polymer reports

Thermomechanical properties of nylon-6,6 annealed in glycerol

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The high temperature properties of samples annealed in glycerol at 195°C for various periods of time and those of variously treated samples were examined by thermomechanical analysis (t.m.a.) and thermal stress/strain analysis (t.s.a.). The sample annealed under much more severe conditions preserves its shape and load strength at temperatures high above the melting point. As the crosslinked sample shows properties resembling those of the severaly annealed sample, while the hydrolysed samples show more deteriorated properties than those of the annealed sample, we can conclude that the severely annealed sample is easily set to a gel accompanying thermal degradation or oxidation during the annealing, which was also indicated by elementary analyses.

Keywords Nylon-6,6; thermomechanical properties; stress–strain curve; crosslinking; gel formation; thermal degradation

INTRODUCTION

Nylon-6,6 crystal annealed in glycerol at high temperatures was found to increase its lamellae fold length by stepwise increments of $\frac{1}{2}$ a monomer unit length with increasing annealing temperature or time. Simultaneously, another distinct layer-thickening process[1] was observed which led to approximately a doubling (or maybe a quadrupling) of the straight stem length of the lamellar crystal annealed under appropriate conditions. New melting endotherms corresponding to these layer thicknesses were observed using differential scanning calorimetry (d.s.c.)[2,3].

In this report, the high temperature properties of these annealed samples were examined by thermomechanical analysis (t.m.a.) and thermal stress/strain analysis (t.s.a.). The strongly annealed sample tends not to melt, but preserves its shape and load strength at temperatures high above the melting point. These properties are compared with those of crosslinked samples, where the crosslinking was introduced by reaction with paraformaldehyde and hydrolysis with acids, where the roles of the crosslinking and tie molecular chains of the inter-crystallites are explained by these comparisons.

EXPERIMENTAL

The glycerol samples were annealed at 195°C for various periods of time using a previously described procedure[3]. The hydrolysed samples were obtained by treating the sample, which had been annealed in glycerol at 195°C for 24 h, in 55% aqueous formic acid and in 10% aqueous hydrochloric acid at 95°C for 24 h. As the annealed and the hydrolysed samples became more porous and brittle, they were subjected to a pressure of 50 Kg cm^{-2} at 210°C in a hot-press to form smooth disc-like sheets. For comparison, nylon-6,6 film which had been obtained by moulding the refined nylon-6,6 at 285°C in a hot-press and quenching in ice-water, was used. The film was *N*-methoxymethylated at 30°C for 24 h in a solution of methanol, paraformaldehyde, potassium hydroxide and anhydrous oxalic acid as applied to nylon-6[4]. This film was cured at 160°C for 5 min to introduce crosslinking between the molecular chains (termed the crosslinked sample).

Thermomechanical analysis (t.m.a.) and thermal stress/strain analysis (t.s.a.), which improved on the t.m.a. by the addition of apparatus accessories for detecting loads on samples, were performed with a Shimadzu thermal analyser TM-30 under a flow of nitrogen at a heating rate of 10°C/min or at selected temperatures, constant to ±0.5°C. T.s.a. measurements were performed by the application of a constant rate of electromagnetic load (25 g/min) on samples and recording the loads and extensions of the samples. The sample dimensions used were usually an initial length of 4 mm, width 2 mm and a thickness (this corresponds to the hot-pressed direction) of about 0.2 mm.

RESULTS AND DISCUSSION

Typical d.s.c. thermograms of nylon-6,6 samples annealed in glycerol at 195°C for various periods of time are shown in *Figure 1* (heating rate 10°C/min). Melting peaks can be seen in *Figure 1* with some peaks about 10°C higher than the main peak and all of these peaks shift discontinuously

