# Crystalline state extrusion of melt-crystallized and solution-grown crystals of nylons-6 and 6,6

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Melt- and solution-grown crystals of nylons-6 and 6,6 have been solid-state extruded to examine the relationships among thermal behaviour, crystallinity, orientation and modulus. Unextruded and extruded samples were examined by thermal analysis, wide-angle X-ray scattering and tensile testing. An extrusion draw ratio (*EDR*) of 4.0 was attained for all samples. At this *EDR*, modulus and crystallinity are linearly related over a wide range up to 60% crystallinity. The highest tensile modulus of 6.7 GPa was attained for both polymers in the extrudates of solution-grown crystals, although crystals in extrudates from precipitates were less oriented. This suggests that the extent of both crystallinity and draw play an important role in the enhancement of modulus.

## INTRODUCTION

Crystalline-state extrusion of high density polyethylenes crystallized from the melt[1] and from solution[2] has provided ultra-oriented morphologies of high tensile modulus. The semicrystalline state of nylons-11 and 12 have also been solid-state extruded[3]. Nylons have higher melting points than polyethylene due to inter- and intramolecular hydrogen bonding. The crystals and mechanics of nylons-6 and 6,6 are thermally more stable than in nylons-11 and 12[4] due to a higher concentration of amide groups, and also have potentially high tensile moduli[5]. Higher crystallinity leads to higher moduli for melt-crystallized nylons[6]. Solution-grown nylon crystals[7–10] have also been shown to exhibit a higher percentage crystallinity[8] than the corresponding melt-crystallized polymers. Higher draw also leads to higher tensile properties with several routes being explored. Reversible plasticizing of nylons with ammonia during draw is one route[11]; a second is to perform the deformation on compacted powders, in order to reduce entanglements[2].

Here, both melt-crystallized and solution grown crystals of nylons -6 and 6,6 have been extruded in the semicrystalline state through conical dies to examine the dependence of thermal behaviour on extrusion draw ratio (*EDR*), and the relationships among modulus, crystallinity and orientation. These solid-state extrudates have been examined by thermal analysis, wide angle X-ray and tensile testing.

## MATERIALS AND EXPERIMENTS

Nylon-6 powder and cylindrical plugs of nylon 6,6 were obtained commercially. For determination of molecular weights, small amounts were solution purified by dissolving in formic acid and precipitation on pouring into water according to the method described by Pennings[10]. Molecular weights were calculated to be $3.0 \times 10^4$ and $3.8 \times 10^4$ for nylons-6 and 6,6, respectively, from intrinsic viscosities of 1.07 and 1.41 in 85% and 90% formic acid, respectively.

Nylon-6,6 rods were melt-crystallized, as received. They were shaved to a diameter $(\varphi)$ of 0.95 cm. Nylon-6 powder was melt-crystallized by slow cooling at a rate of $\sim 1°C$ $min^{-1}$ under an applied pressure of $\sim 200$ atm in the reservoir $(\varphi = 0.95 \text{ cm})$ of an Instron Capillary Rheometer.

Both nylons were dissolved at several concentrations (0.1–25 w/w %) in 1,4-butanediol[10] and then crystallized isothermally or by fast cooling. The obtained suspensions were poured into a 1:1 w/w mixture of methanol and acetone. The precipitates were dried *in vacuo* at 100°C over 48 h and compressed at 120°C and 2400 atm in the rheometer reservoir.

The prepared plugs were solid state extruded at several fixed temperatures and at a constant extrusion rate with a fixed cross-head speed of 0.2 cm $min^{-1}$ through the stainless steel conical dies with an entrance angle of 20°. The extrusions were carried out at several draw ratios of cross-sectional areas for die-entrance-to-exit, i.e. 2, 3, 4 and 5. No lubricant, hydrostatic liquid or plasticizer were used. Extrusion cross-head speeds from 0.01–2.0 cm $min^{-1}$ were tried with no significant improvement in draw.

