The characterization and properties of nylon 13,13

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The physical properties of the nylon with the longest number of methylene segments, nylon 13,13 have been characterized. Studies are reported of thermal analysis, X-ray scattering and for mechanical properties including hardness. The crystal of nylon 13,13 has been found to have a monoclinic form with $a=4.9$ Å, $b=9.22$ Å, $c=34.40$ Å and $\beta=121.08°$. Also, studies were carried out on the mechanical properties of nylon 13,13 that had been uniaxially drawn by solid-state extrusion at 125 and 135°C. The highest draw ratio obtained was 4.5. The maximum melting point, heat of fusion and amorphous density were estimated to be $\geqslant 183$°C, 230 J g^{-1} and 1.01 g cm^{-3}, respectively. The crystallinity, melting temperature and tensile modulus increased with draw ratio. The glass transition temperature of the undrawn polymer was 56°C. For the sample with a draw ratio of 4.0, the tensile modulus and the X-ray crystal orientation function reached 2 GPa and 0.94, respectively.

(Keywords: nylon 13,13; characterization; properties)

INTRODUCTION

Opportunities abound for the possible development of the properties of nylon 13,13. This is because of two features: the composition of nylon 13,13 is the limit among the available nylons, having 11 methylene units per amide repeat; and nylon 13,13 represents a model for functionalized polyethylene. In special applications nylon 13,13 is to be preferred over polyethylene because of its higher melting point and better bonding for adhesives and paint. Previously, nylons with the longest aliphatic segments, namely, nylon 11 and nylon 12, have been studied in this laboratory[1]. The advantages of nylon 13,13 among the nylons include a lower melting point and a slightly lower density, plus the lowest dielectric constant and water affinity[2,3].

The first publications on the synthesis of nylon 13,13 from brassylic acid were in 1968[3–5]. Currently, this material has only been made in pilot plant amounts. Previous information on the basic properties of nylon 13,13 has therefore been limited. This paper reports the preliminary results of characterization and the physical properties of this new material, both before and after uniaxial deformation.

EXPERIMENTAL

Material. Nylon 13,13 was obtained from the United States Department of Agriculture, Northern Regional Research Center, Peoria, Illinois. The viscosity-average molecular weight is 6.8×10^4. The resin was used as received, which was slightly brown from prior cresol solvent recovery.

Thermal analyses were carried out with a differential scanning calorimeter (Perkin–Elmer DSC-7) at a heating rate of 20°C min^{-1} and by dynamic mechanical thermal analysis (d.m.t.a.) at a frequency of 1 Hz and a heating rate of 5°C min^{-1} in the temperature range of -50 to 150°C.

Density was measured with a density gradient column prepared with a toluene–carbon tetrachloride mixture in the range of 0.9400–1.0300 g cm^{-3} at 23°C[6]. The tensile modulus of samples was evaluated with an Instron tensile tester at room temperature at an initial strain rate of 1×10^{-3} s^{-1}.

Microhardness (*MH*) was measured at room temperature using a Leitz tester adapted with a square-pyramidal diamond indenter[7]. The MH was measured perpendicular to the surface expressed as KP/d^2, where d is the length of the impression diagonal, P is the contact load applied and K is a factor equal to 1.854.

WAXS. The crystal structure and the orientation functions of drawn nylon 13,13 samples were studied by WAXS. X-ray diffraction patterns of the specimen were obtained by using Ni-filtered CuKα radiation incident perpendicular to the sample. The crystal system and unit-cell dimensions of the crystal were determined from the end-view X-ray diffraction pattern of a double oriented nylon 13,13 specimen prepared by extrusion drawing followed by cross rolling the uniaxially oriented sample at 140°C. Samples for solid-state extrusions were

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melt moulded at 200°C into a 1 mm thick plate which was held at 200°C for 10 min before quenching in ambient water, and then cut into strips 5 mm wide. The cut strips were put in a split polyethylene billet and inserted into the barrel of an Instron rheometer at temperatures of 125 and 135°C. The details of the solid-state extrusion have been described previously[8–10].

