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Structure and properties of injection-moulded nylon-6

Part 1 *Structure and morphology of nylon-6*

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The microstructure and morphology of injection-moulded nylon-6 has been studied using wide-angle and small-angle X-ray diffraction, optical microscopy and a density measurement technique. A non-spherulitic surface layer consisting of a metastable pseudo-hexagonal γ phase surrounds the moulding and the thickness of the layer is sensitive to mould temperature. This outer structure gives way to a monoclinic α phase containing spherulites between 3 and 6 μm diameter. The central core of the moulding consists almost entirely of the α phase with spherulites 6 μm diameter, approximately. Exposure of nylon-6 to boiling water had no significant effect on the morphology of the moulding but the γ phase in the surface layer was transformed to the monoclinic α phase.

1. Introduction

The resistance to deflection or modulus of a polymer depends upon the nature of the inter-atomic bonds and the packing arrangements of the long chain molecules. Its resistance to collapse or yield strength is to do with the creation under stress of "defects" of some kind, the activation of molecular segments or the formation of kinks in molecules in the structure. The resistance to fracture or toughness is more subtle than the other two bulk properties – it depends upon localized effects; the cavitation process is generally recognized as the initial stage of practically all micro-mechanical regimes of fracture. These cavitation nuclei are small "imperfections" (~ 0.01 to 1.0 μm) in the structure.

The structure and morphology of a polymer is sensitive to the conditions under which it is shaped or moulded. An increase in melt temperature, for instance, decreases the viscosity and the tendency for molecular orientation in the moulding. The occurrence of molecular orientation is complicated by crystallization effects; alignment of polymer chains under stress affects the nucleation and growth of the folded chain lamallae which comprise the bulk of the crystalline solid. The crystalline morphology and degree of crystallization are sensitive to the processing conditions; increasing melt temperature [1, 2], or decreasing cooling-rate [3–5] or moulding pressure [2], for example, increases the size of the spherulite, and a range of structures can be obtained from embryonic spherulites to well-developed stacks of lamellae blocks [6–10]. While yield stress is approximately proportional to the amount of crystallinity, the effect of crystallinity on toughness is more complicated; it seems that a critical degree of crystallinity exists above which the toughness of a semi-crystalline polymer decreases rapidly [3, 6, 11, 12]; and an increase in spherulite size results in a drop in toughness [3, 5].

In Part 1, we attempt to identify the principal microstructural and morphological features, molecular orientation, crystallinity, spherulite size, of an injection-moulded semi-crystalline polymer (nylon-6). The techniques used to characterize

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structure included X-ray diffraction, optical microscopy and density measurement. We then see how processing variables, melt temperature, mould temperature and injection pressure affects structure, and the effect of water. In Part 2 we attempt to determine the distribution of residual stresses in injection-moulded nylon-6, the effect of processing variables, and the effect of water. Finally, Part 3 discusses the relationship between structure, yield strength and toughness.

2. Experimental details

2.1. Material and specimen preparation

Tensile bars of nylon-6 were injection-moulded using Akzo granules‡; the injection pressure was 31 MN m^{-2}; the mould temperatures were 25, 55, 70 and 85° C; the melt temperature was 250° C; and the cycle time was 25 sec.

2.2. X-ray diffraction

Each tensile bar was sectioned at the centre of the gauge length using a jeweller's saw (Fig. 1). Slices 40 μm thick were cut from each section using a base-sledge microtome. The plane of the slice can be defined by the flow direction and the normal to the plane of the moulding, i.e. the *XZ* plane. Wide-angle X-ray diffraction (WAXD) patterns were obtained for each slice in the *XZ* plane by exposing to Cu*Kα* radiation. The direction of the X-ray beam was perpendicular to the plane of the slice. The tube voltage and current were 50 kV and 35 mA, respectively, with an exposure time of 2 h, approximately. The specimen-to-film distance was 75.5 mm. Microdensitometer traces of the diffraction patterns were obtained using a Joyce–Loebl microdensitometer.

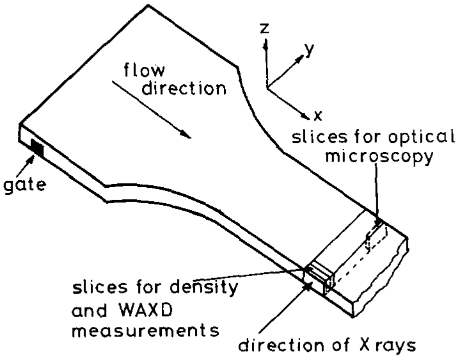

Figure 1 **Injection-moulded tensile specimens showing the sections cut for WAXD, SAXD, optical microscopy and density measurements.**

Small-angle X-ray diffraction patterns were also obtained with the beam in the *Y* direction. In this case, the exposure time was 48 h, approximately.