Thermal analysis of all samples was performed at a heating rate of 10°C $min^{-1}$ in a Perkin–Elmer DSC model IB in order to estimate melting peak temperature $(T_m)$ and the % crystallinity based on a reported[12] heat of fusion $(\Delta H_f)$ of perfect crystals (45 cal/g) for both nylons, see *Table 1*.

Wide angle X-ray diffraction patterns were obtained with the use of nickel-filtered, CuK$\alpha$ radiation.

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*Table 1* Crystallinity of melt-crystallized nylons

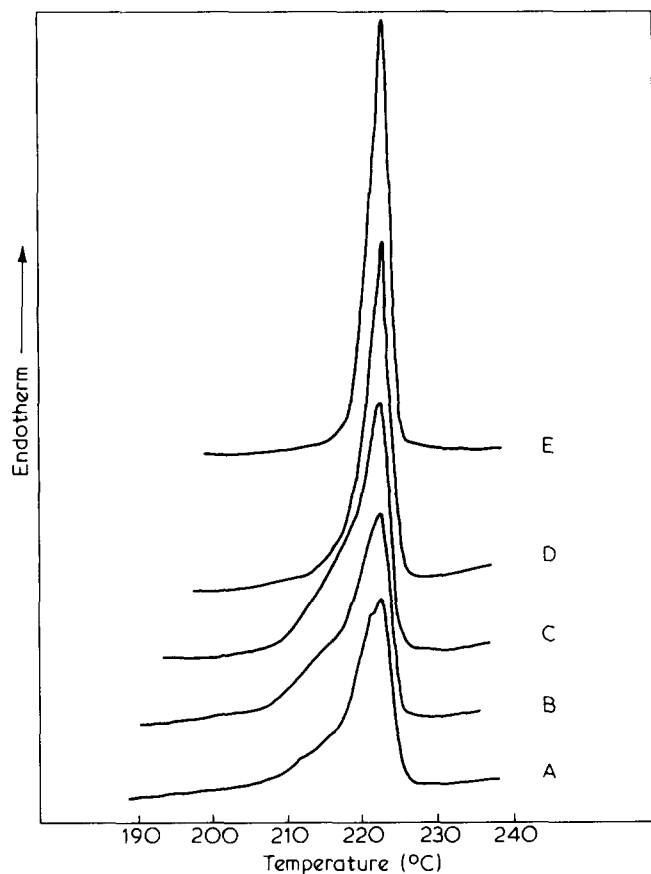| Sample history | % Crystallinity | | |
|---|---|---|---|
| | Nylon-6 | Nylon-6,6 | |
| Unextruded | 28 | 29 | |
| Extruded | at 180°C | at 200°C | at 220°C |
| EDR = 2 | 35 | 37 | 44 |
| 3 | 40 | 41 | 52 |
| 4 | 47 | 47 | 50 |
| Unextruded residue in rheometer | 32 | 32 | 36 |



*Figure 1* D.s.c. melting behaviour of melt-crystallized nylon-6: (a), unextruded; (b), unextruded and annealed at 180°C for 1 h; (c), (d), and (e), extruded at 180°C and at *EDR* of 2,3 and 4, respectively

Tensile moduli were calculated at a strain of 0.2% and at a strain rate of $3.33 \times 10^{-4}$ s$^{-1}$ using an Instron tensile testing machine, model TTCM, equipped with a 10 mm strain extensometer. This intermediate strain was chosen to provide a reliable value after removal in the tensile test or the minor curvature in the as-extruded deformates.

## RESULTS AND DISCUSSION

### Melt-crystallized nylons

Multi-melting temperatures for both nylons-6 and 6,6 have been reported and discussed previously[13-16]. Dumbleton *et al.*[14] reported that at increased annealing temperature and/or time, the temperature and area of the lower melting peak increased for nylon-6,6 while retaining

the higher melting peak; but subsequently the lower melting peak could be transformed to the higher melting peak as the total crystallinity increased. Recently, etching studies have suggested an alternative explanation[17]. The long period of crystallites also increased during this annealing process[14,16].