RESULTS AND DISCUSSION

Physical properties

The thermal properties of nylon 13,13, such as the equilibrium melting temperature (T_m°) and glass transition temperature (T_g), were studied by d.s.c. These studies started with a sample quenched into ice water after melting. In the first run at a heating rate of 20°C min^{-1}, the T_g can be readily seen. The mid temperature for the specific heat jump was taken as the T_g, which was 56°C. At 120°C crystallization takes place and shows an exothermal peak at ~140°C. The melting peak temperature on the thermogram is 174°C, which is the same as a literature value[3]. However, these reported melting temperatures are not the equilibrium values.

For a cross check, dynamic measurements were also carried out by d.m.t.a. at a heating rate of 5°C min^{-1}; the T_g α transition temperature is 57.0°C. The T_g values by the two methods agree within an error of ±1°C.

T_m° was obtained by d.s.c. by measuring the melting point of samples annealed *in situ* at several temperatures below 170°C. From extrapolation according to the Hoffman–Weeks equation, T_m° was obtained directly[11]. The annealing was carried out for 4 h at each annealing temperature, followed by rapid cooling to room temperature with the onset temperature taken as the melting point. The results are shown in *Figure 1*. The extrapolated T_m° is 183°C, which is 9°C higher than the literature value[3].

Using the group contribution method, Van Krevelen has calculated the physical properties, including the heat of fusion and melting temperature, for a variety of polymers. Good correlations with measurement are obtained[12]. For the estimation of the melting temperature and the heat of fusion of nylon 13,13, similar calculations were performed here. Calculations predict that the melting temperature of nylon 13,13 is 187°C, which is 4°C over our measured T_m°. This is close, since it is recognized that odd–even effects occur in the melting points of the nylon family. The heat of fusion is calculated to be 230 J g^{-1} (no data are available for comparison). It is worth noting that for this property of nylons with longer methylene segments, i.e. nylon 11 and nylon 12, Greco and Nicolais carried out the same calculation. They obtained data of 222 and 226 J g^{-1}, for nylon 11 and nylon 12, respectively[13].

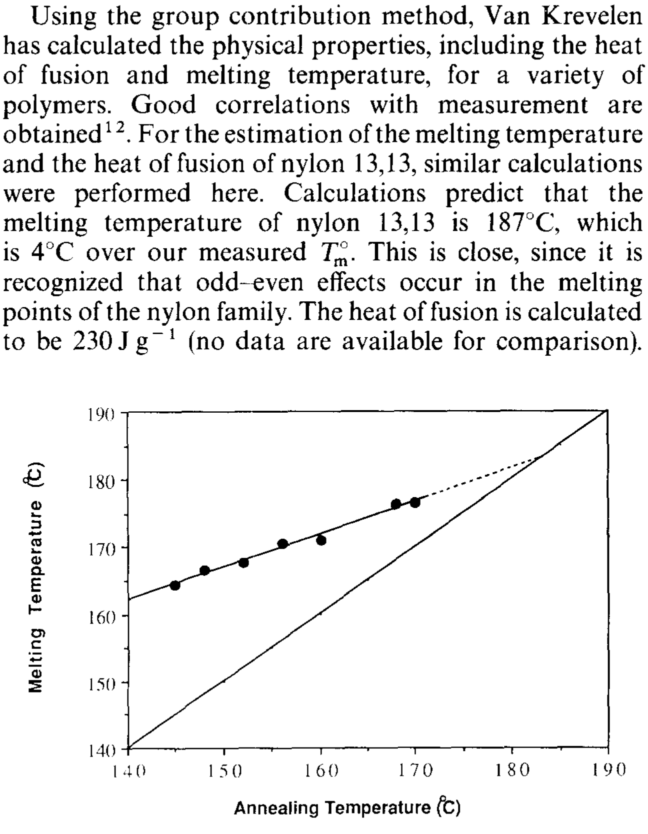

Figure 1 Plot of onset melting temperature *versus* annealing temperature

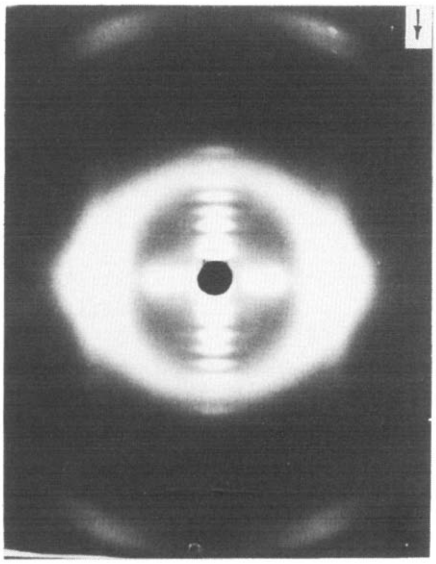

Figure 2 WAXS pattern of uniaxially oriented nylon 13,13 at DR = 4. The arrow indicates the draw direction

