JOURNAL OF MATERIALS SCIENCE 10 (1975) 1127–1136

The effect of polymerization conditions and crystallinity on the mechanical properties and fracture of spherulitic nylon 6

T. J. BESSELL, D. HULL, J. B. SHORTALL
Department of Metallurgy and Materials Science, University of Liverpool, UK

The molecular and structural parameters controlling the mechanical properties, deformation and fracture of spherulitic nylon 6 have been investigated. The nylon was prepared by the anionic polymerization of ϵ-caprolactam and the polymerization conditions were varied to give samples having a range of spherulite diameter, molecular weight and degree of crystallinity. The tensile properties and fracture mode of the nylon varied considerably with degree of crystallinity and polymerization temperature. High crystallinity and low polymerization temperatures below 423 K gave a brittle material. Polymerization above 423 K resulted in a ductile material which showed a yield drop. In this material final fracture was preceded by the formation of inter and trans spherulitic cracks which coalesced to form a large cavity that led to final failure. In nylon having a low degree of crystallinity, fracture was fibrillar in nature and occurred by the ductile drawing of the material to strains greater than 250%.

1. Introduction

The mechanical behaviour of spherulitic semi-crystalline polymers [1, 2] depends on many morphological factors including molecular weight and its distribution, degree of crystallinity, size and type of individual crystalline units and the diameter of the spherulites. In nylon polymers and polypropylene it has been shown [3-5] that there is a marked increase in yield stress and shear modulus with specific gravity and crystallinity. Increasing the spherulite size results in a reduction in yield stress and toughness. However, recent work has cast some doubt on whether or not these changes are attributable to the spherulite diameter alone, since lamellar size [6], intercrystalline links [7] and density of tie molecules [8, 9] also change with the crystallization treatments which are required to produce a range of spherulite sizes.

The morphological parameters also affect the deformation mode and fracture of spherulitic structures. It has been shown that deformation is heterogeneous and depends on the orientation of the crystalline lamellae with respect to the tensile axis [10]. Different modes of deformation have been observed in various zones of the spherulite [10-12]. Samuels [10] considers that the deformation can be divided into three zones within the spherulite. In the radial fibril zone, in which the radius and draw direction are parallel or nearly parallel, the deformation is explained in terms of the extension of the crystal lamellae. Deformation in the equatorial region, in which the tensile axis and radius are perpendicular, is considered to be by separation of the lamellae by extension of the inter lamellar material. Molecular tilting and lamellar slip occur in the intermediate regions, in which the crystals are oriented at some angle to the draw direction. The inhomogeneity of the deformation within the spherulite has been studied in some detail for polyethylene [11, 13] and polyoxymethylene [2, 12]. These observations confirm that different modes of deformation operate in different sectors of the spherulite.

Microscopic examination of polypropylene [14, 15] has shown the presence of arcs or chevrons perpendicular to the tensile axis in the zone of the spherulite [6] in which the radius and tensile axis are parallel. These arcs are observed to extend over an angle of approximately 15° on either side of the draw direction. The nature of these arcs is not fully understood although they have the characteristic appearance of crack- or craze-like features. Presumably they result from the inability of the lamellae to undergo the plastic strains imposed upon them. Since these features do not extend beyond an angle of about 15° to the draw direction it is concluded [14, 15] that molecular tilting and lamellar slip occur at angles greater than 15° allowing the material to undergo larger plastic strains.

The purpose of this present work is to examine the effect of morphological changes and structural variables on the mechanical deformation behaviour of bulk spherulitic nylon 6, with particular emphasis on the effect of polymerization and crystallization variables on the mechanical properties and cavitation type failure in the polymer.

2. Experimental details: sample preparation

The anionic polymerization of ϵ-caprolactam was carried out using sodium hydride as catalyst and acetyl caprolactam as initiator and has been described fully elsewhere [16, 17]. After stirring to disperse the initiator, the solution of molten monomer, catalyst and initiator was cast into a glass sided mould in an oven at the required polymerization temperature. Polymerization and solidification were allowed to take place in the oven in an atmosphere of dry nitrogen. A range of polymerization temperatures from 393 to 473 K, and a series of crystallization treatments, were used. The mould gave a sheet sample 4.5 mm thick from which tensile specimens were cut. These specimens were polished on successively finer grades of emery paper and given a final polish using 0.3 µm alumina powder. The fracture strength determinations and fracture surface studies were made using curved neck specimens having a neck radius of approximately 50 mm. The elastic modulus was determined using parallel sided specimens having a gauge length of 20 mm. Because of the very significant effect that absorbed water has on the mechanical properties of polyamides water pickup was kept to a minimum. The specimens were stored under vacuum at all times prior to testing and were only removed for surface preparation. All polishing operations were performed dry. Tensile tests were performed at room temperature on an Instron testing machine using a cross-head speed of 2 mm min^{-1}.

The degree of crystallinity of the nylon samples was determined from the specific gravity using the following equation [18].

$$\frac{V_c}{V} = \frac{\rho - \rho_a}{\rho_c - \rho_a}$$

where ρ, ρ_a and ρ_c are the densities of the sample, amorphous polymer and crystalline polymer respectively. The values of ρ_a and ρ_c were taken as 1.10 and 1.23 respectively [19].