Both nylons are known to exhibit polymorphism. Nylon-6 has $\alpha$, $\beta$, and $\gamma$ crystal forms, depending on preparation[18,19]; and nylon-6,6 exhibits $\alpha$ and $\beta$ crystal forms[20]. It is known[4,18,20] that slow crystallization for both polymers produces the $\alpha$ form which is the most stable and does not convert to other forms on annealing or drawing. Slow crystallization was performed on both nylons in this study. Annealing effects at 180° and 200°C for 1 h on the melting for unoriented nylons-6 and 6,6 are shown in *Figures 1* and *2*. Annealing increased the crystallinity and lowered the melting peaks but did not produce a complete conversion of the lower melting peaks to the higher melting peaks, as reported for lower temperature and shorter annealing time. Results in *Figures 1* and *2* are also representative of unoriented (unextruded) residual samples left in the capillary reservoir of the Instron Rheometer after a portion had been solid-state extruded.

The extrudates of different *EDR*'s were obtained in the steady state after 1 h by use of dies of different exit diameter. Melting behaviour as seen in *Figures 1* and *2* shows the effect of *EDR* at fixed extrusion temperatures $(T_E)$. The higher melting peak for both nylons remained constant. However, the lower melting peaks increased with *EDR* and subsequently were converted to the higher
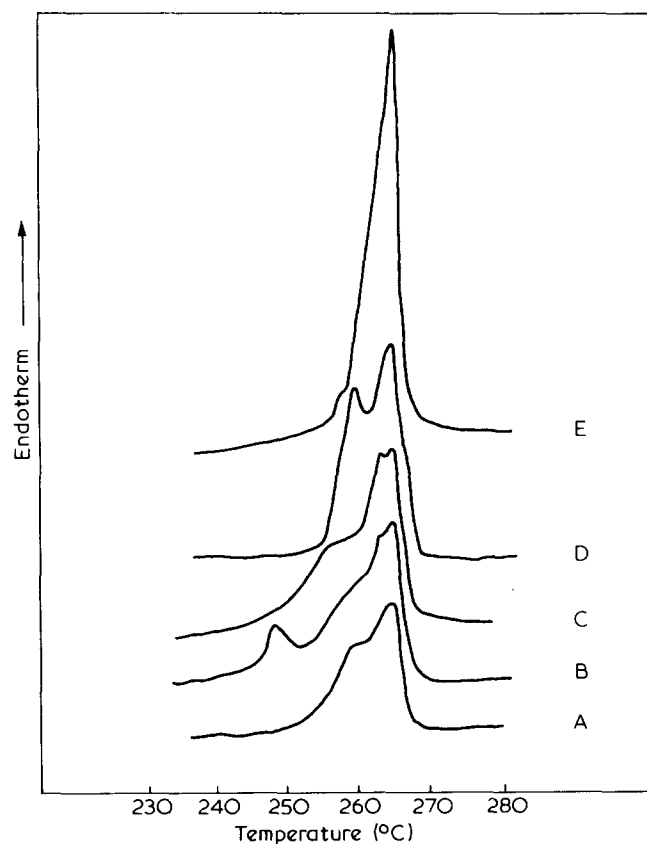


