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Tensile Deformation of Nylon 66 Fibers at −196°C

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Synopsis

Nylon fibers tested in tension at −196°C show ductile strains up to 75%. The ductility is a complicated function of draw ratio, because decreasing work hardening with decreasing draw ratio leads to a point of instability where necking begins. The necks presumably initiate fracture, have the appearance of cracks, and have been previously seen on fibers drawn in various organic liquids. Recovery experiments showed that molecular motions involved in low temperature deformation differ from those involved in ambient temperature deformation.

INTRODUCTION

Polymers generally have a brittle temperature below which they show only elastic deformation before fracture. It has been shown that the brittle temperature is not related in any simple way to the transition temperatures and that it depends on the strain rate and the nature of the stress field. The subject has been reviewed by Vincent.[1]

It is known that nylon in bulk form is brittle below −60°C to −85°C[2] and that the brittle temperature and brittle strength of highly drawn fibers depend on the severity of localized defects.[3]

The present observations show that brittle or ductile behavior depends also on the degree of molecular orientation. The results suggest that nylon, in fiber form, is tough or ductile at very low temperatures along with the other crystalline polymers polyethylene, polycarbonate, and poly(tetrafluoroethylene).[1]

EXPERIMENTAL

Two types of nylon 66 fiber were obtained in the undrawn condition from the Chemstrand Corporation (now Monsanto Textiles Division). One was an 86-μm-diameter (60 denier) monofilament containing some titanium dioxide, and the other was a type A05 tire cord yarn of 140 filaments each of 62 μm diameter. Both these fibers contained a few per cent of plasticizer and stabilizer. The possibility that these impurities influence the results deserves future investigation.

Molecular orientation was achieved by drawing[4,5] on a two-roller drawing machine. Between the rollers, the yarn passed through a tube flushed with N_2 at 220°C. A hot pin was used instead of the tube to draw the monofilament. The feed roll surface speed was 10.6 ft/min. These conditions gave uniformly drawn fibers even at low draw ratios.

The diameter and birefringence of single fibers from samples of various draw ratios were measured with a polarizing microscope and a graduated quartz wedge compensator.

Measured fibers, with a 3-cm gauge length, were extended at a constant strain rate, 11%/min, while immersed in liquid N_2 (−196°C). An Invar frame minimized errors due to thermal expansion. The force was measured by a calibrated and stabilized nonbonded strain-gauge force transducer of negligible compliance with a readout on a $^1/_4$-sec strip chart recorder. A measurement of strain was obtained from the clamp separation, and the clamp error was held to a few percent of the measured strain by clamping no more than a 2-mm length of the fiber. Clamp damage of the fibers was avoided by using lead facings, and optimum performance was obtained by using a preset torque wrench to tighten the clamps. The clamps were so constructed of Invar and nylon, which has a relatively high thermal expansion coefficient, that when they were cooled they tightened up further.

The water content of the fibers varied according to the equilibrium condition with relative humidity from 30% to 50%. This may have affected the results.

RESULTS AND DISCUSSION

Characterization of Drawn Fibers

The drawing procedure produced uniform fibers free from lacunae,[5] except at the very highest draw ratio. Comparison of the fiber diameter with the machine draw ratio (roller speed ratio) showed that, assuming constant fiber density, the relaxation of fiber length after drawing was negligible. Therefore the machine draw ratio was taken to be equal to the ratio of the final length to the initial length of the fiber. For the A05 yarn, the curve of birefringence (Δn) versus machine draw ratio (λ) followed the empirical formula[6]

$$\Delta n = \Delta n_0(\lambda\lambda_1 - 1)/\lambda\lambda_1$$

where $\lambda_1 = 1.11$ is an effective draw ratio of the as received fiber (chosen to suit the initial birefringence) and $\Delta n_0 = 0.072$ is de Vries[6] value for the birefringence at infinite draw ratio.

