

# Evaluation of the structural behaviour of annealed nylon 6 fibres from density measurements

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Nylon 6 fibres were annealed in the temperatures range 80–185 °C for times from 1–10 h, and the density of the annealed fibres was measured by a system based on the theory of vibrating strings. The fibre diameter was also determined, using the laser forward diffraction technique. Differential thermal analysis (DTA) measurements were used to determine the glass transition temperature and the melting point of nylon 6. Some annealed samples were subjected to X-ray diffraction to clarify the variation of crystallinity with the annealing conditions. The mechanism of structural variations for nylon 6 fibres due to the annealing process is discussed, and structural details for crystalline and non-crystalline phases of a polymer are suggested. The behaviour of the number of oriented chains, number of crystallized nuclei, relative amount of recrystallized material and the shrinkage ratio with annealing time is proposed to explain the thermal structural variations.

## 1. Introduction

Recently, polymers have been considered commercially, as one of the most fundamental materials. The technical importance of polymers is based on the ability to produce polymers with different characteristics, such as steel hardness, sponge softness, glass transparency, etc. The main polymer feature, for these widely different products, is its flexible structure, which can be controlled either by chemical construction or by technical processing. Thus, the most important parameters with which to characterize an anisotropic property of an oriented, polycrystalline polymer are the fraction of each phase present, the intrinsic property of each phase and the orientation function of each phase. In general, the fraction of each phase present in the polymer is determined by density or X-ray diffraction measurements [1].

For density determination of the fraction of each phase present, the density of the crystalline and amorphous phases must be known individually. While the density of the crystalline phase can be determined using X-ray data, the evaluation of the density of the amorphous phase is sometimes a very formidable task. This is because only a relatively small number of crystalline polymers can be produced in the amorphous state. For many crystalline polymers the determination of amorphous phase density is carried out by extrapolation of the temperature dependence of the density of the melt to room temperature [2]. The density of the polymer sample may be determined by any of a number of standard experimental methods, including pycnometry, hydrostatic weighing and the use of a density gradient tube [3].

The most available technique for changing the polymeric structure is the annealing process [4–7]. The

effects of annealing increase drastically with temperature, but also depend on the time the sample is held at the annealing temperature. To understand annealing effects, their molecular source must be known [8, 9].

In this work, the mechanism of changes in the molecular structure of nylon 6 fibres, due to annealing, is discussed, based on density measurements carried out for nylon 6 fibres annealed at different temperatures for different times. The suggested structural behaviour is supported by the X-ray diffraction data.

## 2. Experimental procedure

### 2.1. Annealing of samples

Long bundles of nylon 6 fibres were loosely folded in a cocoon form with free ends. Several samples were distributed in small glass bottles, and then left in an electric oven and heated at a constant temperature ranging from 80–185 ± 1 °C for different annealing times ranging from 1–10 h. The samples were then left to cool at room temperature, 28 °C. Thus for each annealing temperature, there was a set of ten samples annealed at different times.

### 2.2. Differential thermal analysis (DTA) measurements

The greatest number of applications of DTA in recent years has been in the area of polymeric materials. This technique is routinely used to measure glass transition temperatures,  $T_g$ , melting points,  $T_m$ , and numerous other parameters. Several DTA instruments were developed mainly for use in polymer measurements. In

the present work, a Shimadzo thermal analyser model DT-30B was used.

### 2.3. X-ray diffraction

The X-ray diffraction technique was used in this work to examine the crystallinity and the crystalline structure of the crystalline phase in the annealed samples. X-ray diffraction examinations were done with a Shimadzo X-ray diffraction DX 30 with conventional  $\text{CuK}_\alpha$  (0.1542 nm), at 45 kV and 35 mA. The scan-speed was adjusted at  $5 \text{ deg min}^{-1}$ .

### 2.4. Density measurements

For the measurement of fibre density, a special measuring system was constructed. The apparatus for this system was based on the concept of vibrating strings. It is well known that when a string is stretched by a tensional force,  $T$ , and put in contact with a vibrator which vibrates at right angles to the axis of the string, a definite length,  $l$ , of the string will vibrate stationary as the resonance condition between frequencies of vibrator and string is achieved. Let  $f_0$  be the resonance frequency, then