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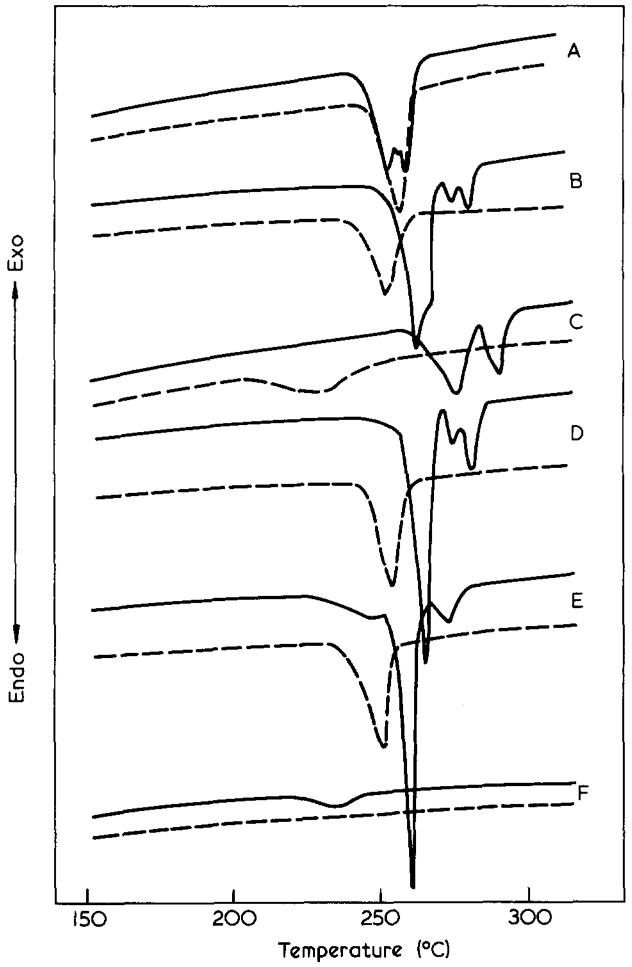

Figure 1 D.s.c. heating curves annealed and variously treated samples. (A), Unannealed; (B) and (C), annealed at 195°C for 24 h and for 265 h, respectively. (D) and (E), treated by hydrolysing sample (B) in 55% HCOOH and in 10% HCl solutions, respectively. (F), Crosslinking introduced after *N*-methoxymethylating the nylon-6,6 film for 24 h. The second runs of d.s.c. heating curves are shown as broken lines on the first runs

to higher temperatures as the annealing time becomes longer[2,3]. The second heating curves are shown as broken lines on the respective first heating curves. The first heating curve for nylon-6,6 film almost corresponds to the second heating curve for the unannealed sample (A). Every sample shows a single melting peak, whose temperature decreases from 260°C to 230°C and whose area becomes smaller as the annealing time increases, implying that the level thermal decomposition increased during the annealing. Viscosity average molecular weights ($\bar{M}_v$) were measured at 25°C in a 90% formic acid solution by using a Ostwald viscometer. $\bar{M}_v$ values decreased steeply from 18000 (unannealed) to 7000 (annealed for 24 h) and the minimum was around 4000 (annealed somewhere between 48–75 h). The sample annealed for the longest time (e.g., 265 h) became insoluble in all solvents, implying that a gelation-type reaction occurred during the annealing[5,6].

In *Figure 1* (D) and (E) are the heating curves for the samples hydrolysed in formic acid and in hydrochloric acid, respectively and the main sharp peak for curve D appears at a temperature about 10°C higher than that for curve E. The second heating curves (shown as broken lines) show the single melting peaks and the lowered melting temperatures parallel to the first heating curves. The $\bar{M}_v$ values decreased from 7000 (B) to about 4000 (D) and 2000 (E). F is the curve for the crosslinked sample and it shows a very small melting peak at the lower temperature of 235°C and the crosslinked sample became insoluble in all solvents. The second heating curve for the crosslinked sample does not show any detectably melting peaks, because it became almost amorphous and hard to crystallize due to the crosslinking.