*Figure 2* D.s.c. melting behaviour of melt-crystallized nylon-6,6: (a), unextruded; (b), unextruded and annealed at 220°C for 1 h; (c), (d) and (e), extruded at 220°C and at *EDR* of 2, 3 and 4, respectively
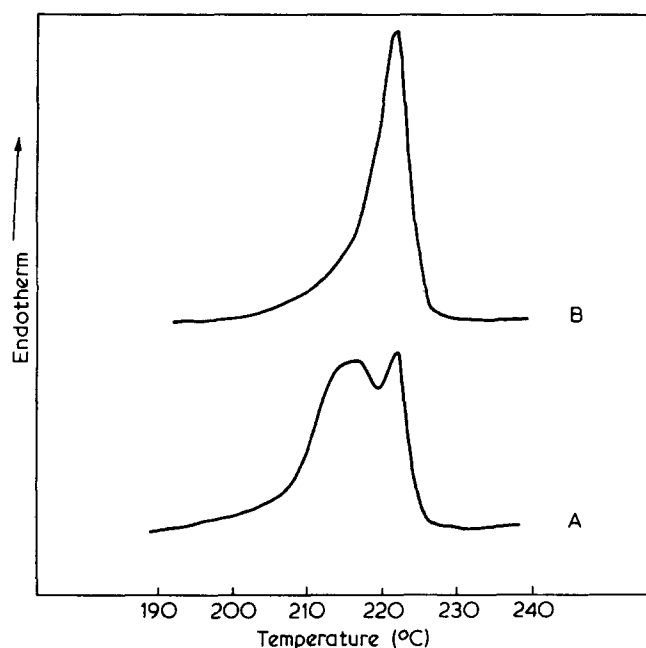
*Figure 3* Melting behaviour of nylon-6 precipitates from 8% solution: (a), unextruded; (b), extruded at 200°C at *EDR* of 4

melting form. Crystallinity accordingly increased. These results suggest that the drawing effect on melting may be similar to that of annealing.

### Solution-grown crystals

The solution-grown crystals (*SGC*) of nylon-6 from 1,4-butanediol produced the α-form[10], as confirmed in *Figure 8b*. These solution-grown samples of nylon-6 were prepared by isothermal crystallization at 128°C from 0.1 and 1% solutions and by fast cooling to room temperature from 8 and 25 wt % solutions. Fast cooling crystallization was also performed on nylon-6,6 to obtain precipitates from 8 and 25 wt % solutions. This produced a melting behaviour different from the melt-crystallized samples and from the samples precipitated at lower concentrations, as seen in *Figure 3*. The lower $T_m$ corresponds to 70% of the total area for the 8% solution-precipitate. This differs markedly from the shoulder or tail on the melting curves of the melt-crystallized samples and precipitated at lower concentrations. Nylon-6 precipitated from 0.1 and 1% solutions exhibited single melting peaks with a $T_m$ of 222°C, the same as the higher $T_m$ of the melt-crystallized sample.

Similar and clearer behaviour was observed for nylon-6,6, as can be seen in *Figure 4*. The higher melting peak of solution-grown crystals, as shown in *Figure 4*, may be due to the melting of the reorganized crystals formed during the d.s.c. scan. The higher melting peak of the *SGC* may not therefore correspond to the higher melting peak of the extruded samples, see *Figure 4b*. The larger area of the lower melting peak is associated with the fast crystallization which produces smaller crystallites.

Precipitated and compacted nylon-6 and 6,6 were solid-state extrudable at 200° and 240°C to an *EDR* of 4.0. The limits of temperature and draw are most likely due to the crystallinity level, as shown in *Table 2*. Extrudates of nylon-6 precipitate from 0.1–25% solutions exhibited single melting peaks. However, extrudates of nylon-6,6 showed double peaks with the lower peak converted only partially to the higher peak. Complete transformation of

crystallites of nylon-6,6 are likely to require more extensive drawing since complete transformation was attained for nylon-6. The % crystallinity for both nylons is high after extrusion as seen in *Table 2*.

