Isothermal Crystallization Measurements on Poly(ethylene Terephthalate) by Differential Enthalpic Analysis

BERNARD MILLER, *Textile Research Institute, Princeton, New Jersey*

Synopsis

The process of solid-phase crystallization in poly(ethylene terephthalate) has been followed by means of differential enthalpic analysis. Kinetic data for the process has been obtained for isothermal annealing from 100 to 115°C., showing induction times and first-order rate dependence. For the material studied, undrawn polyester filaments, an activation energy of 44 kcal./mole was determined. The technique used provides more direct monitoring of the crystallization phenomenon than that achieved with other methods.

Introduction

It is well known that amorphous poly(ethylene terephthalate) (PET) shows a solid-phase crystallization exotherm during differential thermal analysis. This usually appears at 140–150°C., depending on the scanning rate. By using a differential scanning calorimeter, it is possible to obtain quantitative values for the heat of crystallization from the area under this peak. The extent of crystallization (i.e., the number of bonds formed) will be directly proportional to this measured heat value. However, the process actually starts considerably below the above temperature interval, but is not detectable by DTA because of the low rate of heat evolution. Mayhan et al.[1] have reported the isothermal growth of crystalline PET at 96.5°C. They obtained kinetic data from ultraviolet transmission values for amorphous films in silicone oil. Earlier, Cobbs and Burton[2] utilized infrared transmission measurements to obtain crystallization data for melt-cast films for the range 120–240°C. Both of these studies, as well as those on other polymers,[3,4] have relied on changes in light transmission to observe the onset and the growth of crystals. There were some difficulties in interpreting the data and in insuring isothermal conditions for rate processes that, at some temperatures, have half-lives of only a few minutes. Prior to these studies, Kolb and Izard[5] used density measurements to follow crystallization but emphasized that increasing density could not be quantitatively related to increasing crystallinity. It would therefore be useful to have another method for obtaining such data, especially one that measures the crystallization phenomenon directly.

We have been able to do this over a limited temperature range by determining the reduction in exothermic peak area found on post-annealing thermal scanning.   If one can measure the maximum heat of crystallization under specific scanning conditions for a given polymer sample, any premature crystallization will cause something less than this maximum value to appear when the exotherm occurs.   The effect is shown diagrammatically in Figure 1.

Experimental Procedure

A Perkin-Elmer differential scanning calorimeter was used for all of the thermal scans and annealing treatments.   The polymer was an undrawn polyester yarn with an intrinsic viscosity of 0.99.   Each sample was weighed into the standard aluminum dish and closed with a cover.   Any previous mechanical and thermal history was considered to be erased by the first step in the experimental sequence in which it was taken up to 290°C. and held there in the molten state for 10 min.   In preliminary tests it was determined that no appreciable differences in subsequent crystallization could be observed if longer molten state conditioning times were used.   The sample was then removed and allowed to cool rapidly against ambient room temperature.   (It was not possible to achieve the same quenching within the instrument by turning the temperature programming dial manually to room temperature.)   After at least 10 min. at room temperature, the sample was returned to the instrument chamber, which had been preset at 45°C., and programmed at 20°C./min. to the desired annealing temperature.   It was held at that temperature for a given time, after which the temperature dial was returned manually to 50°C.   Thermal equilibrium was established in about 4–5 min. and the sample was then thermally scanned at 20°C./min. through the crystallization exotherm and the melting endotherm to 290°C.   The procedure could then be repeated with either the same or different annealing conditions.
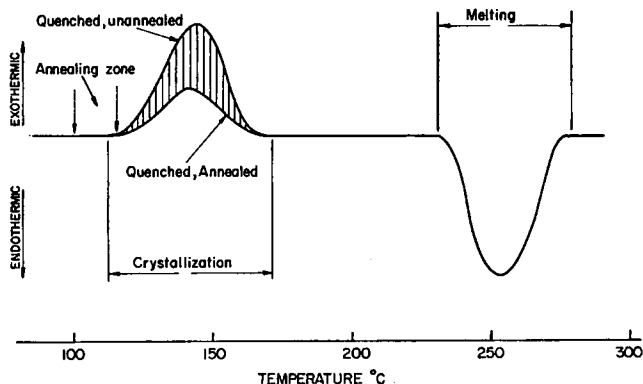

Fig. 1. Suppression of crystallization exotherm by annealing.