Typical t.m.a. curves for these samples are shown in *Figure 2* when the load was 0.5 g. The unannealed sample broke at around 245°C, which corresponds to the temperature of melting. Samples B and D became soft at temperatures around 260°C and sample D was suddenly broken at 264°C, while the sample B continued to extend at the higher temperatures. Sample E shows a sharp breaking point at the lower temperature 248°C. As both samples are broken at the start of their melting temperatures, it could be considered that the tie molecular chains of the inter-crystallites were severed by the hydrolyses. The difference in the breaking temperatures reflects the severity of the hydrolyses. The sample with longest annealing (C) can preserve its load strength even at temperatures above the melting point. The crosslinked sample (F) shows a similar curve to that of (C), and this implies that the severely annealed sample can easily set to a gel. The second run curves of the t.m.a. for (C and F) are shown as broken lines (C′ and F′), which heated to a temperature of 310°C under a 0.5 g load then cooled down. Both show gently-sloping curves, because the extensible regions have already been extended and the load is supported by the network of crosslinked regions in the samples.

Typical t.s.a. curves for film (a), the sample annealed for 265 h (b) and the crosslinked sample (c) are shown in *Figure 3*. The film continues to extend by over 100% (maybe to 100–200%) to 225°C, and then it becomes weak and difficult to extend above 230°C and therefore difficult to plot the stress-strain curve at 242°C. However, the annealed and the crosslinked samples can extend to a much larger extent (over 100%) until around 250°C, and above this temperature both become difficult to extend any further but do show a fair strength over wide ranges of temperature. Both samples display similar curves,

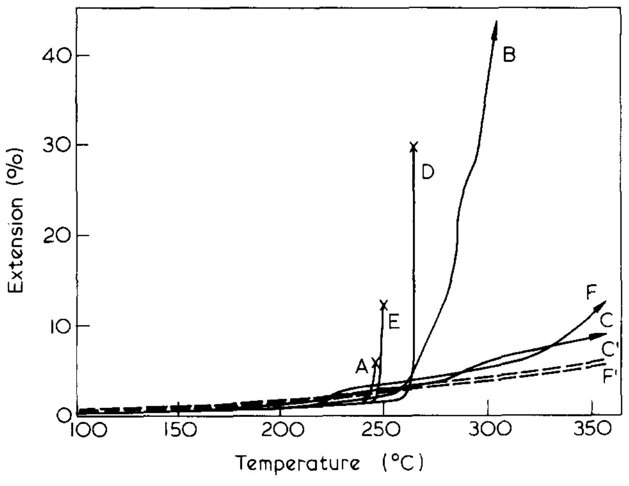

Figure 2 Typical t.m.a. curves of the samples corresponding to those in *Figure 1*. The broken lines (C′ and F′) show the second running curves for the t.m.a. of samples C and F, respectively. (X) shows the broken point and (→) means the sample continues to extend

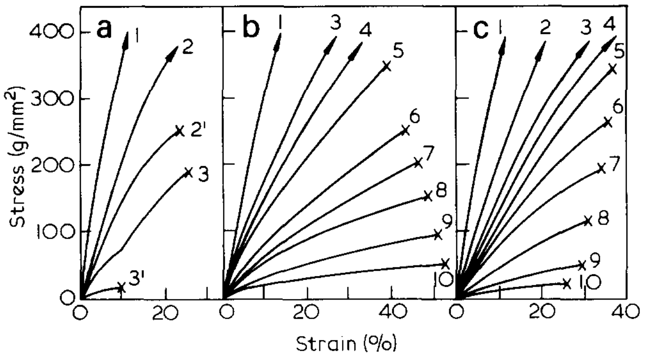

Figure 3 Stress–strain curves of typical samples (a: nylon-6,6 film, b: annealed at 195°C for 265 h, and c: crosslinked sample) obtained from t.s.a. measurements at various temperatures: 1, 220°C; 2, 230°C; (2', 235°C); 3, 240°C; (3', 242°C); 4, 250°C; 5, 260°C; 6, 285°C; 7, 300°C; 8, 315°C; 9, 330°C; 10, 345°C

however, that annealed extends to larger extent than the crosslinked sample, above the melting temperatures. Connecting these thermomechanical properties of both samples with the thermal properties (*Figure 1*), we can conclude that the difference between them is that in the crosslinked sample the crosslinkages are introduced not only in the amorphous region but also in the crystalline regions, while in the annealed sample the crosslinkages are preferentially introduced in the amorphous regions accompanied by thermal degradation, whereas the crystalline regions remain unaltered.