### Extrudate properties

Conventional drawing effects on deformation[21,22] and mechanical properties[23,24] have been reported for these nylons. Higher draw provides higher orientation of both crystalline and amorphous regions. Nylons can absorb water in their amorphous component. However, the tensile modulus of oriented nylon-6,6 conditioned at 50% RH is similar to that of dried samples, although the change from dryness to water saturation causes a ×4 decrease in modulus because of the plasticizing action[25]. Our experiments were performed below 50% humidity. Thus, after preparation of solid plugs, sample drying was not performed in this study. Both crystallinity and tensile modulus increase with *EDR*, both for melt-crystallized nylon-6 and 6,6, as seen in *Figures 5* and *6*. The highest readily-obtainable *EDR* was 4 for all samples, either melt-crystallized or precipitated. EDRs over 4 produced spiral fractures in the extrudates. In comparable tests, nylon-12[3]
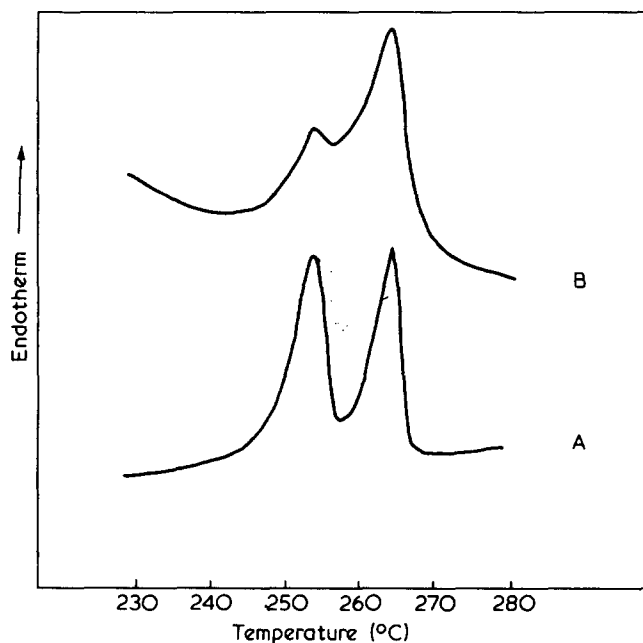


*Figure 4* Melting behaviour of nylon-6,6 precipitates from 8% solution: (a), unextruded; (b), extruded at 240°C and at *EDR* of 4

*Table 2* Crystallinity of solution-grown nylons and their solid-state extrudates

| wt % Concentration | % Crystallinity | | | |
| --- | --- | --- | --- | --- |
| | Nylon-6 | | Nylon 6,6 | |
| | Unextruded | Extruded* | Unextruded | Extruded** |
| 0.1 | 61 | 63 | – | – |
| 1.0 | 58 | 61 | – | – |
| 8.0 | 54 | 57 | 54 | 56 |
| 25 | 53 | 55 | 53 | 53 |

* at 200°C to *EDR* of 4
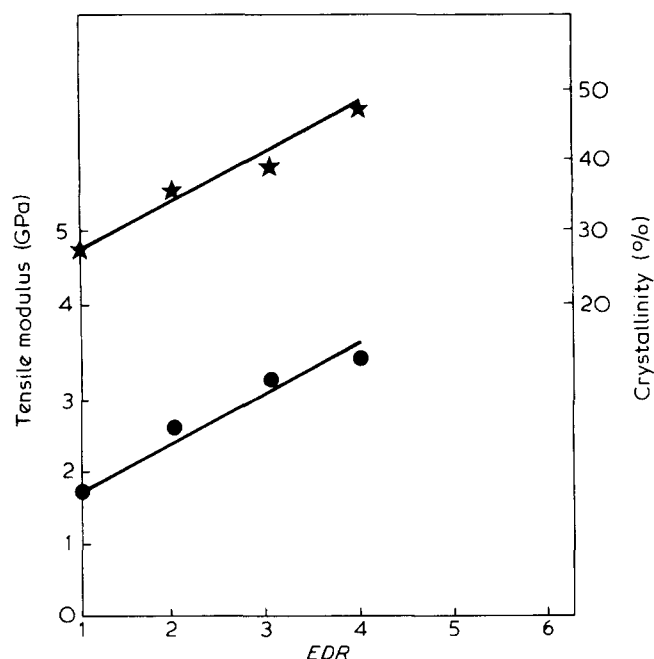** at 240°C to *EDR* of 4
Uncertainty ±1% in crystallinity