The specific gravities were measured using a density column with an aqueous solution of calcium chloride. The measurements were carried out at 298 K and the results had an accuracy of ± 0.001.

The molecular weight and molecular weight distribution were measured using gel permeation chromatography with *o*-chlorophenol as solvent at a temperature of 363 K.

The spherulitic size was measured from optical micrographs of ultramicrotomed thin sections and etched bulk specimens. The diameters of spherulites were determined individually by measuring the length of a line through the spherulite nucleus and the adjoining boundary. No measurements were taken from spherulites in which a distinct central nucleus was not apparent so as to avoid measuring the size of sections through spherulites. Approximately one hundred measurements were taken from each sample and from these the mean and standard deviation were calculated, assuming a normal distribution.

3. Results and discussion

3.1. Effect of polymerization conditions

The variation in some physical properties of nylon 6 as a function of polymerization conditions is presented in Table I. The samples were allowed to crystallize isothermally for 1 h at the polymerization temperature. With the exception of the material polymerized at 473 K, the crystallization treatments resulted in specific gravity values of about 1.155 and degrees of crystallinity of 0.4. The mean spherulite diameter increased approximately linearly with increasing polymerization temperature. The molecular weight is dependent on the catalyst and initiator concentrations [17]. At low polymerization temperatures, these concentrations were increased to maintain a high conversion rate of monomer thus raising the number of lactam anions available for polymerization and thereby decreasing the molecular weight. At high polymerization temperatures, the catalyst and initiator concentration was decreased, and this resulted in an increased molecular weight as shown in Table I.

The variation in polymerization conditions resulted in significant differences in the mechani-

TABLE I The effect of anionic polymerization conditions on the physical properties of nylon 6

Polymerization and crystallization temperature (K)	Catalyst and initiator concentrations (molar. prop.)	Specific gravity	Degree of crystallinity	Spherulite Diameter,		Molecular weight	
				mean (μm)	standard deviation (μm)	$MN \times 10^3$	MW/MN
393	0.02	1.152	0.402	14	6	9.5	2.3
413	0.0125	1.153	0.407	24	8	7.7	1.8
423	0.01	1.154	0.416	36	6	14.9	2.0
433	0.0075	1.155	0.420	46	12	23.4	2.4
453	0.005	1.155	0.421	63	12	39.1	2.3
473	0.005	1.144	0.336	78	14	26.2	2.4

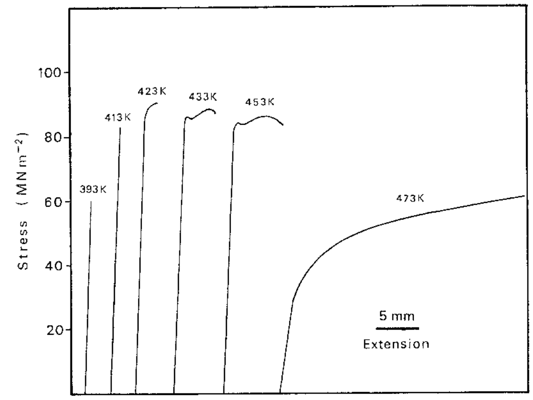

Figure 1 The stress-extension curves of nylon 6 polymerized between 393 and 473 K.

cal properties of the nylon. Fig. 1 shows the variation in stress-extension behaviour of the polymer when tested in tension. At the lower polymerization temperatures brittle behaviour is observed with no yield point, but as the polymerization temperature is increased the material becomes more ductile and a well-defined yield point is observed after polymerization at 433 K. When polymerized at 473 K the polymer extends approximately 300%. The elastic modulus and the yield and fracture stresses are shown as a function of polymerization temperature in Fig. 2. The modulus and yield stress are fairly constant between 413 and 453 K but as the polymerization temperature is raised the true fracture stress and toughness increases.

Previous work on nylon 66 [3] and polypropylene [5] has shown that toughness and impact resistance are reduced as the spherulite diameter is increased. This is attributed to weakening of the inter-spherulite boundaries resulting from a reduction in the density of tie molecules and diffusion of low molecular weight material to the boundary region during crystallization [7-9]. However, the results presented here show that samples having the larger spherulite diameter, produced by higher polymerization temperatures, were tougher than those having small spherulites. Therefore, it seems unlikely that the observed increase in toughness is due to variations in spherulite size alone, and that higher polymerization temperatures do not weaken the spherulite boundaries.

The changes in ductility are more likely to be due to the effect of polymerization temperature on the molecular weight and degree of crystallinity. For polymerization temperatures between 393 and 453 K there is little change in crystallinity but a significant increase in M_N from 9.5 to 39.1×10^3. Thus, the increase in ductility in this range can be attributed to an increase in M_N. Polymerization at 473 K produces a marked decrease in crystallinity with only a small change in M_N indicating that the large increase in ductility between 453 and 473 K is due to this factor. The small variation in yield stress between 413 and 453 K is in agreement with the results for polypropylene samples [6] which had differing spherulite size but similar crystallinity and lamellar thickness.