$$f_0 = (p/2l) (T/m)^{1/2} \quad (1)$$

where  $p$  is the number of resonance modes within the string's length,  $l$  ( $p = 1$  for the fundamental mode) and  $m$  is the mass per unit length of the string [10]. The sample was clamped at one end while the other end (connected to small scale pan) passed over a small frictionless pulley, Fig. 1. The clamp, C, and pulley, W, were fixed to an optical bench, B. An electromagnetic pulse transmitter (vibrator), T, as well as a piezocrystal transducer, R (receiver) were also fixed tightly to B. The sample, S, was tightened by mass,  $M$ , and left in contact with T and R. The vibrator, T, was stimulated by sinusoidal electric pulses from the adjustable frequency pulse generator, G. Pulses from G were also supplied to the frequency counter, FC, to be counted, and to the first channel, CH1, of the double-beam cathode ray oscilloscope, CRO, to be taken as the reference wave. The frequency of the vibrator, T, was increased, from zero, up to the resonance frequency,  $f_0$ , at which points on the sample (from T to R) were vibrated with the same frequency,  $f_0$ . Thus R receives pulses with a maximum amplitude. Pulses from R were magnified using a low-noise pre-amplifier

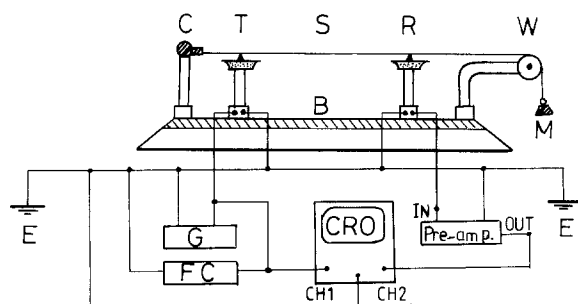


Figure 1 Schematic diagram for the constructed density measuring system.

whose output signals were supplied to the second channel, CH2, of the CRO. The received wave, on CH2, thus possesses maximum amplitude only at resonant modes of the sample (odd modes were observed out-of-phase, while even modes were observed in-phase with the reference wave) when the vibrator's frequency was increased.

Using such a system allows the determination of the fundamental resonance frequency,  $f_0$ , of a certain length,  $l$ , of the sample ( $l$  is the distance between T and R) when it is loaded by a mass,  $M$  (g). Then the mass per unit length,  $m$ , of the sample under test could be calculated from Equation 1. An accurate value of  $m$  could be obtained as an average over several modes of resonance.

From the obtained value of  $m$ , the density,  $\rho$ , of the sample material can be easily calculated. If the sample is taken as a bundle of  $N$  individual fibres per bundle,

$$\rho = gM/4\pi Nl^2 r^2 f_0^2 \quad (2)$$

where  $g$  is the acceleration due to gravity, and  $r$  is the radius of an individual fibre.

### 2.5. Measurement of the fibre diameter

In this work, the fibre diameter,  $d$ , was measured by the technique of laser beam forward diffraction [11–13]. In this technique the following formula was considered

$$d = \pm \lambda L/x \quad (3)$$

where  $\lambda = 632.8 \text{ nm}$ , the wavelength of the He–Ne laser used,  $x$  is the distance from the centre of the obtained diffraction pattern to the first minimum, and  $L$  is the distance between the fibre and screen on which the pattern was produced. Each sample was examined at several positions and the average value was considered.

## 3. Results and discussion

The DTA measurement of unannealed nylon 6 fibres showed that the glass temperature,  $T_g$ , of nylon fibres is  $47^\circ\text{C}$ , while the melting point  $T_m$  is  $210^\circ\text{C}$ . Therefore, the range of annealing temperatures was selected from  $80\text{--}185^\circ\text{C}$  in order to avoid any phase transition during the isothermal annealing process, and to keep samples in their fibrous form throughout the whole measurements.

The measurements of fibre diameter showed no observable changes, after annealing at different temperatures.

The colour of the nylon 6 fibres was visually observed to change from light yellow to dark brown with increasing annealing temperature and annealing time, although, as the annealing temperature and time were increased, the fibres became more brittle; for these reasons it was impossible to measure the density of samples annealed at  $185^\circ\text{C}$  for periods longer than 6 h, due to the partial production of ash on the samples.

Fig. 2a–g show the density variations of seven sets of nylon 6 fibres with annealing times from 1–10 h.

