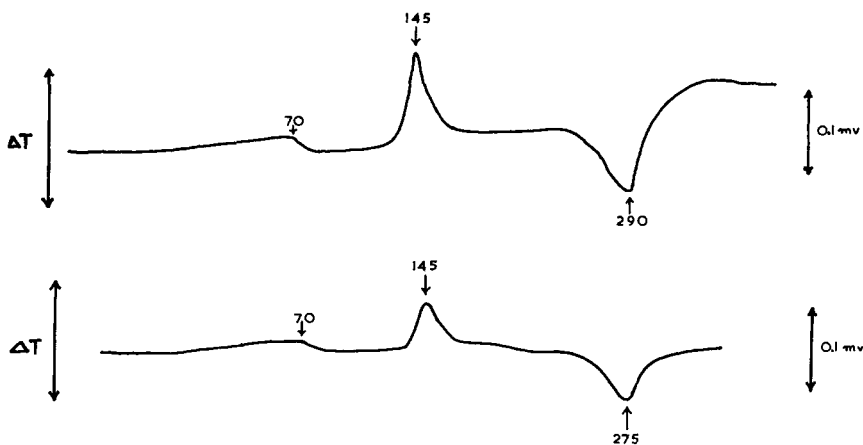

Fig. 1. (Top) DTA curve for amorphous PET (open).
Fig. 2. (Bottom) DTA curve for amorphous PET (sandwich).

However, under the conditions of the present investigation, no appreciable loss in weight is observed until a temperature above the observed melting point (275°C.) has been achieved, as indicated in Figure 7. Thus, it would appear that although there is appreciable crystallization at 140°C., the process continues to higher temperatures. Further support for this contention is obtained from work on rates of crystallization,[8] where an increase of temperature was found to produce an increase in the degree of crystallization, the period of time chosen for comparison being ten half-times, i.e., ten times greater than the period required to obtain half the limiting value of crystallization at a given temperature. Above the indicated melting temperature there is a distinct difference in the shape of the two curves shown in Figures 1 and 2, and it would seem reasonable to suggest that in the open sample the exothermic behavior is a result of oxidative degradation.
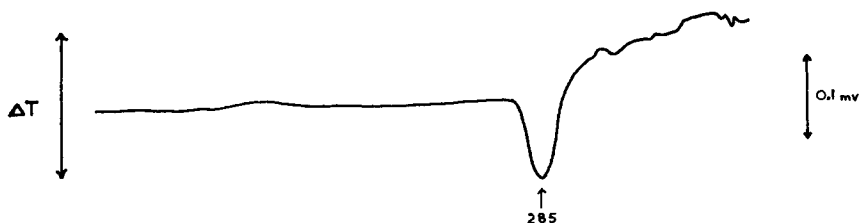
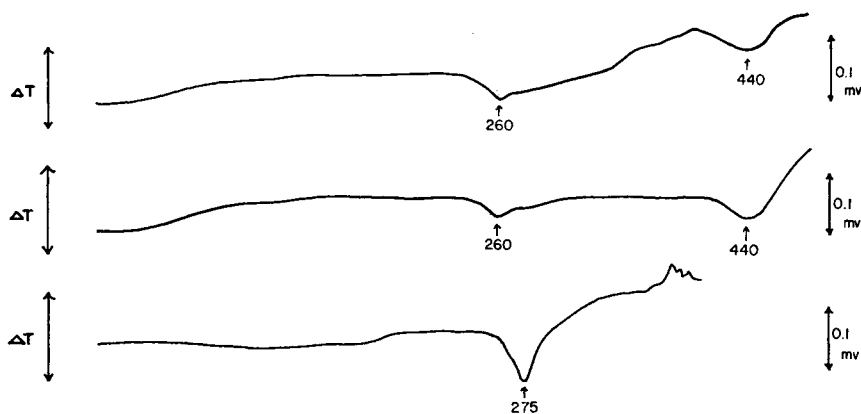Fig. 3. DTA curve for heat-crystallized PET (open).

Fig. 4. (Top) DTA curve for cold-drawn PET (sandwich).
Fig. 5. (Middle) DTA curve for cold-drawn heated PET (sandwich).
Fig. 6. (Bottom) DTA curve for acetone-crystallized PET (open).