Dropping the temperature back to 50°C. after annealing was necessary in order to establish a base line for determining the area under the crystallization peak. Slower scanning rates could be used but served to decrease the precision of the measurements.

Results

Annealing was performed at 100, 105, 110, and 115°C. The heats of crystallization and melting were obtained by planimeter measurements of the appropriate areas, taking into account any instrument factors such as recorder chart speed, etc.), that would influence the values. For each temperature a series of scans was accumulated in which the crystallization exotherm decreased as the annealing time was lengthened.

To convert the experimental results into values reflecting the amount of crystallization that took place during annealing it is necessary to decide on a value for the maximum heat of crystallization. One possible choice is to use the result obtained directly for a similarly quenched and scanned, but unannealed sample. (In effect, this would be a zero annealing time exotherm.) The difference between this value and that for any other run would give a quantity proportional to the number of crystalline bonds formed during annealing. Referring to Figure 1, this would correspond to the shaded area. Another possible interpretation is to consider that the melting endotherm is a more accurate measure of the maximum crystallinity and to use the measured heat of fusion, with a reversed sign, as the equivalent of it. For this purpose, an individual value for each scan was available, from which the exotherm could likewise be subtracted. These treatments are identified as methods 1 and 2, respectively, and
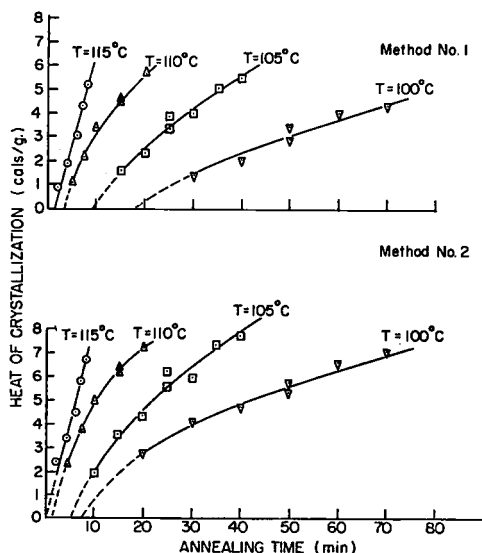
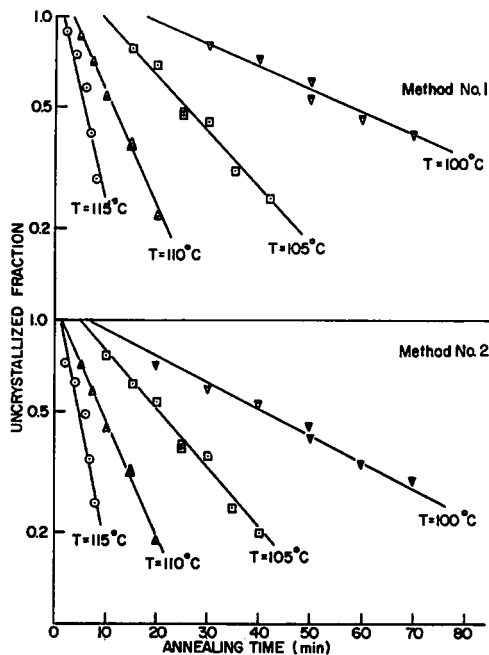

Fig. 2. Progress of crystallization with time.

Fig. 3. Fraction of amorphous polymer remaining.

results are shown in Figure 2. Both methods appear to produce the expected first-order growth rates, after induction periods that are temperature-dependent. Examples of reproducibility are shown by values for the same annealing times. When the logarithm of the fraction of uncrystallized (amorphous) polymer was plotted as a function of time (Fig. 3), the resultant linear plots for each temperature reiterated the first-order kinetics.