3.2. Effect of degree of crystallinity

Samples polymerized at 453 K were subjected to varying crystallization and annealing treatments to give specimens having a range of crystallinity from 0.20 to 0.45. The samples had a mean spherulite diameter of approximately 60 μm and a number average molecular weight of about 35×10^3 with a molecular weight distribution M_W/M_N of 2. The stress-extension behaviour of these samples is presented in Fig. 3 which shows that at high degrees of crystallinity (0.44) the polymer is brittle. At intermediate crystallinities (0.42 to 0.37) the stress extension behaviour is characterized by a yield drop, with extensions to failure of the order of 50 to 80%.

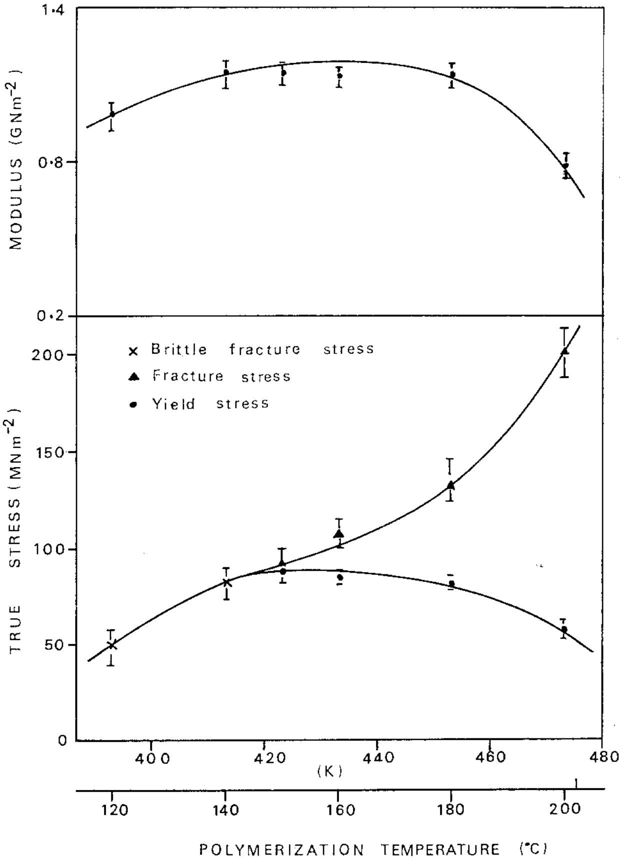

Figure 2 Dependence of elastic modulus, yield and fracture stress on the polymerization temperature of nylon 6.

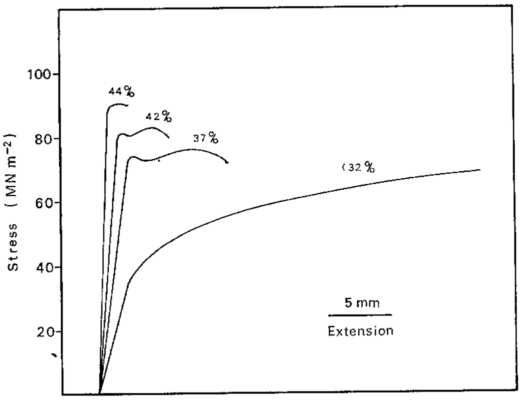

Figure 3 Stress-extension behaviour as a function of crystallinity for nylon 6 polymerized at 453 K.

At low crystallinity, the polymer shows no yield drop and large extensions to failure.

The area under the load-extension curve is a measure of the energy required to fracture the specimen and in this investigation this quantity (expressed in arbitrary units) has been taken as the toughness of the material. The elastic modulus, yield and fracture stresses and toughness are shown as a function of specific gravity and crystallinity in Fig. 4. There is a marked change in slope of the stress and toughness curve at about 33% crystallinity without any corresponding change in the tensile modulus. This indicates that the crystalline material has an effect on the initial elastic response to applied stress throughout the range of crystallinities investigated. However, below 33% crystallinity the yield stress and toughness are insensititive to the amount of crystallinity which suggests that in this range the yield strength of the nylon is controlled by the flow of amorphous material. The yield stress in this range is about 40 MN m^{-2}.