2.3. Optical microscopy

Slices of about 5 μm thickness were cut using an ultramicrotome and examined using a transmission optical microscope. Each slice was submerged in an oil film on a microscope slide and viewed in plane polarized light. A few of the surfaces were etched in a solution of 10% formic acid in methanol and viewed in reflected light. A Nomarski interference technique was used to enhance the contrast.

2.4. Density measurements

Density measurements were made on slices prepared in a similar manner to those used in the X-ray diffraction study. Each slice was immersed into a density gradient column consisting of a mixture of carbon tetrafluoride and toluene. Readings were taken 24 h after immersion.

3. Results and discussion

3.1. Density measurements

The variation of density through the thickness of nylon-6 for mould temperatures of 25 and 85° C is shown in Fig. 2. The density profile for a specimen moulded with a mould temperature of 25° C can be divided into four main regimes; (1) a surface layer of 200 μm thickness, approximately, having a density of 1.120 g cm^{-3}; (2) a region extending between 200 and 600 μm below the surface where density is directly proportional to thickness; (3) a region between 600 and 2000 μm below the surface where density is slightly sensitive to thickness; and (4) a central core in which density is constant at 1.132 g cm^{-3}. Where a hot (85° C) mould is used, the surface layer of constant density is absent and the density curve is shifted to the left.

If we assume a relationship between density and degree of crystallinity α of the form

$$\alpha = (\rho - \rho_a)/(\rho_c - \rho_a)$$

where ρ_a is the density of amorphous nylon-6 (1.080 g cm^{-3} [13]) and ρ_c is the density of the crystalline unit cell of nylon-6 (1.230 g cm^{-3} [14]) then we can replot the data in the form of percentage crystallinity versus distance from the surface

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‡ **These are granules of nylon-6 containing a high concentration of a nucleation agent to produce small spherulites.**

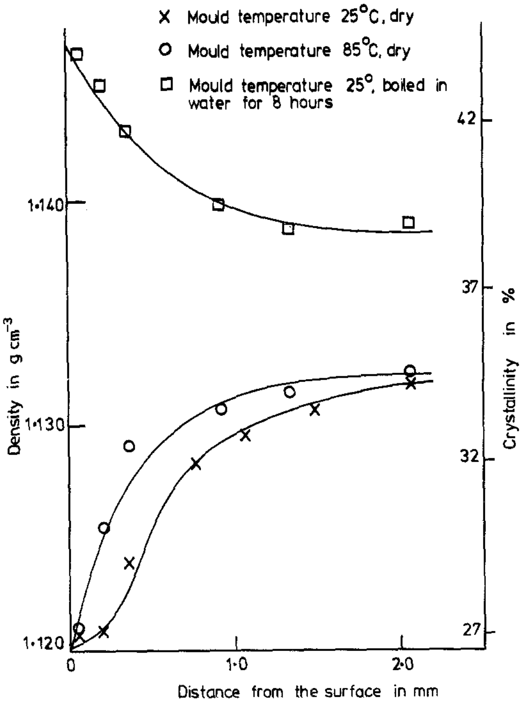


Figure 2 Density profile through the thickness of a nylon-6 moulding.

of the moulding. The material close to the surface has a crystallinity of 27%, approximately, and the centre of the moulding has a crystallinity of 35%, approximately, for both mould temperatures used (Fig. 2).

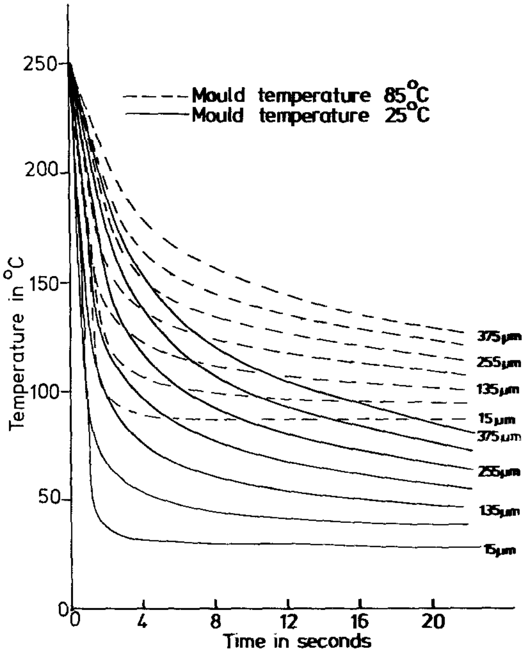


Figure 3 Theoretical cooling curves at different points in a nylon-6 injection moulding.