From the thermogram of the quenched sample it can be seen that a totally amorphous nylon 13,13 cannot be obtained. Based on our calculated heat of fusion, the crystallinity of the quenched sample is 20% by d.s.c. This means that, due to the long methylene segments, the crystallization rate of nylon 13,13 is very fast.

The crystal structures found in the nylon family are complex. Polymorphism, i.e. α, β and γ forms, exists in the aliphatic nylon family. These structures are interconvertible by chemical, thermal or mechanical treatment[14]. The γ form is the characteristic structure of over half the aliphatic polyamides. The structure deviates from the planar zigzag to allow essentially complete hydrogen bond formation among amide units. This conformation can theoretically form strain-free intermolecular hydrogen bonds with the chains fully extended. This is the common structure for odd–even, even–odd and odd–odd nylons and sometimes occurs for even and odd nylons. The γ form is more stable in the polyamides with odd numbers of CH_2 groups, while the α and β forms are more stable in those with even numbers[14].

The crystal structure was studied by WAXS. An X-ray diagram of an oriented nylon 13,13 sample is shown in *Figure 2*. It is characterized by a single strong equatorial reflection instead of a pair of strong reflections observed from the well crystallized α form of nylons. This pattern tells us that nylon 13,13 crystals closely resemble the γ form of nylon 12[15]. This form is so stable that no transition to the α form was observed even when the nylon 12 sample was subjected to draw at a temperature of 135°C. It is thus concluded that the stable crystal form of nylon 13,13 is the γ form. The end-view X-ray scattering pattern of a drawn and cross rolled specimen is shown in *Figure 3*. This diagram confirms that the γ form crystal system of nylon 13,13 is monoclinic. The c-axis period was estimated from the layer line reflection of a uniaxially oriented specimen, and the a and b parameters were

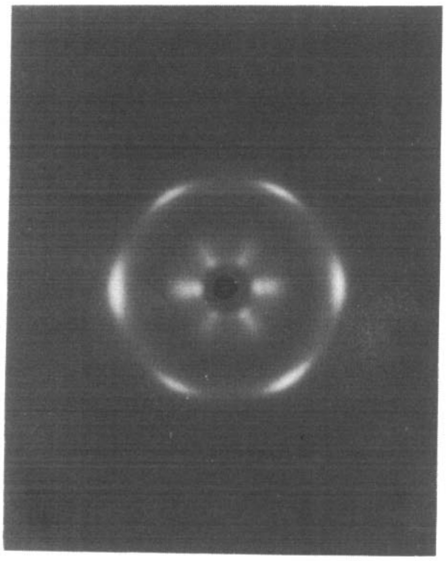

Figure 3 End-view WAXS pattern of double oriented nylon 13,13

obtained from doubly oriented samples. The unit cell parameters of the monoclinic crystal are as follows: $a = 9.22$ Å, $b = 4.94$ Å, $c = 34.47$ Å and $\beta = 121.08°$. The unit cell has two $H[-NH(CH_2)_{13}NHCO(CH_2)_{11}CO-]OH$ monomer units. The chain repeat distance in this crystal is less than the calculated fully extended chain by 0.4 Å. This is caused by a small chain twisting in the unit cell.

The crystal density of nylon 13,13 calculated from the unit cell is 1.04 g cm^{-3}. With this data, the density of the amorphous phase was also calculated with the aid of crystallinity measurements by d.s.c. The crystallinity and density of samples annealed at several temperatures were measured by the separate d.s.c. and density column methods. From this calculation, the density obtained for the amorphous phase of nylon 13,13 is 1.01 g cm^{-3}.