The importance of crystallinity in controlling the yield stress of anionic nylon is also shown in Fig. 5 which gives the dependence of yield stress on specific gravity for samples having varying polymerization temperatures, molecular weights and spherulite diameters. Although the yield stress of crystalline polymers may be considered

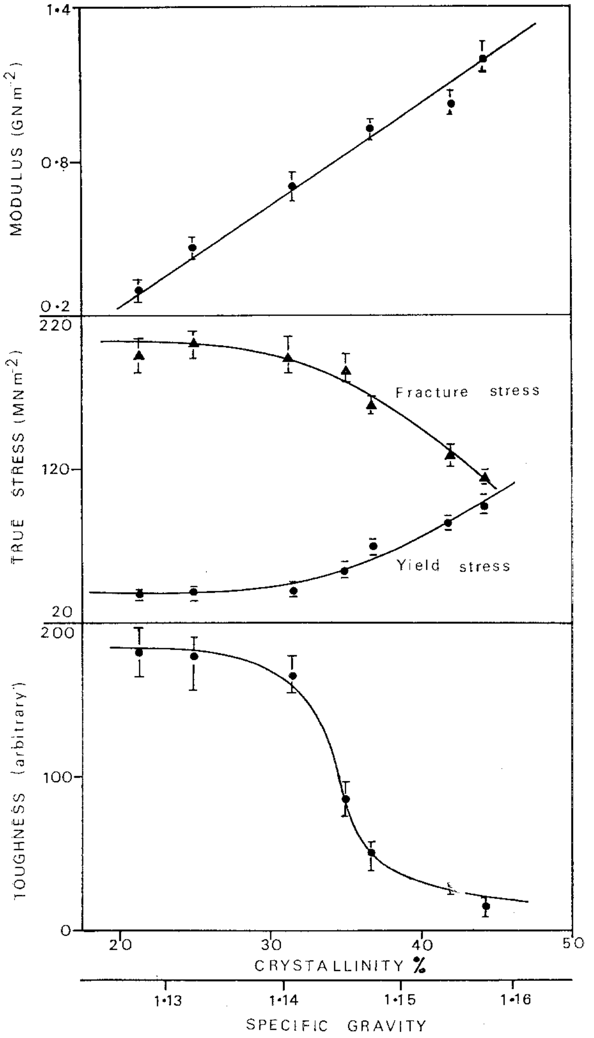

Figure 4 Variation of elastic modulus, yield and fracture stresses and toughness with specific gravity and crystallinity.

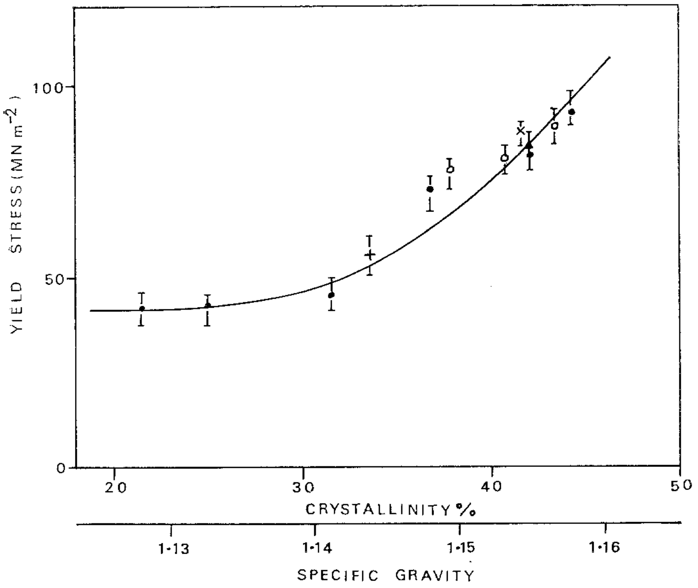

Figure 5 Dependence of yield stress on degree of crystallinity for nylon 6 having a range of polymerization temperatures: +, 473 K; ●, 453 K; △, 433 K; ×, 423 K; ○, 413 K. (The variation of spherulite diameter and molecular weight with polymerization temperature is given in Table I.)

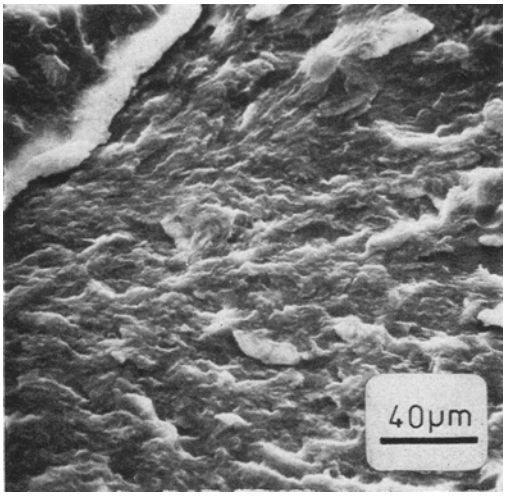

Figure 6 Scanning electron micrograph showing the brittle fracture of nylon polymerized at 393 K.

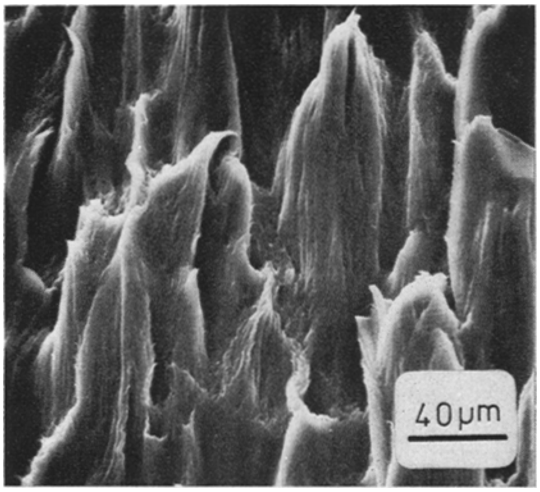

Figure 7 Scanning electron micrograph showing the fibrillar fracture mode of nylon 6 polymerized at 473 K.

to be due to the response of the various microstructural units such as spherulites, lamellae, tie molecules and amorphous volume to the applied stress, the results in Fig. 5 show that the most important is the degree of crystallinity. However, the spread of experimental data in Fig. 5 is perhaps an indication of the effect of these other microstructural units. The contribution of factors such as lamellar thickness and distribution has not been determined.