Young's moduli of these samples plotted against temperature are shown in *Figure 4*. The sample was repeatedly extended by a constant load to a maximum load of 20 g at each temperature until 210°C, above this temperature the maximum load was reduced to 5 g so that the residual strain could be controlled to within 2%. The moduli of these samples decreases at the glass-transition temperatures (40°–60°C). These moduli decrease once more at temperature above 150°C with the exception being that of the crosslinked sample, where the crystal form begins to transform in a reversible fasion from the triclinic to the cylindrical hexagonal form[7,8]. The moduli of the film and the crosslinked sample decrease steeply near the melting temperatures (above 220°C), and the film is broken at temperatures above 242°C, while the crosslinked sample can preserve its shape and load strength. The annealed sample begins to melt above 260°C and its modulus decreases steeply, however, it seems to level off at temperatures above 280°C. The modulus of the crosslinked sample decreases much more rapidly than the annealed sample above 320°C, because of the residual stress of the annealed sample remains when it has been hot-pressed. When the crosslinked sample was thermoset under a load of 0.5 g above 320°C, it shows a higher modulus than the annealed sample as one would expect from the second running curves of the t.m.a. shown in *Figure 2*.

Elementary analyses of the annealed and the variously treated samples are shown in *Table 1*. The N atom content largely decreases and O atom content remarkably increases as the annealing time increases, while those of H and C atoms hardly change. The hydrolysed and the crosslinked samples show a slight decrease in levels of N, C and H atoms and an increase in O atom content, reflecting the changes in chemical compositions. For comparison, the atom levels for the severely annealed sample carbonized at 350°C for 5 min (in N_2 atmosphere) are also shown. As can be seen, the levels of N, H and O atoms have greatly decreased, whilst that of the C atom have increased, reflecting the carbonization process. These results demonstrate that the annealed sample was not carbonized, but was thermal decomposing or oxidizing by degrees as the annealing conditions became severer along with the successively occurring gelation-type reactions. The studies have, with respect to thermal decomposition and gel formation in molten nylon-6,6[5,6], shown that the rate of gelation increases with the release of NH_3 (or CO_2) from polymer chains with the formation of reactive groups accompanying thermal degradation. Here, samples were merely swollen in glycerol under mild conditions, however, it was concluded that the reactive groups occurred (maybe accompanying the release of NH_3) after the milder thermal degradation, and reacted with those of the neighbouring chains to form crosslinkages.

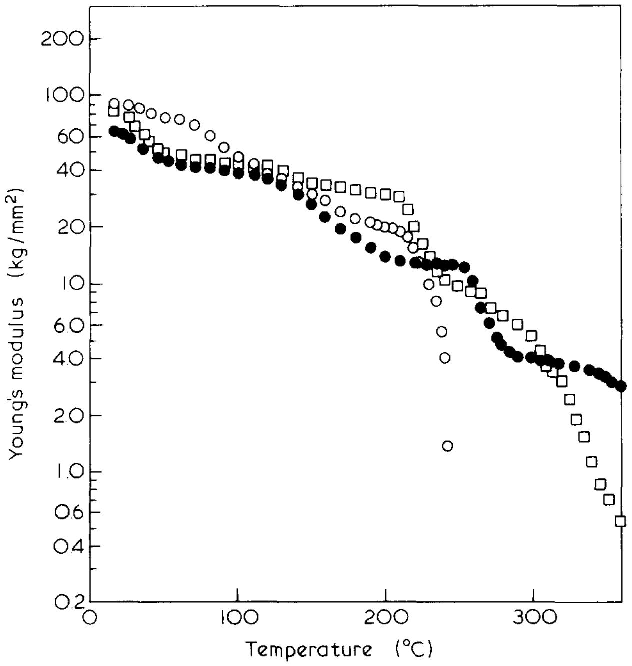

Figure 4 Young's moduli of typical samples against the temperature (obtained from t.s.a.). ○, ● and □ correspond to A, B and C in *Figure 3*, respectively

Table 1 Elementary analysis of the samples annealed at 195°C for various periods of time and various treatments