*Figure 5* Increase in tensile modulus and crystallinity with extrusion draw ratio for melt-crystallized nylon-6 extruded at 180°C: (●), tensile modulus; (★), crystallinity
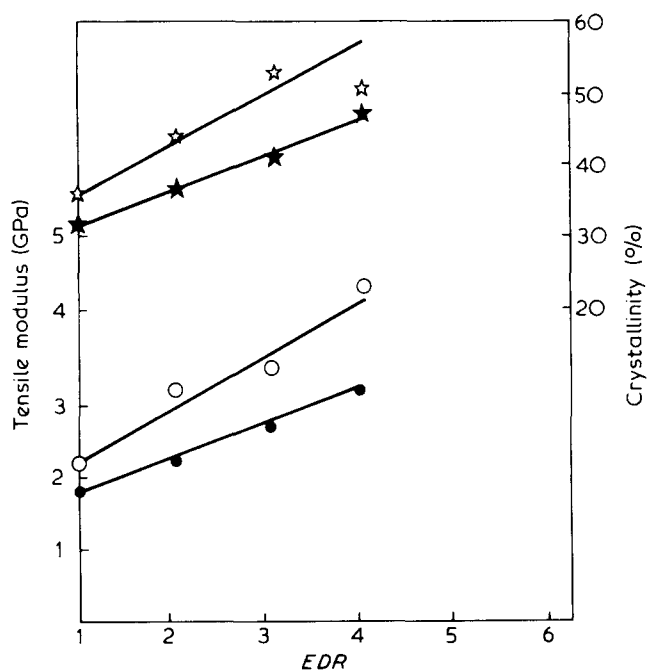


*Figure 6* Increase in tensile modulus and crystallinity with extrusion draw ratio for melt-crystallized nylon-6,6: (●) and (★), tensile modulus and crystallinity for extrudates at 200°C (filled symbols), for extrudates at 220°C (open symbols)

has been solid-state extruded at EDR up to 12 without fractures and high density polyethylene[1] to an EDR of 36. The lower draw ratio obtained here for nylons-6 and 6,6 is likely to be due to high concentrations of amide groups leading to extensive interchain hydrogen bonding. Thus, the studies on deformation of nylons containing plasticizers with polar chemical groups have been reported to reduce yield stress and deformation[26]. On reversibly plasticizing with ammonia an EDR of 12 has been attained for nylon-6[11] resulting in 53% crystallinity and a

tensile modulus of 13 GPa. Importantly, however, no higher draw ratios for nylons-6 and 6,6 appear to have been reported. The highest moduli obtained for extrudates of melt-crystallized nylons-6 and 6,6 were 3.3 and 4.3 GPa, respectively. This nylon 6,6 extrudate is well oriented according to wide angle X-ray diffraction patterns. A similar X-ray pattern was observed in the nylon-6 extrudate.

An increase in crystallinity was observed with EDR for both nylons. The starting crystallinity for melt-crystallized nylons-6 and 6,6 is ～30%, as shown in Table 1. Samples of both polymers annealed at 180° and 200°C increased slightly in crystallinity. Crystallinity increased by ～20% on solid state extrusion to an EDR of 4 for both melt-crystallized polymers. However, the initial crystallinity for solution-grown nylons-6 and 6,6 is remarkably high, 50–60%, as shown in Table 2. On solid-state extrusion, the crystallinity stays high, increasing slightly. This suggests that ～60% may be crystallinity saturation for these nylons and conditions. Extrusion of melt-crystallized nylon-6,6 at 220°C produced a higher modulus and crystallinity, due to annealing, than that at 200°C. This suggests that the higher crystallinity is responsible for a higher modulus. *Figure 7* shows that relationship of tensile modulus to crystallinity is at a fixed EDR of 4 for melt-crystallized and precipitated samples. The highest modulus, as obtained for both nylons, is 6.7 GPa, ～70 g/den, for solution-grown samples. This maximum modulus is larger than commonly used for these nylons in tire cord, ～50 g/den, higher than attained by melt crystallization[3] in the range ～8 GPa, recently reported for these same nylons[27].