Low-Temperature Tensile Tests

Tensile tests at −196°C were made on three to six fibers from each sample of the A05 yarn. True stress–strain curves for the fiber from each sample which underwent the largest strain at fracture are shown in Figure 1. (The stress values were based on the instantaneous cross section by assuming uniform extension and constant fiber density.) For draw ratios below 1.8, the stress–strain curve shows a fairly sharp yield and a short region of plastic deformation at constant load. This ductile behavior is quite surprising in view of the low temperature of the test. (Compare T_g ~80°C and T_m = 265°C.) It is even more remarkable than when the

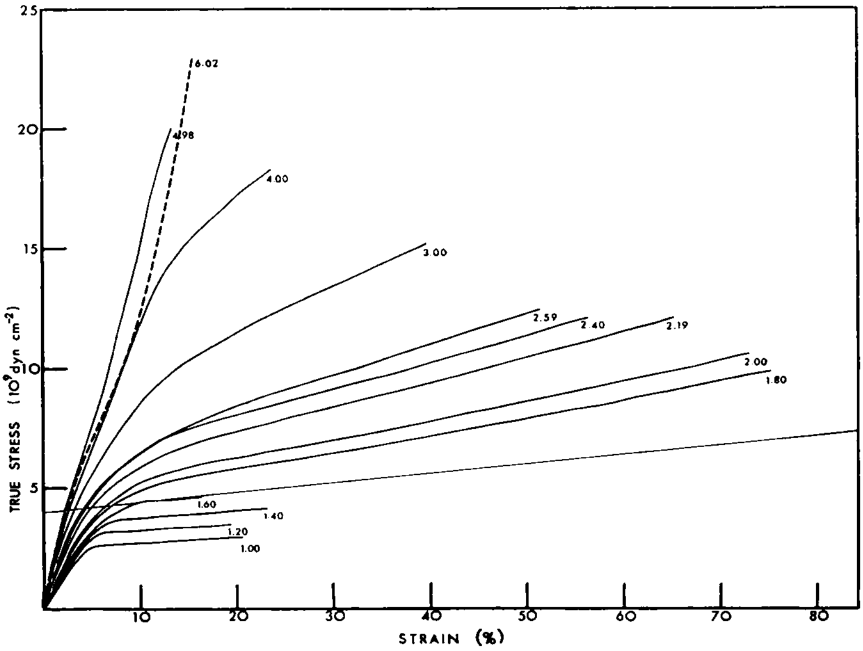


Fig. 1. True stress–strain curves at −196°C for nylon 66 fibers of various draw ratios. (The inversion of the 4.98 and 6.02 curves is due to nonuniform drawing.)

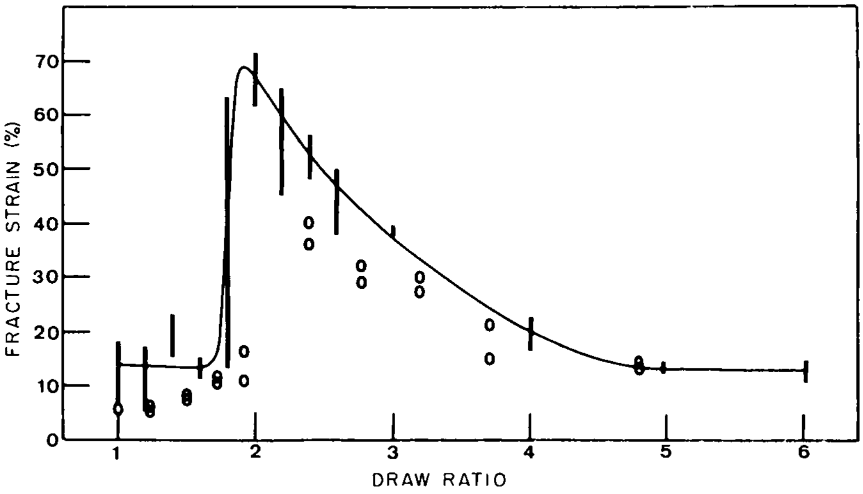
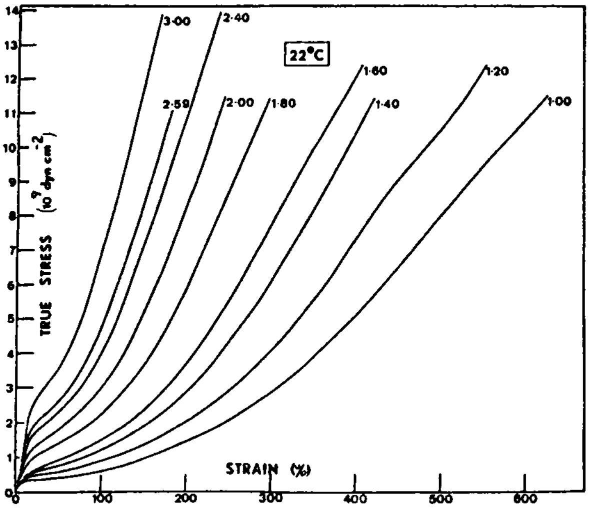