The DTA curve for the heat-crystallized sample (Fig. 3) is similar to those obtained by previous workers and, apart from drawing attention to the expected exothermic behavior just above the melting range, presents no points for discussion. It is not clear why the observed melting point of 260°C. should be lower than for the investigation involving amorphous PET.

Figure 4, relating to a cold-drawn sample appears to suggest, on the basis of the observed baseline, that there is no pronounced crystallization process in the region of 140°C. as for amorphous material and that the sample is probably already completely crystallized. Previous work involving x-ray diffraction studies[9] on drawn film and on a similar specimen which was subsequently heated at 140°C. for 30 min. showed that in the former case orientation without resolution occurred, whereas with the latter, disorientation with good resolution resulted. From the results it was difficult to compare absolute levels of the degree of crystallization, although it is felt that at least in part, the differences in resolution may be due to differences in crystallite size, or strain. A separate investigation has shown that a cold-drawn sample heated for 30 min. at 140°C. has the same density, and presumably the same degree of crystallinity as an originally undrawn amorphous sample heated under the same conditions, i.e., 1.377 g./cc. Figure
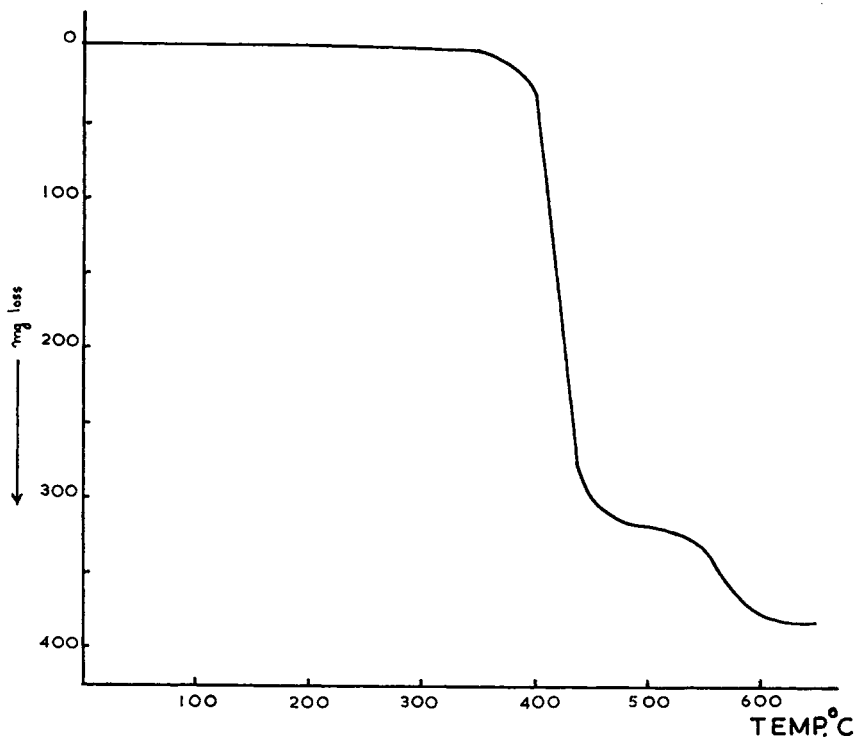
Fig. 7. TGA curve for PET.