The toughness is particularly sensitive to degree of crystallinity especially in the range 0.3 to 0.35 (Fig. 4). Changes of this kind cannot be described in terms of homogeneous deformation processes in the material and explanations must be sought in terms of the local deformation processes which lead to crack nucleation and propagation.

3.3. Fracture behaviour

Stereoscan microscopy reveals that three types of tensile fracture morphology can be identified and these are illustrated in Figs. 6 to 8. Fig. 6 shows brittle failure which is typical of samples having a low polymerization temperature, a high degree of crystallinity and low toughness. Fast crack propagation has resulted in a planar

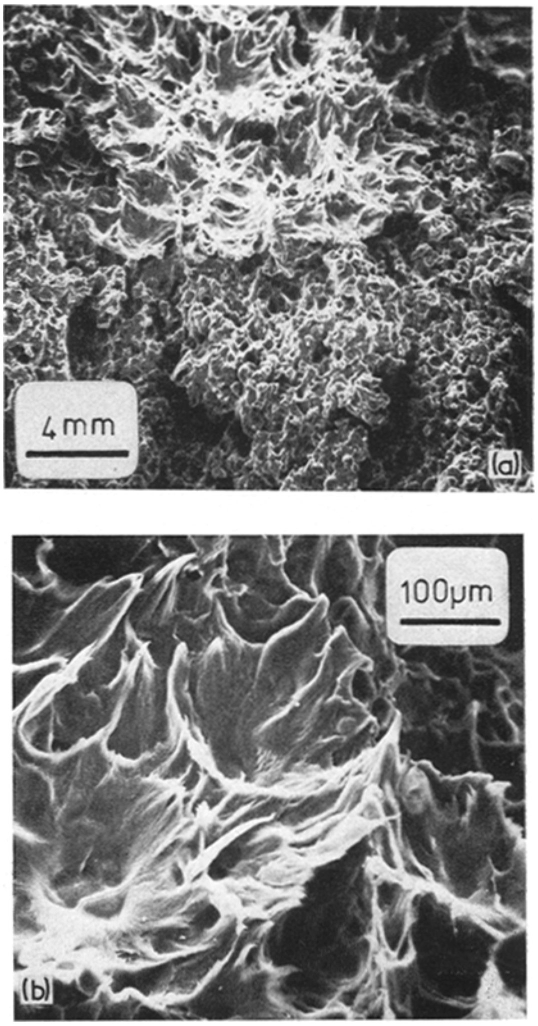

Figure 8 Scanning electron micrographs showing the mixed mode of failure of nylon 6 polymerized at 453 K. (a) Low magnification photograph of fibrillar nucleation zone and interspherulitic propagation region. (b) High magnification photograph of interspherulitic region.