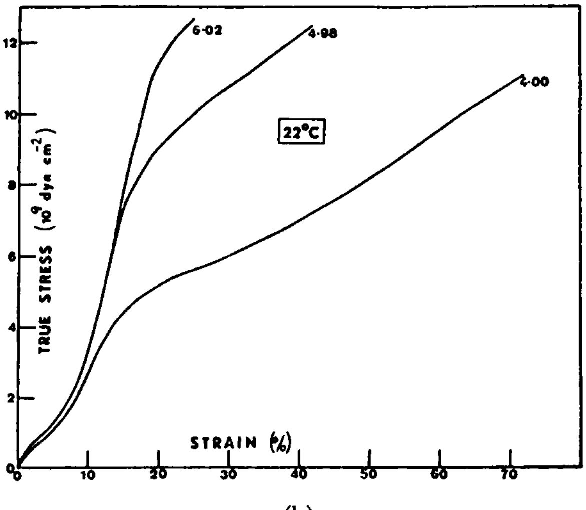
Fig. 2. Dependence of fracture strain at −196°C on draw ratio of nylon 66 fibers. Circles represent monofilament, bars represent yarn.

draw ratio exceeds 1.8, there is a sudden large increase in the extent of plastic deformation up to a strain of 75%. As the draw ratio increases beyond 1.8, the ultimate strain decreases, the ultimate stress increases, and the slope of the plastic region (work hardening rate) increases. It was noted that, unlike results obtained on nylon 6,[7,8] the ultimate force or load was not independent of draw ratio.

For draw ratios between 1.8 and 2.4, there was visible necking at the point of fracture; for other draw ratios, there was none.



(a)



(b)

Fig. 3. True stress–strain curves at 22°C: (a) draw ratios 1–3; (b) draw ratios 4–6.

The discontinuity in behavior at 1.8 draw ratio confirmed the results of preliminary experiments on the monofilament. Fracture strain versus draw ratio, for both fiber types, is shown in Figure 2. The bars are two standard deviations long and are centered on the mean value.

Stress–strain curves at 22°C are shown for comparison in Figure 3. It was noted that the total draw ratio at fracture was constant within 20%.

Necking Instability

The sudden reduction of ductility at 1.8 draw ratio probably reflects a mechanical instability. Localized necking occurs[9–12] when $d\sigma/d\epsilon \leqslant \sigma/(1 + \epsilon)$, where σ is true stress and ϵ is strain. This condition is not satisfied at any point on the low-temperature stress–strain curves of the highly drawn samples. The work hardening rate decreases with draw ratio until at 1.8 it becomes possible to satisfy the necking condition. This is shown graphically in Figure 1 by the straight-line tangent which, when projected, passes through the point of zero stress and −100% strain. If it is assumed that this local deformation soon leads to fracture, then the observations can be accounted for. The ductility transition at 1.8 draw ratio is thus an example of the general hypothesis[13] that a fracture process can often be an instability in deformation.

Multiple Breaks

Multiple breaks[14] occurred in the draw ratio range below 1.8 but not in the high range. This is in accord with reduced ductility below 1.8 draw ratio.

Cracks

Cracks as shown in Figure 4a and apparently identical to those produced by Woods[15] and Hookway[16] upon drawing in various organic liquids were formed in the low draw ratio range more profusely the greater the fracture strain. Appearances suggested that the cracks did not weaken the fibers; the point of fracture (possibly a secondary fracture) was often found to occur in a region that was free from cracks when there was a region of high crack density nearby. This point deserves further investigation, since it is not in accord with the above major hypothesis that necking leads to early fracture. Cracks that went only a small part of the way around the fiber were sometimes found exclusively in the draw ratio range of 1.8 to 2.4.

Generally, the cracks were isolated as shown in Figure 4a, but very occasionally regions of concentrated cracks as in Figure 4b were seen, and in rare cases a conventional neck was formed. In one of these, the draw ratio deduced from diameters inside and outside the neck was 2.0. It was noted that when a fiber with isolated cracks was stretched a second time at room temperature, sharply bounded necks as illustrated by Woods[15] were formed.