5, which shows the DTA curve for a cold-drawn and then heated sample is virtually the same as Figure 4 and thus tends to confirm that the cold-drawn sample is indeed crystalline, and therefore invalidates a possible alternative suggestion that the absence of an observed crystalline peak may be due to a cancellation of a heat change, due to such behavior, by mechanical energy associated with shrinking. Apart from visual appreciation that shrinkage does occur on heating, a separate experiment, in which the thermogravimetric apparatus was modified so that the balance arm could register movement due to contraction of a cold-drawn test piece rather than by weight changes, showed that relaxation occurs as low as 50°C. However, the energy associated with relaxation must be small or marginal over a wide temperature range owing to the similarities of Figures 4 and 5. If the above interpretation is correct, it seems curious that the cold-drawn sample has the same degree of crystallinity as the heat-crystallized sample. At higher temperatures the results are in general agreement with those of Schwenker and Beck, and it appears from this and from the TGA studies that the behavior above the melting temperature is largely independent of the physical nature of the material below this temperature. The TGA results themselves confirm that degradation occurs above the melting temperature (Fig. 7) and that, from the point of view of weight loss, it is taking place at a maximum rate just over 400°C. and approaches a minimum about
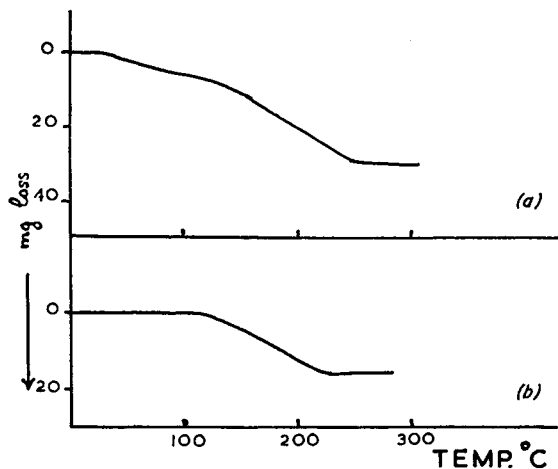
Fig. 8. TGA curve for acetone-crystallized PET: (a) nonevacuated; (b) evacuated.

440°C. It would therefore appear that the DTA peak at the latter temperature may be indicative of a transition from one exothermic reaction, presumably associated with degradation to another which may be final oxidation of carbon.

The DTA curve for the acetone-crystallized sample suggests that complete crystallization has taken place prior to analysis (Fig. 6). The TGA curves (Fig. 8) show that acetone is evolved continuously over a wide temperature range from about 130°C. and above for both the evacuated and unevacuated samples. At temperatures below these, only the latter shows appreciable weight loss with a sharp increase in the rate about 130°C. Figure 8 also indicates that acetone is still being given off almost to the melting temperature of the crystallized polymer. This serves to emphasize difficulties experienced with kinetic studies of liquid-induced crystallization, where one is forced to adopt approximate methods of calculation in the determination of sample density because of this high degree of retention.[5] A comparison of Figures 6 and 8 show that, although acetone is being evolved at temperatures above about 170°C., the DTA curve baseline is linear. This observation may have some relevance in connection with foregoing remarks on the influence of a continuous process upon the baseline.

References

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Résumé

On a étudié le téréphthalate de polyéthylène amorphe, étiré à froid, cristallisé par recuit et à l'acétone, par l'analyse thermique différentielle (DTA) et par l'analyse thermogravimétrique (TGA). Les résultats de l'analyse thermique différentielle montrent que dans le cas de polymère amorphe une cristallisation secondaire prolongée suit un processus primaire à des températures de l'ordre de 140°. Quant au polymère étiré à froid, le traitement thermique ne montre pas les différences que l'on a observées auparavant lors d'une étude par rayons-X. L'analyse thermogravimétrique montre que l'on ne doit pas considérer le pic endothermique observé à haute température lors de l'étude par analyse thermique différentielle comme associé à un phénomène de dépolymérisation. On a observé un degré élevé de rétention d'acétone dans le matériel recristallisé en présence d'acétone.

Zusammenfassung

Amorphe, kalt gereckte, hitzekristallisierte und acetonkristallisierte Proben von Polyäthylenterephthalat wurden mittels Differentialthermoanalyse (DTA) und thermogravimetrischer Analyse (TGA) untersucht. Aus der DTA geht hervor, dass im Falle der amorphen Substanz auf einen Primärprozess im Bereich von 140°C ein länger dauernder "sekundärer" Kristallisationsprozess folgt. An kalt gereckten Polymeren kommen bei der Hitzebehandlung die in früheren Röntgenbeugungsuntersuchungen beobachteten Unterschiede nicht zum Ausdruck. Aus der TGA geht hervor, dass eine bei der DTA bei hoher Temperatur beobachtete endotherme Zacke nicht direkt einer Depolymerisation zugeschrieben werden kann. An acetonkristallisierten Proben wurde starke Acetonretention festgestellt.