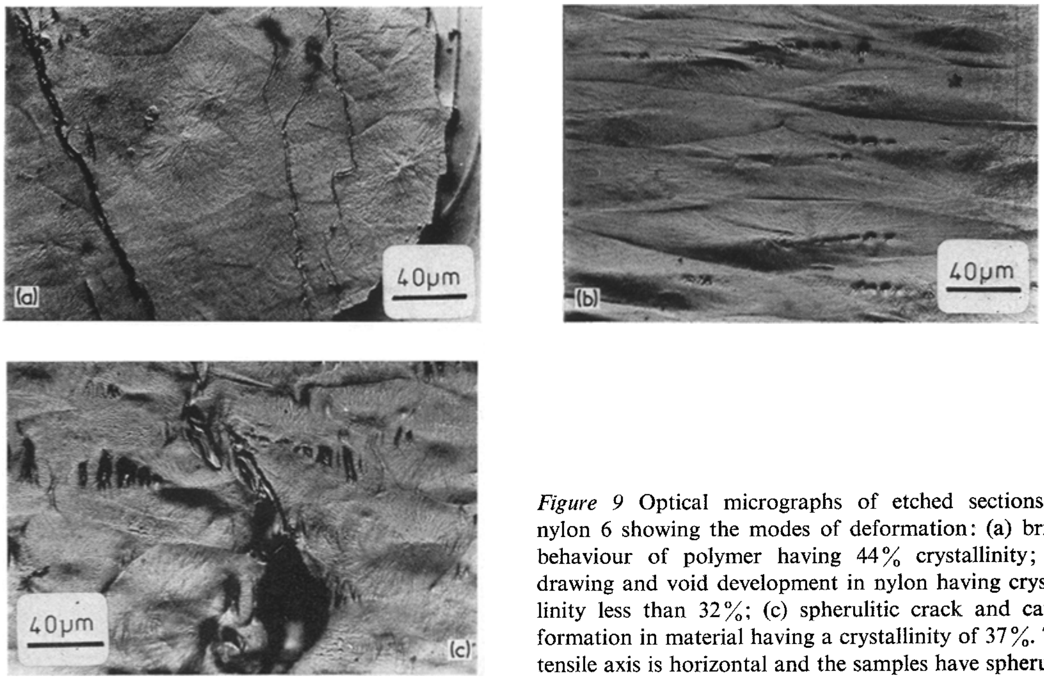

Figure 9 Optical micrographs of etched sections of nylon 6 showing the modes of deformation: (a) brittle behaviour of polymer having 44% crystallinity; (b) drawing and void development in nylon having crystallinity less than 32%; (c) spherulitic crack and cavity formation in material having a crystallinity of 37%. The tensile axis is horizontal and the samples have spherulite diameter of 60 μm and molecular weight, MN 35 × 10^3.

appearance, with little observable interaction between the spherulitic structure and the crack path. The second mode of fracture, shown in Fig. 7, has a highly drawn, fibrillated surface and is observed in samples having low crystallinity with extensions to failure greater than 250%. The topography is very similar to that observed in TPX [20], in which the fibrillar fracture surface is attributed to a coalescence of small voids in a stress whitened zone. In the third mode of fracture, illustrated in Fig. 8a, the fracture surface is divided into two distinct regions; a central fibrillar zone covering up to 30% of the total fracture surface, in which the fine structure is similar to that shown in Fig. 7 and an outer zone of interspherulitic failure (Fig. 8b). This mode of failure occurred in samples of intermediate crystallinity which gave a yield drop when tested in tension.

The effect of degree of crystallinity on the fracture processes in nylon 6 is shown in Fig. 9. In each example the nylon has a mean spherulite diameter of approximately 60 μm and a molecular weight M_N of about 35 × 10^3. Fig. 9a shows a section through a fractured specimen of a sample having a crystallinity of 44%. Fracture has occurred by the propagation of transspherulitic cracks. Many secondary cracks extending over large distances occur below the main fracture surface and the general appearance is similar to fracture observed in thin films of nylon [21]. The highly deformed spherulitic structure shown in Fig. 9b is typical of the nylon having crystallinity of 32% or less. The development of small voids along the tensile axis can be observed and it is the coalescence of these voids which gives rise to the fibrillar appearance of the final fracture surface shown in Fig. 7.

A section through a specimen with a mixed fibrillar and interspherulitic mode of fracture is shown in Fig. 9c for a partially fractured 37% crystalline specimen. The fracture consists of a large central cavity which has propagated within and between spherulites. These results show that the degree of crystallinity has a pronounced effect on the amount of deformation which precedes fracture and on the mode of crack propagation.

The sequence of events leading to failure of samples in the intermediate range, i.e. degree of crystallinity 35 to 42%, was examined by deforming a series of specimens to various strains and then sectioning and etching. The results are summarized in Fig. 10 which shows a typical stress-strain curve. The first sign of cracking was observed after the yield drop. Fine cracks formed within the spherulites normal to the

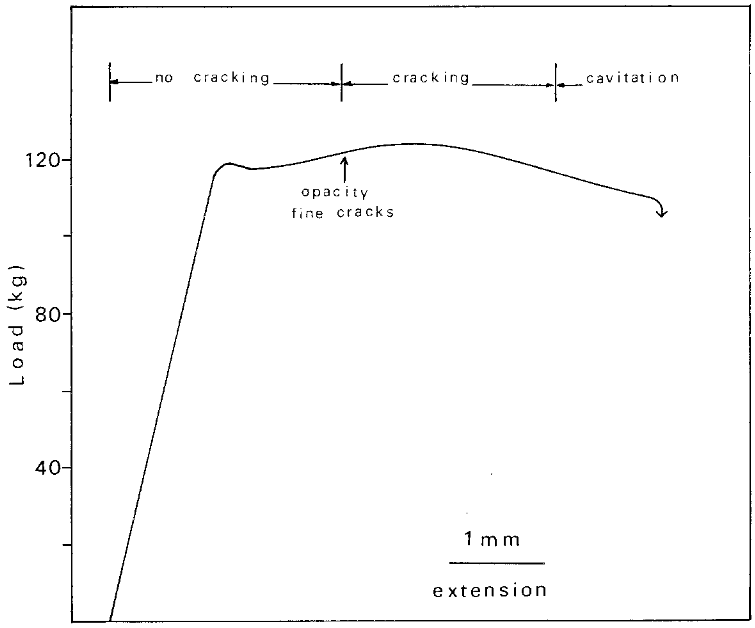

Figure 10 Load-extension behaviour of nylon 6 polymerized at 453 K with a degree of crystallinity in the range 35 to 42% showing the stages of deformation at which spherulitic cracking and cavitation occur.