Bosch and his co-workers used a plot such as Figure 3 to obtain half-lives and rate constants for crystallization at each temperature. Treating our results in the same way produced values as shown in Table I. An

TABLE I
Kinetic Data for Isothermal Crystallization

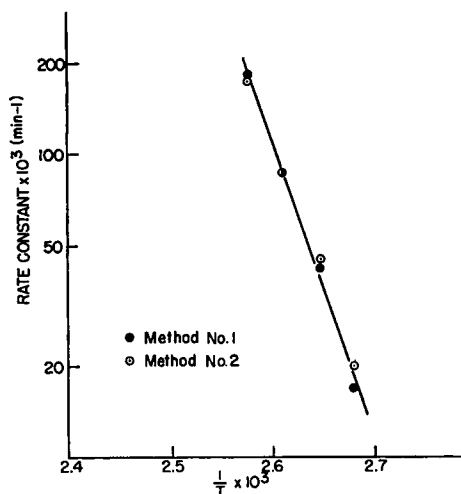| Temperature, °C.	Calculation method	Half-life, min.	Rate constant $k \times 10^3$, min.$^{-1}$
100	1	41.0	16.9
	2	34.8	20.0
105	1	16.5	42.0
	2	15.5	44.7
110	1	8.0	86.6
	2	8.0	86.6
115	1	4.0	173
	2	3.8	183

Fig. 4. Rate constant dependence on temperature.

Arrhenius plot (Figure 4) showed a good linear correlation for both calculation methods. Activation energy based on the average slope was 44 kcal./mole.

Evaluation of the Technique

It would seem that this procedure supplies a quick, though limited in range, method for following such polymer crystallization. Induction times and half-lives obtained in this way correspond to those previously reported from light transmission measurements. The value for activation energy is somewhat higher than the 37 kcal./mole found by Mayhan et al., which may be related to the fact that the latter had the polymer immersed in silicone oil during crystallization. There is also the possibility that average molecular weight can influence the activation energy (our polymer had almost double the intrinsic viscosity). Cobbs and Burton reported 20 kcal./mole, but their experiments did not cover the same temperature range. Collier and Baer calculated an activation energy of 64 kcal./mole for self-diffusion of PET, using the Avrami theory for bulk crystallization.

It must be emphasized that this technique could not be expected to reveal anything meaningful about early nucleating phenomena. However it does seem to be reliable for studying the later phases of crystallization, and, if nothing else, can be useful as a check on the interpretation of other, more indirect measurements.

References

1. K. G. Mayhan, W. J. James, and W. Bosch, *J. Appl. Polymer Sci.*, **9**, 3605 (1965).
2. W. H. Cobbs and R. L. Burton, *J. Polymer Sci.*, **10**, 275 (1953).
3. J. J. Kean and R. S. Stein, *J. Polymer Sci.*, **20**, 327 (1956).

4. J. R. Collier and E. Baer, *J. Appl. Polymer Sci.*, **10,** 1409 (1966).

5. H. J. Kolb and E. F. Izard, *J. Appl. Phys.*, **20,** 571 (1949).

Résumé

On a suivi le degré d'avancement de la cristallisation de la phase solide du téréphtha-late de polyéthylène au moyen de l'analyse enthalpique différentielle. Les résultats cinétiques de ce processus ont été obtenus par recuit isothermique de 100 à 115°C, montrant des temps d'induction et une dépendance de vitesse de premier ordre. Pour les matériaux étudiés, des filaments de polyester non-étirés, on a trouvé une énergie d'activation de 44 kcal/mole La technique utilisée permet de diriger plus directement le phénomène de cristallisation qu'en utilisant d'autres méthodes.

Zusammenfassung

Der Fortschritt der Kristallisation in fester Phase wurde bei Polyäthylenterephthalat durch Differential-Enthalpieanalyse verfolgt. Kinetische Daten für den Prozess wurden bei isothermer Temperung zwischen 100°C und 115°C erhalten; diese zeigen Induktions-perioden une eine Abhängigkeit nach bester Ordnung. Für das untersuchte Material, ungereckte Polyesterfäden, wurde eine Aktivierungsenergie von 44 kcal/mol bestimmt. Das verwendete Verfahren liefert eine direktere Aufzeichnung des Kristallisations-phänomens, als sie mit anderen Methoden erreicht wird.