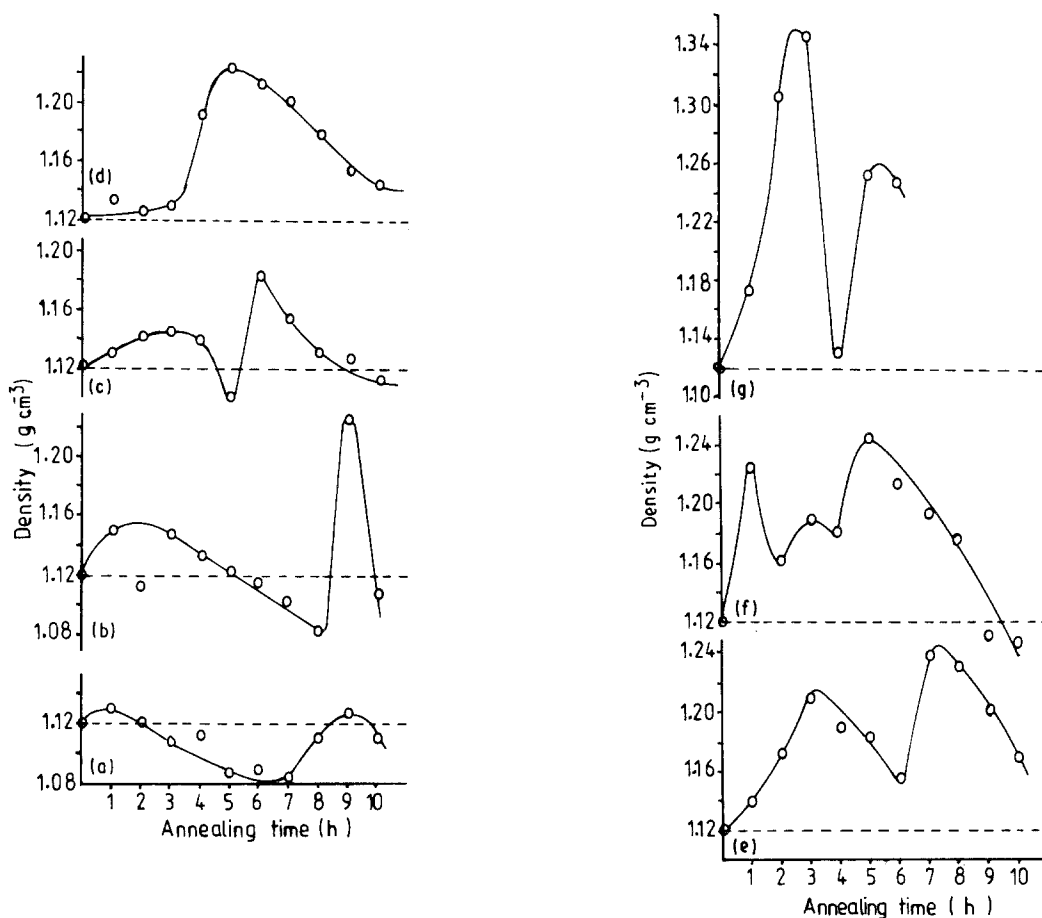


Figure 2 Density variations of nylon 6 fibres isothermally annealed at (a) 80 °C, (b) 100 °C, (c) 120 °C, (d) 140 °C, (e) 160 °C, (f) 170 °C and (g) 185 °C.

Each set was annealed at a selected temperature: (a) 80 °C, (b) 100 °C, (c) 120 °C, (d) 140 °C, (e) 160 °C, (f) 170 °C, and (g) at 185 °C. The interpretation of physical variations associated with isothermal annealing of metals was, in general, fulfilled, but the interpretation of similar variations is somewhat problematical when a polymer undergoes isothermal annealing. These difficulties are due to the anisotropic features of the polymer.

Most studies, which involve variations of physical properties, considered polymers as an anisotropic polycrystalline medium, i.e. consisting of crystalline regions suspended in an amorphous medium which is partially oriented. Thus the polymeric molecular chains were classified into only three structural classes: crystalline, oriented amorphous and disordered amorphous structures. These three structural classes are insufficient, from our point of view, to explain the results obtained, Fig. 2. We suggest further sub-classifications for the interphase distribution of polymer molecular chains and the proposed classification is shown schematically in Fig. 3.

In order to explain the widely different variations shown in Fig. 2a–g, it was essential to take the following assumptions into account.

1. All thermally structural variations may be considered irreversible, at temperatures higher than the glass transition temperature.
2. The most compact non-crystalline structure is not essentially the ordered structure or, in other

words, the oriented macromolecular structure may not be the most compact non-crystalline structure.

When a polymer is annealed, its structural behaviour is due to accumulation of several structural processes. These processes may be summarized as: (a) disorientation, (b) recrystallization by nucleation, (c) recrystallization by growth, (d) shrinkage, and (e) crystal decomposition. They are natural responses for both annealing temperature and time [1, 8, 14–16]. To give an acceptable explanation for all variations in Fig. 2, we have to estimate, individually, the weight of each structural process during an isothermal annealing treatment at different temperatures.