Drawing by solid-state extrusion

In the nylon family, hydrogen bonding substantially enhances both the melt flow activation energy and viscosity level. The hydrogen bonds act effectively as temporary crosslinks during the short time-scales of deformation involved in flow at high shear rates[16]. The lower nylons, such as nylon 6,6 and nylon 6, are difficult to solid-state extrude because of their abundant hydrogen bonding, which inhibits sliding displacement along consecutive hydrogen-bonded planes, a common deformation mode[17]. Therefore, nylon 13,13 may be more ductile than these lower nylons. Solid state co-extrusions were performed with a split polyethylene billet for nylon 13,13 in the barrel of an Instron rheometer at two different temperatures below the melting point (125 and 135°C). Compared with results on nylon 6 and nylon 6,6, this higher nylon proved to be relatively flexible. As a consequence, it can be extruded at a temperature 50°C below its melting point. The extrusion pressure was ~10 MPa, which was much less than required for the extrusion (~500 MPa)[1] of nylon 11 and nylon 12 at 190°C. The highest draw ratio (DR) obtained at 135°C is 4.5, which is almost the same as for nylon 6[18-20], nylon 11 and nylon 12[1]. This suggests that the amorphous phase is extended, the crystals oriented, both in the draw direction, but that the crystals are not disrupted and act as restraining crosslinks.

Results of extrusion draw from quenched samples are shown in *Figures 4–8*. The relationship shown for several physical properties of nylon 13,13 is given as a function of DR. *Figure 4* shows a rise in T_m with DR up to about 169°C at a DR of 4. This represents an 8°C increase over the undrawn samples (DR = 1). The percentage crystallinity, as measured by d.s.c., *versus* DR is shown in *Figure 5* to increase with DR from 20 to 34% at a DR of 4.

The crystal orientation function was measured by WAXS as a function of draw (*Figure 6*). The results

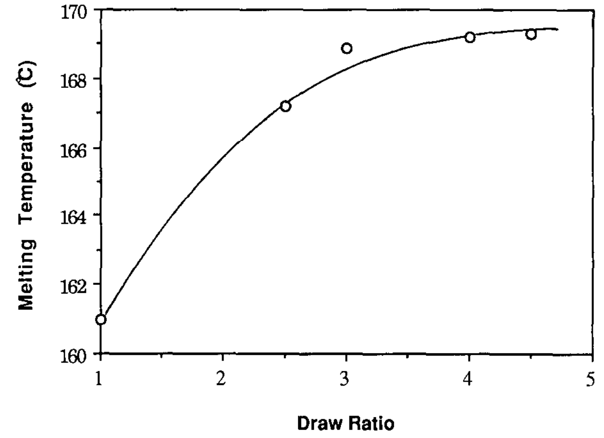

Figure 4 Plot of melting temperature onset of extrudates *versus* draw ratio

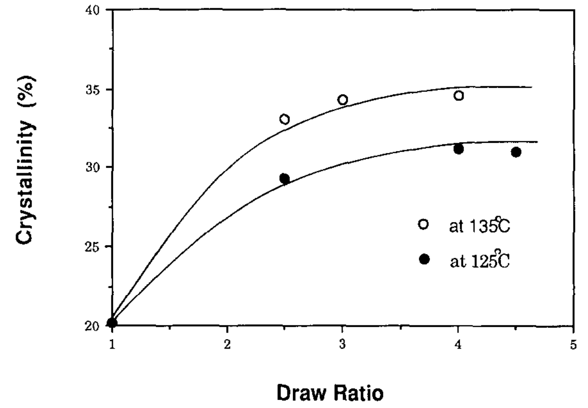

Figure 5 Plot of percentage crystallinity of nylon 13,13 *versus* draw ratio

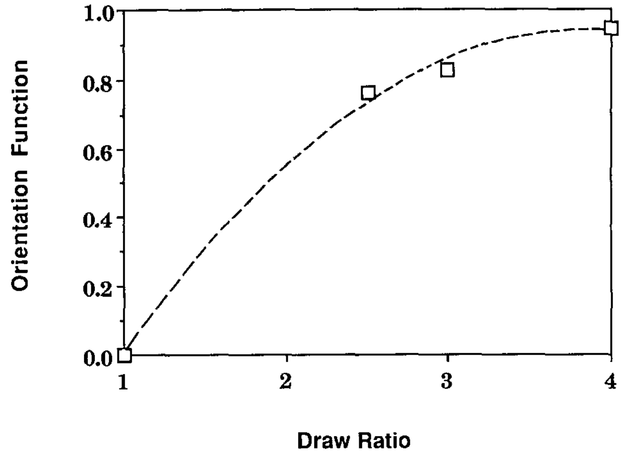

Figure 6 Plot of crystal orientation function of extrudates drawn at 135°C *versus* draw ratio