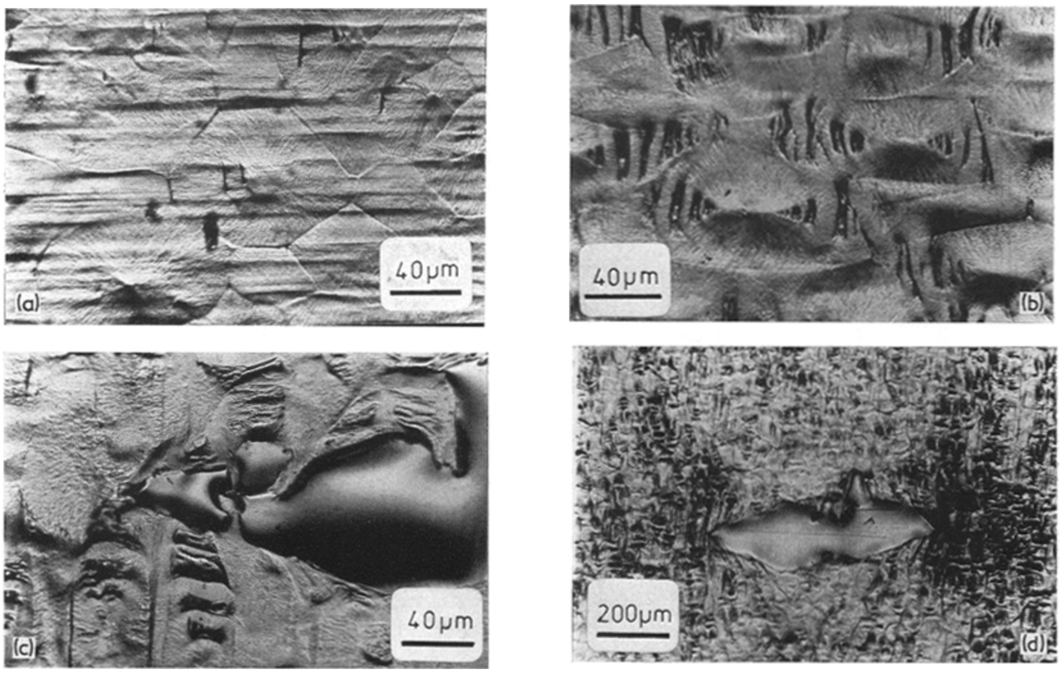

Figure 11 Optical micrographs showing the development, broadening and extension of cracks in nylon 6. (a) Fine cracks formed within spherulites. (b) Elongated spherulites and wide cracks within spherulites. (c) Large cavity caused by the coalescence of spherulitic cracks. (d) Tip of a large crack showing the growth of a cavity by successive coalescence of spherulitic cracks.

tensile axis as illustrated in Fig. 11a. As the strain increased the spherulites elongated, more cracks formed and existing cracks widened (Fig. 11b). In the latter stages of deformation cracks in adjacent spherulites started to coalesce to form a large cavity (Fig. 11c). The propagation of the cavity by coalescence is shown in Fig. 11d. At some critical stage the mode of cavity growth

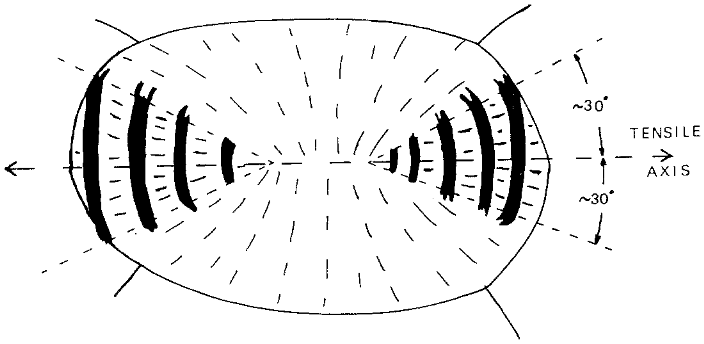

Figure 12 Schematic diagram showing the relation between the spherulitic cracks and the tensile axis.

changed and final fracture occurred rapidly mainly by interspherulitic crack propagation.

The occurrence of cracks in particular sectors of the spherulite, with reference to the orientation of the tensile axis as illustrated in Fig. 12, is consistent with previous results [10-13] which show that the mode of deformation of the spherulite is dependent on the position of the tensile axis. Such cracks have not been reported previously for bulk spherulitic polymers although features referred to as chevron markings have been observed in the same zones in deformed polypropylene [14-15]. The angular extent of the cracks shown in Fig. 12 is somewhat greater than the extent of the chevron markings but this could be due to the amount of spherulitic deformation which occurs before the onset of cracking.

The reasons for the different deformation mechanisms within the spherulite are not fully understood. However, electron microscopy and X-ray diffraction experiments have shown a variation in the deformation of the lamellae depending on their orientation to the tensile axis [2, 10-12] and more rigorous studies of the changes in the electron diffraction patterns of deformed thin films of polyethylene are in progress [13]. The position of the cracks within particular zones of the spherulite suggest that in these regions the lamellae are unable to accommodate the applied strain by plastic deformation. The amount of strain in different parts of the spherulite will depend on the availability of deformation modes such as inter and intra lamellar slip and the orientation of the tensile axis.