### 3.1. Disorientation

The amount of disorientation of the non-crystalline chains depends on the annealing temperature and time. The greater the annealing temperature for a given time in a given medium, the greater would be the expected disorientation [1]. Therefore, one may deduce that the disorientation process is a consequence of the thermal energy transferred to the medium. Thus, it is expected that the degree of disorientation may be directly proportional to the amount of energy given to the polymer. Because the thermal energy gained is the resultant of temperature and time of heating, a certain degree of disorientation at a given temperature and time can be again observed at higher temperature but shorter time. Also, because a given

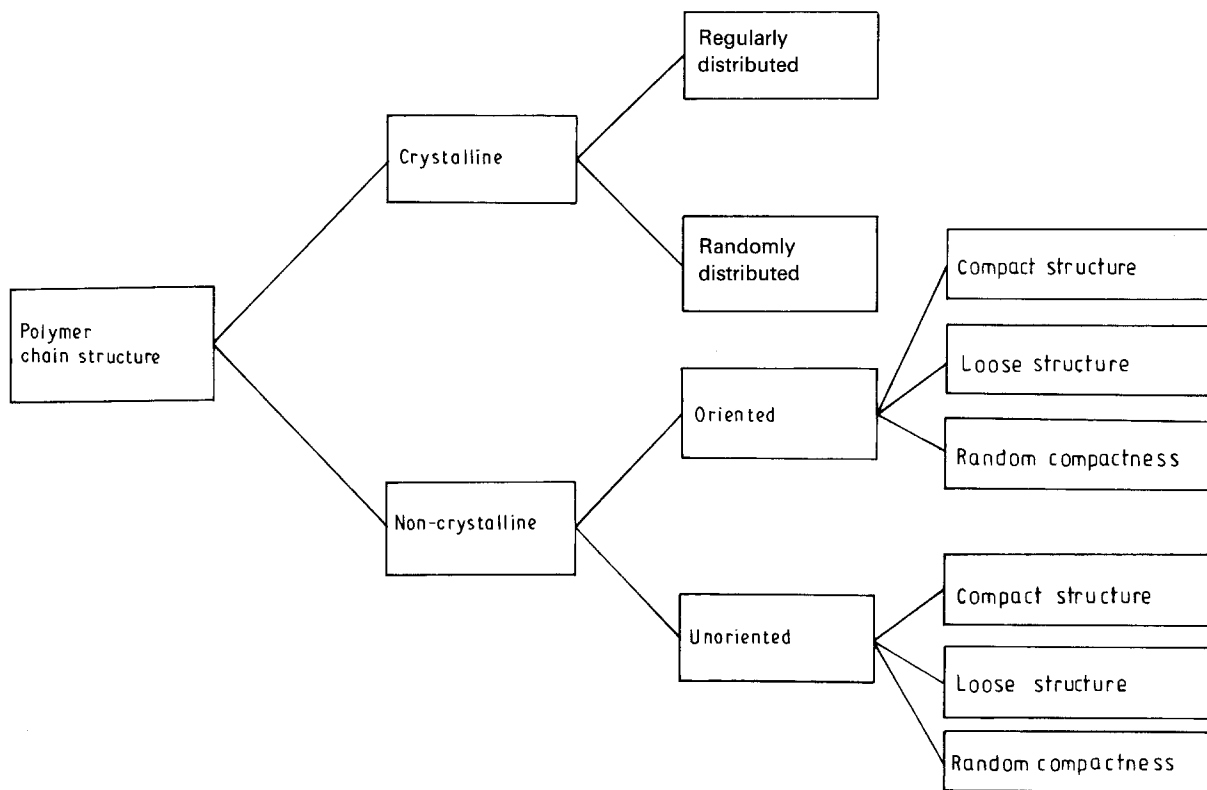


Figure 3 Schematic representation of the suggested details of the polymer macromolecular chain structures.

polymer sample contains a finite number of ordered chains, the disorientation process should end after a certain energy value which depends on the initial orientation, as well as the nature of the medium. Therefore, we suggest Fig. 4a to show the change of disorientation process during the isothermal annealing treatment.

In order to estimate the density variations associated with the disorientation process, the suggested details of the oriented polymer phase in Fig. 3 should be considered. The density response to the disorientation depends on the initial compactness of the oriented chains. It may be considered that the given mobilizing thermal energy causes chains to displace as well as to rotate about some axis perpendicular to the chain backbone at a point which may be taken as the chain's centre of mass. So, if the initial oriented structure was compact, it will disorient to a loose structure and hence, the density decreases. Because the disorien-

tation process is limited by the number of ordered chains present, the decrease in density should show a stability after a certain annealing time, depending on the annealing temperature, Fig. 4b. The density may not show any variation when the initial orientation and the final disoriented structures were of random compactness.