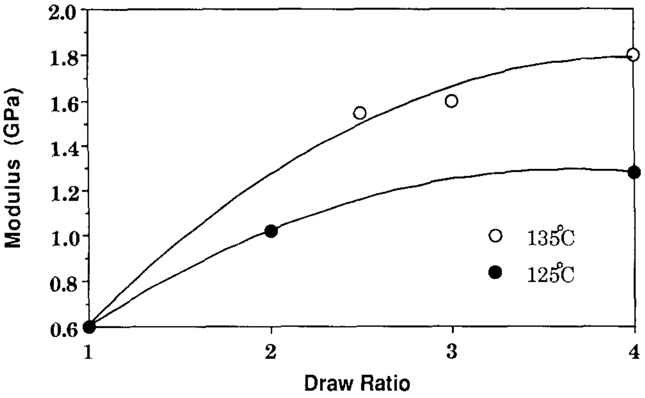

Figure 7 Plot of modulus *versus* draw ratio

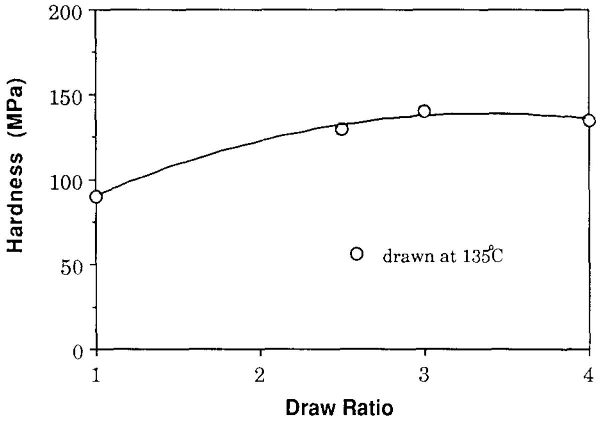

Figure 8 Plot of microhardness of nylon 13,13 *versus* draw ratio

indicate that the crystalline chain orientation develops more rapidly with DR than in high density polyethylene. It is very interesting to find that at DR of 4, the orientation function reached a saturated value of 0.944 at the draw temperatures studied.

Since extrusion is performed at a temperature lower than the crystallization peak temperature, an increment of crystalline content is generated by the stress. The crystal perfection of the extrudates is almost the same as a DR of >2.5, as judged by their melting temperature. So, a rapid increase in orientation function with DR is expected.

After extrusion, the tensile properties of nylon 13,13 are improved. *Figure 7* is a plot of Young's modulus against DR. The moduli increase from 0.6 GPa for moulded samples to 1.8 GPa for the extrudate with a DR of 4. From *Figure 5* it can be seen that, for property development, the higher draw temperature is more favourable. It is also interesting to find that the hardness increases with DR (*Figure 8*). The crystallinity increase due to draw is a reasonable explanation.

The influence of the initial crystallinity of nylon 13,13 on its extrusion was also studied. A sample was annealed at 140°C in a vacuum oven for 24 h: the crystallinity obtained was ~40%. The subsequent extrusion was unsuccessful when attempted in the same way as for the quenched sample. This can be explained in terms of the increased crystallinity which acts as a crosslinking point to prevent the chain slippage. The limitation of draw for this sample is 4, which may also be explained by the crystallinity formed on extrusion draw.

From this study, the conclusion may be drawn that samples with lower crystallinity and higher extrusion temperature favour draw.

CONCLUSIONS

In this initial study it has been found that the crystal of nylon 13,13 has a γ monoclinic form with unit cell crystal dimensions of $a = 9.22$ Å, $b = 4.94$ Å, $c = 34.47$ Å and $\beta = 121.08°$. The T_m° and the T_g of nylon 13,13 are found to be 183 and 56°C, respectively. The mechanical properties and density of nylon 13,13 extrudate increase with uniaxial DR. The solid state deformability of nylon 13,13 is much easier, requiring lower force than for lower members in the nylon family.

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