Extrudates of the nylon-6,6 precipitate are less oriented than that of melt-crystallized samples, yet the modulus of the extruded nylon 6,6 precipitate is higher. The well developed spots for the 002 plane, *Figure 8a*, are worth noting. Similar results were obtained for nylon-6. This indicates a major role for crystallinity, in addition to drawing, in determining the tensile modulus of these solid-state extruded aliphatic nylons.
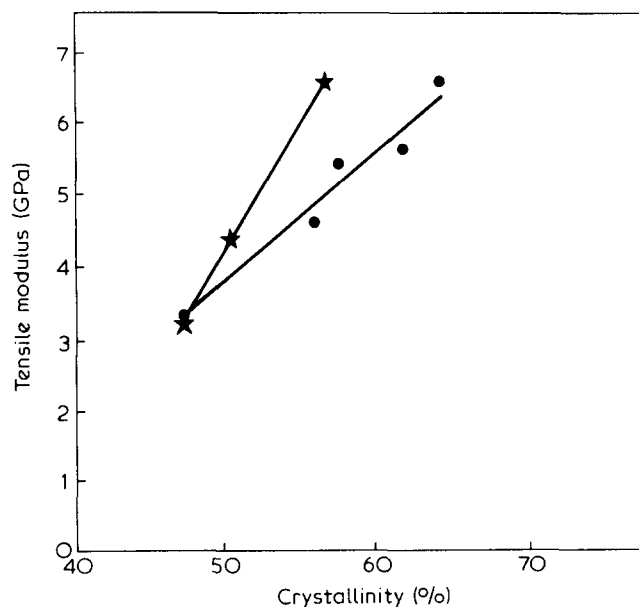


*Figure 7* Relationship of tensile modulus to crystallinity for nylons-6 and 6,6 at a fixed draw ratio of 4: (●), nylon-6; (★), nylon-6,6

## CONCLUSIONS

Solution-grown crystals of nylons-6 and 6,6 have been solid-state extruded. The thermal properties, crystalline orientation and tensile moduli of these extrudates are compared with solid-state extrudates of melt-crystallized nylons.

(i) From the dual melting peaks for each nylon, the concentration of crystallites having the highest melting isotherm were increased by solid-state extrusion.

(ii) The highest initial crystallinities, for precipitates of 50–60%, increased only slightly on solid-state extrusion to a draw ratio (EDR) of 4.

(iii) At an EDR of 4, the measured tensile moduli for both polymers increased linearly with crystallinity up to 60%.

(iv) Extrudates of precipitates for both polymers were less oriented at an EDR of 4 than for the corresponding melt-crystallized samples. The former none-the-less exhibited higher moduli. This indicates that crystallinity as well as drawing plays an important role in tensile modulus development.

(v) The highest moduli, obtained from the extrudates of precipitates, for each nylon-6 and 6,6 is 6.7 GPa. Extrudates of the same EDR of 4 for melt-crystallized samples of the same nylons-6 and 6,6 were 3.3 and 4.3 GPa. These values therefore are at the high end of conventional drawing processes for these polymers.

(vi) Crystalline-state extrusion of aliphatic nylons as compacted powders, *versus* solid plugs, offers an alternative and a potential complement to deformation with a reversible plasticizer, viz ammonia, to produce extensive draw and enhanced tensile properties.

## ACKNOWLEDGEMENTS

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