### 3.2. Recrystallization by nucleation

As the time of isothermal annealing increases, the rate of nucleation first increases and then decreases [16]. This means that the number of thermally produced nuclei is rapidly increased up to a fixed value after a certain given thermal energy. This fixed value depends on the initial structure of the non-crystalline part as well as on the annealing temperature. Therefore, the authors suggested that Fig. 5a represents the

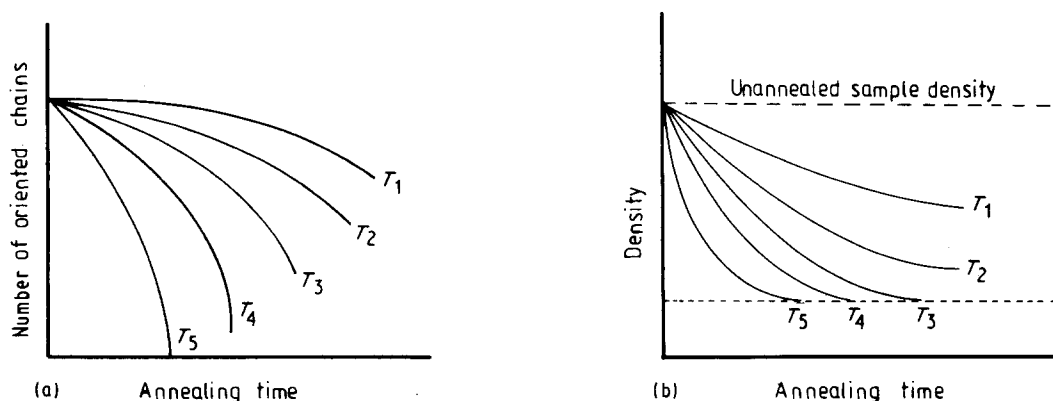


Figure 4 Diagrammatic representation of the deduced behaviour of (a) the number of oriented chains, and (b) the density of a polymeric medium undergoing thermal disorientation at different temperatures ( $T_1 < T_2 \dots < T_5$ ).

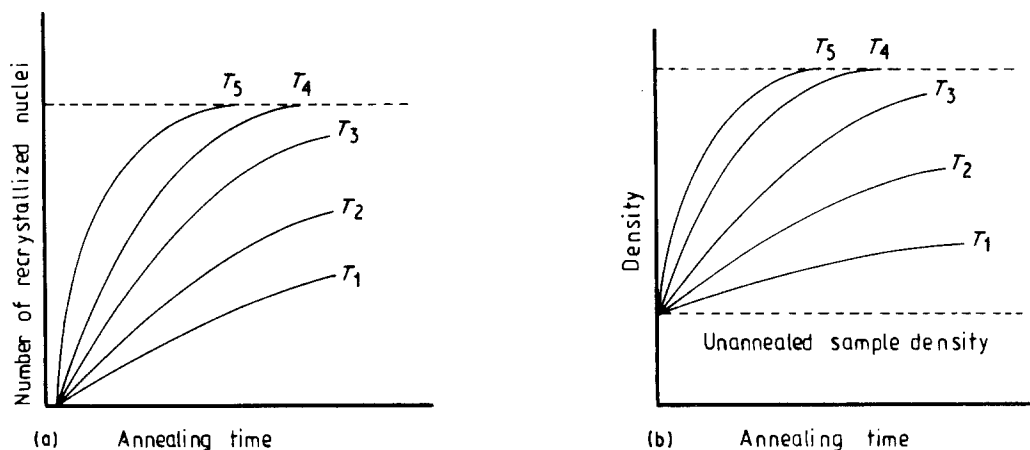


Figure 5 Diagrammatic representation of the deduced behaviour of (a) the recrystallized nuclei and (b) the density of a polymeric medium undergoing thermal recrystallization by the nucleation process at different temperatures ( $T_1 < T_2 < \dots < T_5$ ).

number of nuclei as a function of annealing time at different annealing temperatures.

The density variations due to the nucleation process are expected as in Fig. 5b, where the density of nuclei was considered higher than both oriented and un-oriented non-crystalline phases.

### 3.3. Recrystallization by growth of nuclei

A number of relationships were proposed to describe the kinetics of isothermal recrystallization. The most generalized of them was that proposed by Avrami [16]

$$X = 1 - \exp(-Bt^k) \quad (4)$$

where  $X$  is the relative amount of recrystallized material,  $B$  and  $k$  are the coefficients depending, respectively, on the temperature and the nature of nucleation as well as on the growth of nuclei, and  $t$  is the annealing time. For a one-dimensional process (as fibres),  $1 \leq k \leq 2$ . On the other hand, the growth of recrystallized nuclei is a thermally activated process. For a given time, the effect of temperature on the process is described by the Arrhenius equation