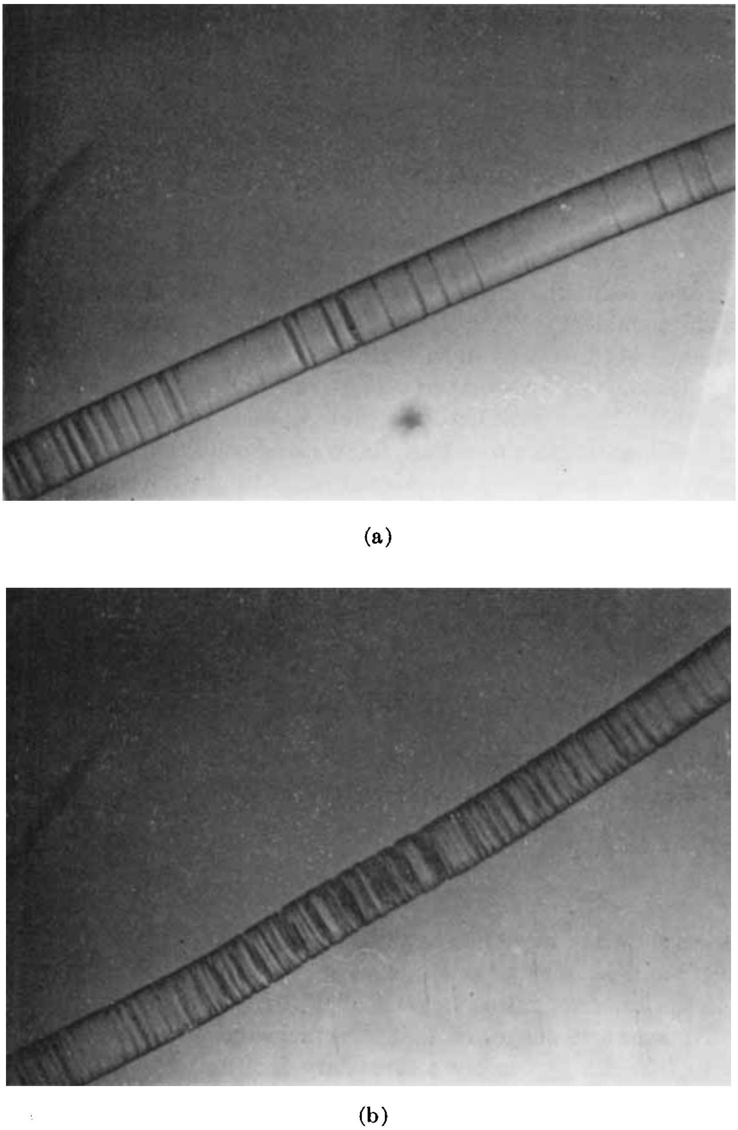


Fig. 4. Cracks formed during deformation at −196°C of nylon 66 fibers with draw ratio between 1 and 1.8: (a) isolated; (b) concentrated.

The stress–strain curve analysis given above and the observations of cracks are consistent with Hookway's suggestion[16] that crack formation is an extreme case of necking under conditions unfavorable to ductility.

It has been shown that thermal runaway[17] is important in nylon fibers of a similar type, but in the present work it probably did not occur because the fiber diameter was an order of magnitude smaller and thermal contact was by a liquid rather than a gaseous medium.

Recovery

Further observations on undrawn fibers showed that the plastic part of the strain was essentially permanent, but only at the low temperature. In a typical case, an elastic strain of 7% was followed by a plastic strain of 13%, at which point a reduction of strain of 7% reduced the stress to zero. In the next 2 min at zero tension, only about 1% of plastic strain was recovered. When the fiber was heated to room temperature, however, all the plastic strain was recovered within 2 min. This was true within experimental error of about 1% and involved a correction for thermal expansion. The complete recovery of strain occurred even though cracks were formed in the fiber.

This rather surprising observation indicates that the simple concept[16] of a crack being a type of neck is not adequate. Either the cracks are more extended at low temperature than the room temperature observations indicate, or else the plastic strain occurs outside the crack.

A 2-min "anneal" at room temperature was also found to have an effect on the stress–strain curve of the highly drawn fibers. The deviation from linearity, Figure 1, was eliminated by cycling at −196°C. After 2 min at room temperature and cooling again, the original nonlinear curve could be retraced.

It appears that molecular motions other than purely elastic can be activated by tensile stress in both drawn and undrawn nylon 66 fibers at −196°C. These molecular motions are not the same as would be produced by the same strain at room temperature, because in the slightly drawn fibers, a 20% room temperature strain would not recover completely at room temperature in 2 min; and in the more highly drawn fibers, the stress level of a fiber strained partly at room temperature and partly at −196°C depends on how the strain is proportioned between the two temperatures.

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