Sample	Atom content (%)			
Annealing time (h) or treated	N	C	H	O
0	12.15	62.57	9.82	15.46
24	11.98	62.53	9.67	15.82
75	11.40	62.53	9.64	16.43
265	10.78	62.01	9.48	17.73
Hydrolysed in				
HCOOH	11.53	62.50	9.54	16.43
HCl	11.52	61.42	9.55	17.51
Crosslinked	11.52	62.33	9.64	16.51
Carbonized* at				
350°C	9.66	70.06	8.97	11.31
Theoretical				
$(C_{12}H_{22}N_2O_2)_n$	12.38	63.68	9.80	14.14

* The sample annealed at 195°C for 265 h was held in the t.m.a. furnace at 350°C for 5 min to carbonize

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The use of differential scanning calorimetry to study polymer crystallization kinetics

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A Tektronix-31 programmable calculator interfaced to a Perkin Elmer differential scanning calorimeter, model 2, substantially improves the accuracy of measuring the time-dependent development of the degree of crystallinity (× 10) and hence improves the quality of the rate data. Storing energy flow data at preset time intervals directly into the memory of the calculator improves the accuracy of the measurement of time, and enables the evaluation of the onset of crystallization and the baseline of the calorimeter initially. This substantially improves the measurement of the degree of crystallinity developing with time by integrating the energy flow data over the time interval from the onset of crystallization. Polyethylene samples are studied since their rate constants have a marked temperature dependence which enables the accuracy of the analytical procedure to be assessed. Primary and secondary crystallization processes are separated.

Keywords Interface; differential scanning calorimetry; base-line corrections; microprocessor; crystallization; kinetics

INTRODUCTION

In previous publications[1,2] the use of differential scanning calorimeters (d.s.c.) to measure isothermal crystallization rate parameters has been assessed and compared with conventional dilatometry[3]. In general it was concluded that whilst the apparent temperature control of the Perkin-Elmer d.s.c., model 2, was satisfactory, i.e. ± 0.025 K, its greater sensitivity than the d.s.c.-1B was not being used to its full potential since the thermal rate-time data were displayed on a 1-10 mV recorder with a limiting response of $\sim 1\%$. Interfacing the calorimeter to a digital millivoltmeter, and hence to a microprocessor, enables this increased sensitivity to be realized.

This report considers various experimental procedures which are available with this computer interface, which assists in the analysis of isothermal crystallization rate data.

EXPERIMENTAL

Polyethylene fractions, Marlex 60, supplied by Philips Petrochemical Co. Ltd., were used. Their molecular weight characteristics are listed in *Table 1*. Dilatometry has been described elsewhere[3].

A Perkin-Elmer d.s.c., model 2, was used to study the crystallization behaviour of moulded polymer samples of 5–30 mg weighed to 0.01 mg, and sealed in aluminium pans under nitrogen. The d.s.c.-2 was interfaced to two computers—a Perkin-Elmer Scanning Autozero and through a Perkin-Elmer microvoltmeter to a Tektronix-31 programmable calculator. The output from the calorimeter was also displayed on a 10 mV Recorder.

The scanning autozero stored the calorimeter baseline without a sample, as a function of temperature, and subsequently subtracted it from subsequent determinations with samples. It substantially improved the linearity of the corrected baseline of the calorimeter over a wide temperature range.

The Tektronix-31 programmable calculator stored the corrected calculator output—digitalized by the Perkin-Elmer interface at a programmed time interval. The data was stored as a composite number of temperature and energy flow rate. Up to 400 data points could be stored for each isothermal crystallization run at preset time intervals.

Isothermal temperatures of the d.s.c.-2 were calibrated from the melting characteristics of zone-refined stearic acid, m.pt. 343.2 K, and benzoic acid, m.pt. 395.2 K, and ultra pure indium, m.pt. 429.8 K, by extrapolating to zero

Table 1 Polyethylene characteristics

Serial number	Molecular weight x10^{-3} $\bar{M}_n$	$\bar{M}_w$	D*
A	19.0	142.0	7.4
B	25.0	41.0	1.6
C	32.0	99.0	3.1
D	78.0	165.0	2.1

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