$$G = G_0 \exp(-Q_g/RT) \quad (5)$$

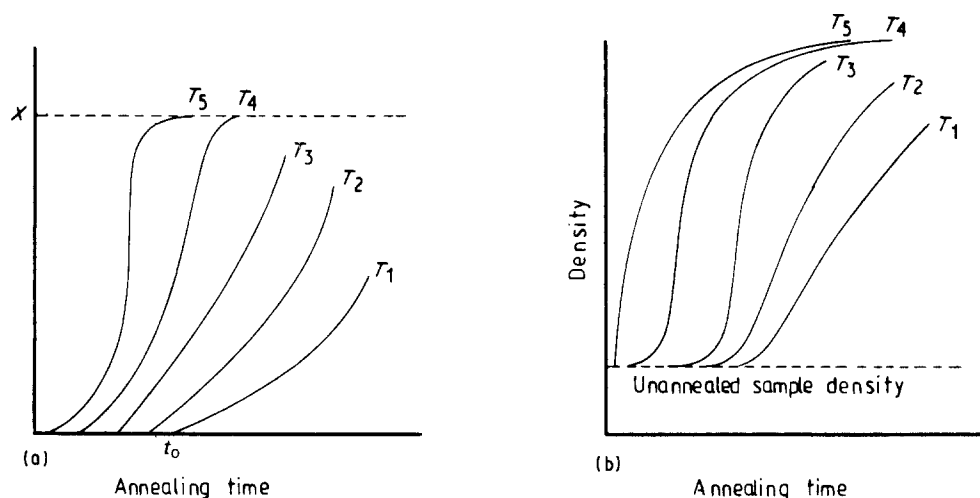


Figure 6 Diagrammatic representation of the deduced behaviour of (a) the recrystallized volume and (b) the density of a polymeric medium undergoing thermal recrystallization by the growth of nuclei at different temperatures ( $T_1 < T_2 < \dots < T_5$ ).

where  $G$  is the rate of crystal growth and  $Q_g$  is the effective activation energy of growth.

The expression is strictly valid only in temperature ranges where  $Q_g$  and the pre-exponential factor,  $G_0$ , are constants. However, because  $Q_g$  decreases with increasing temperature, this also increases growth rate.

Therefore, from the time and temperature dependence of the recrystallized volume by growth, given in Equations 4 and 5, one may expect the change of  $X$ , during an isothermal annealing process and at different temperatures, to be as shown in Fig. 6a. Then the density response for the recrystallization by growth can be estimated as in Fig. 6b, where new nuclei appear and grow after a definite incubation period,  $t_0$ , which is shorter at higher annealing temperatures.

### 3.4. Shrinkage

Because shrinkage means a volume contraction, and due to the conservation of mass, an increase in the medium density is expected to be associated with the shrinkage process.

Studies carried out by Samuels [1], showed that the ratio of shrinkage is related to the disorientation occurring during thermal annealing. He found also that

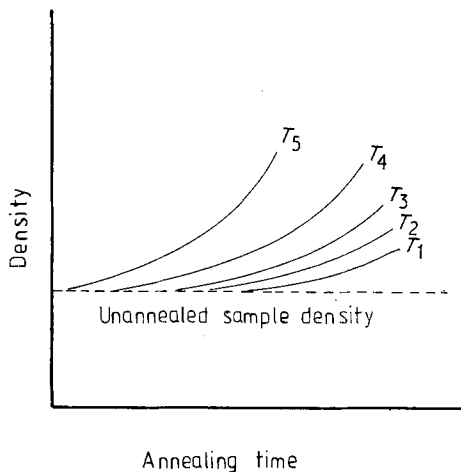


Figure 7 The expected behaviour of polymer density due to shrinkage associated with isothermal annealing at different temperatures ( $T_1 < T_2 < \dots < T_5$ ).

the shrinkage ratio increases as the annealing temperature increases. Hence, it is estimated that on shrinkage, the ordered structure is destroyed into a compact disordered structure.

Fig. 7 shows the deduced density response due to the shrinkage process.

### 3.5. Crystal decomposition

Fig. 8 shows the observed decrystallization of nylon 6 fibres when annealed for 6 h at different temperatures, where the X-ray diffraction intensity was reduced as the annealing temperature increased for the same period. Fig. 9 shows the X-ray diffraction intensity of nylon 6 fibres annealed at 140 °C for different annealing periods. It is clear from Fig. 9 that increasing annealing time also causes crystal decomposition