An important additional effect in nylon spherulites is likely to arise because of the high density of hydrogen bonding within the polyamide [22]. X-ray studies have demonstrated [23] that the (010) planes which contain the hydrogen bonds are aligned parallel to the spherulite radius. The hydrogen bonding will, therefore, affect the deformation of the lamellae especially when the applied stress is acting along the spherulite radius and hydrogen bond direction. This effective strengthening parallel to the applied stress will limit the ability of the lamellae to deform and increase the likelihood of crack nucleation perpendicular to the tensile direction.

4. Conclusions

This work has shown that in anionically polymerized spherulitic nylon 6, the mechanical properties in tension depend upon the polymerization conditions which affect the degree of crystallinity, the spherulite size and the molecular weight. Increases in the molecular weight and spherulite diameter effected by raising the polymerization temperature produce a change from a brittle to a ductile, tough polymer.

In specimens which have a constant molecular weight and spherulite size, the most important factor affecting the mechanical properties is the crystallinity, and three modes of fracture are identified which depend on the crystallinity:

(1) Brittle behaviour in which a planar brittle fracture occurs before substantial yielding can occur. This takes place at high degrees of crystallinity (about 0.44).

(2) Behaviour in which the load extension curve shows a yield drop with fracture after about 75% extension. This takes place at intermediate crystallinity (0.42 to 0.37) and specimens show mixed fibrillar and interspherulitic fracture.

(3) Behaviour in which the extension to failure exceeds 250% and a completely fibrillar fracture topography is obtained. This takes place at low crystallinity of about 32% or less.

The toughness and fracture stress decrease with increasing crystallinity and the yield stress and elastic modulus increase with crystallinity, in the specimens which have a constant molecular weight and spherulite diameter. There is a transition in the toughness and yield and fracture stress curves at about 35% crystallinity.

The cracks which occur in deformed nylon 6 spherulites are oriented perpendicular to the tensile axis and extend over an angle ± 30° with respect to the tensile axis. The coalescence of these cracks creates a large central cavity which produces the drawn fibrillar appearance of the fracture surface.

Acknowledgements

The authors wish to acknowledge the award of a Science Research Council Studentship (T.B.) and the help of the Rubber and Plastics Research Association who carried out the molecular weight determinations.

References

1. P. I. VINCENT, *Plastics* **28** (1963) 107.
2. K. J. O'LEARY, Ph.D. Thesis, Case Western Reserve University (1967).
3. H. W. STARKWEATHER, G. E. MOORE, J. E. HARRISON, T. M. RODER and R. E. BROOKS, *J. Polymer Sci.* **21** (1956) 189.
4. H. W. STARKWEATHER and R. E. BROOKS, *J. Appl. Polymer Sci.* **1** (1959) 236.
5. J. VAN SCHOOTEN, M. VAN HOORN and J. BOERMA, *Polymer* **2** (1961) 161.
6. L. S. REMALY and J. M. SCHULTZ, *J. Appl. Polymer Sci.* **14** (1970) 1871.
7. M. D. KEITH, F. J. PADDEN and G. R. VADIMSKY, *J. Polymer Sci. A2* **4** (1966) 267.
8. M. D. KEITH and F. J. PADDEN, *J. Appl. Phys.* **35** (1964) 1270.
9. F. P. PRICE and R. W. KILB, *J. Polymer Sci.* **57** (1962) 395.
10. R. J. SAMUELS, *J. Macromol. Sci. Phys. B* **4** (1970) 701.
11. T. ODA, S. NOMURA and M. KAWAI, *J. Polymer Sci. A* **3** (1965) 1943.
12. K. J. O'LEARY and P. H. GEIL, *J. Macromol. Sci. Phys. B* **2** (1968) 261.
13. M. BEVIS and P. ALLAN, "Surface and Defect Properties of Solids", Vol. 3. (Specialist Periodical Reports, The Chemical Society, 1974) Ch.3.
14. J. L. WAY and J. R. ATKINSON, *J. Mater. Sci.* **6** (1971) 102.
15. *Idem, ibid* **7** (1972) 1345.
16. G. B. GECHELE and G. STEA, *Europ. Polymer J.* **1** (1965) 91.
17. T. BESSELL and J. B. SHORTALL, *ibid* **8** (1972) 991.
18. H. G. KILLIAN, *Kolloid Z.* **176** (1961) 49.
19. A. MULLER and P. PFLUGER, *Plastics* **24** (1959) 350.
20. T. W. OWEN and D. HULL, *Polymer* **14** (1973) 476.
21. P. H. HARRIS and J. H. MAGILL, *J. Polymer Sci.* **54** (1961) 547.
22. D. R. HOLMES, C. W. BUNN and D. J. SMITH, *ibid* **17** (1955) 159.
23. A. KELLER, *ibid* **17** (1955) 351.

Received 7 October 1974 and accepted 13 January 1975.