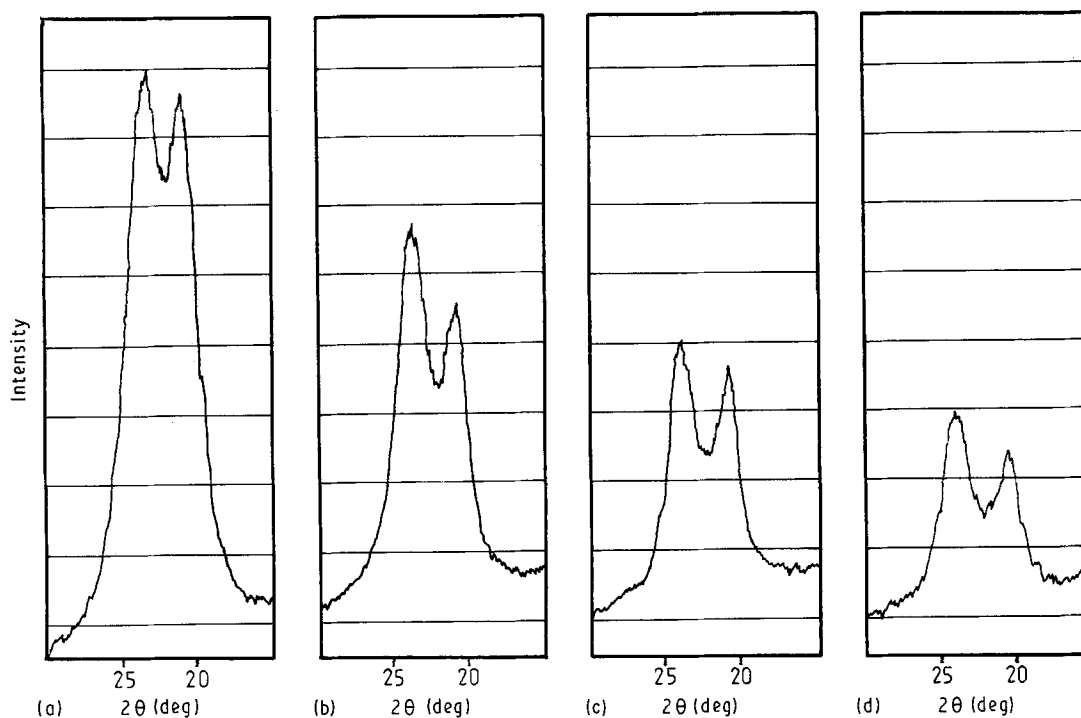


Figure 8 X-ray diffraction patterns of nylon 6 fibres annealed for 6 h at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 170 °C.

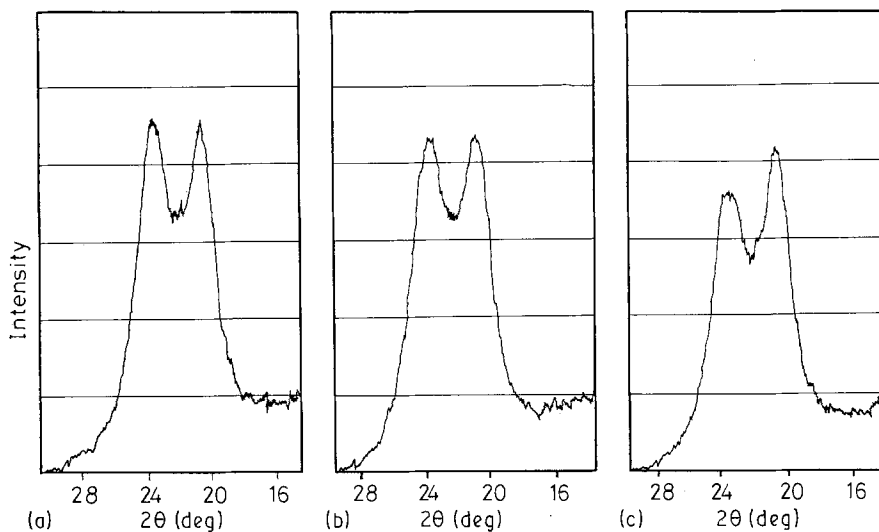


Figure 9 X-ray diffraction patterns of nylon 6 fibres annealed at 140 °C for (a) 6 h, (b) 8 h and (c) 10 h.

which is associated with a decrease in the density of the medium, where the density of the crystalline portion,  $\rho_c$ , was considered to be the highest density in the polymer.

The reduction in the X-ray diffraction intensity,  $I$ , does not essentially mean a decrease in crystallinity, because  $I^{1/2} \approx \rho_c - \rho_{am}$ , where  $\rho_{am}$  is the density of the amorphous region [17]. Thus  $I$  may be reduced due to an increase in  $\rho_{am}$  by annealing. In most polymers,  $\rho_c$  is higher than  $\rho_{am}$  by about 10%, but in the present data (Fig. 8) it is clear that  $I$  is reduced by a much higher percentage, which ensures the occurrence of crystal decomposition by annealing at high temperatures.

From the previous review of the most of the structural processes associated with the isothermal annealing treatment, it is clear that two processes (disorientation and crystal decomposition) cause a fall in the density of a polymer medium, while the other three structural processes cause an increase in the density. Thus, the complex variations in density of nylon 6 polymer when isothermally annealed (Fig. 2a–g), could be explained on the basis of a combination of the structural processes previously discussed. For example, in Fig. 2e, the fast increase in nylon 6 density with annealing time in the range  $0 < t < 3$  h is due to the recrystallization by nucleation and the growth of nuclei with a weight much greater than the density fall due to disorientation of the non-crystalline portion which occurred simultaneously in that annealing range. The peak point at  $t = 3$  h represents the maximum crystallinity of nylon 6 when annealed at  $160^\circ\text{C}$ . The fall in density in the time interval  $3 \text{ h} \leq t \leq 6 \text{ h}$  is due to the decomposition of some crystals while most of oriented non-crystalline part was disordered. It is clear that the point at  $t = 6$  h did not reach the density of unannealed sample due to the effect of shrinkage, which may cause a remarkable increase in the density after 6 h annealing at  $160^\circ\text{C}$ . The second increase in density within the interval  $6 \text{ h} \leq t \leq 7.5 \text{ h}$  may be due to the end of the disorientation process while the shrinkage process produces a greater effect. The second peak at  $t = 7.5$  h is due to the most compact unoriented chain structure but, of course, not to higher crystallinity. Fig. 10a and b show that the amount of crystal at the second peak ( $t \approx 7$  h) is lower than that at the first peak ( $t = 3$  h). The fall in density during annealing for longer than 7.5 h is due to crystal decomposition, which is the most dominant structural process at high temperatures and long annealing times.

This explanation of Fig. 2e can be applied to the other components of Fig. 2. The behaviour of nylon 6 density, which still needs additional explanation, was represented by points lower than the density of the unannealed sample. If these points were produced at low annealing temperatures, they would indicate that the disorientation structural process is the predominant process at their positions, while, at high temperatures, these lower density points would mean decomposition of most crystals, including those initially present in the samples during the fabrication process.

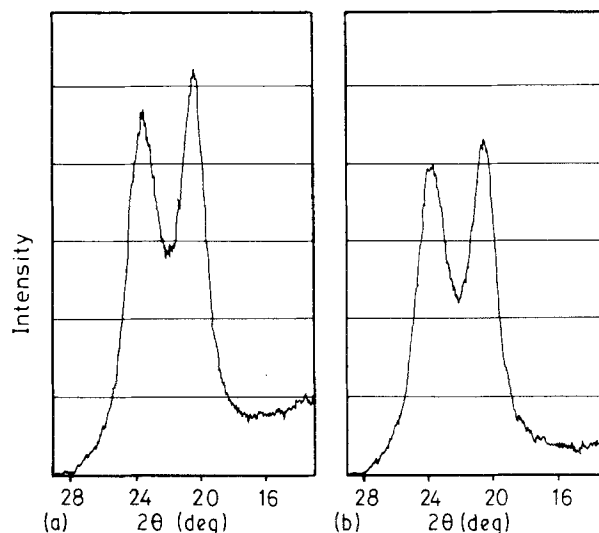


Figure 10 X-ray diffraction patterns for nylon 6 samples annealed at  $160^\circ\text{C}$  for (a) 3 h and (b) 7 h.

#### 4. Conclusions

1. The constructed density measuring system (as a resonance technique) is an accurate (expected error is below  $\pm 1\%$ ), easy, quick and non-destructive technique. Moreover, this technique can equally well be used to measure the mass per unit length of any yarns or textile long ribbons.

2. The fine-density measuring system, used in this work, is recommended as a non-destructive technique for the determination of the linear density of individual fibre specimens. Although not very suitable for measurements on, for example, cotton fibres because of the within-specimen variability, it has been used, extensively, in work on man-made fibres.

3. The macromolecular structure of nylon 6 fibres is strongly affected by the isothermal annealing treatment.

4. The density of nylon 6 depends, critically, on the annealing conditions.

5. The suggested details of polymeric chain distributions (Fig. 3), are sufficient for interpretation of the thermal, or mechanical structural variations.

6. From the X-rays diffraction measurements, it was found that the type of crystal in nylon 6 was not affected by the annealing conditions used.

7. The annealing process affects other physical properties (electrical, mechanical, colour, optical, . . . etc.). Further studies can be carried out in order to detect which properties are improved by annealing.

We conclude that the density measurement offers valuable information on the structure and structure variations of a polymer when it is subjected to external energy. The non-destructive feature of the presented density measuring technique is promising. The density measurement is an important parameter not only as a quality test for the final polymeric products, but also as an estimation base for the polymer's variations due to the applied physical and chemical effects.

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