The crystallinity profile curves may be explained in terms of the rate of cooling of the polymer melt. Fig. 3 shows a plot of theoretical cooling curves for nylon-6 based on an analysis of Carshaw and Jaeger [15] (Appendix 1). In the surface layer of the specimen the cooling-rate is rapid for a mould temperature of 25° C and crystallization of nylon-6 is limited. Below the surface ($> 200\,\mu$m), the rate of diffusion of heat is reduced and additional crystallization is possible. A higher mould temperature (85° C) results in a lower cooling rate of the polymer melt and for a given depth beneath the surface of the moulding we observe a higher crystallinity. The slow rate of heat transfer at the centre of the moulding allows an equilibrium crystallinity to be achieved which is 35%, approximately.

3.2. Optical microscopy

Photomicrographs prepared from slices of nylon-6 are shown in Figs. 4 and 5. The surface layer of the moulding has a non-spherulitic structure; a few isolated spherulites have formed beneath the surface layer; and the central region has a spherulitic structure. Using a mould at 25° C has produced a

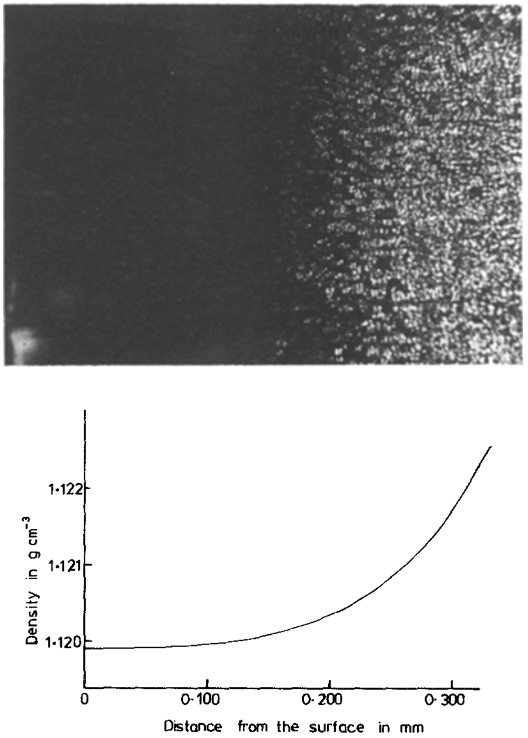


Figure 4 The spherulitic morphology of a moulding and density profile close to the surface of the moulding for a mould temperature of 25° C.

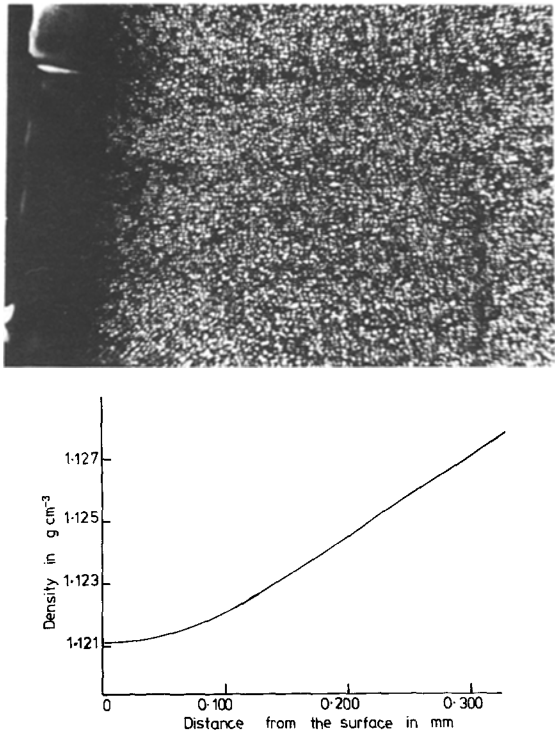


Figure 5 The spherulitic morphology of a moulding and density profile close to the surface of a moulding for a mould temperature of 85° C.

non-spherulitic surface layer 150 μm thick and a transition zone extending for a further 120 μm. Increasing the mould temperature to 85° C has reduced the extent of these two zones, by one-third, approximately, but the size of the spherulites in both cases are similar, between 3 and 6 μm in the transition zone and about 6 μm in the central region.

Inone [16] has shown that the time for the growth of a spherulite depends upon primarily melt temperature and if a nylon-6 melt is cooled from above its melting point to below about 110° C in less than 3 sec, then no spherulites will form.

If we look at the theoretical cooling curve for the nylon-6 (Fig. 3) at a point 150 μm below the surface of a moulding for a mould temperature of 25° C and at a point 45 μm below the surface for a mould at 85° C, we see the curves intersect at 110° C and 1.5 sec. It suggests that no spherulites are likely to form in the nylon-6 provided the melt cools from 250° C to 110° C in less than 1.5 sec; slower cooling-rates will result in the growth of spherulites. This is in agreement with our findings.

The inflection in the density curve close to the surface of the moulding with distance corresponds to the appearance of spherulites (Figs. 4 and 5).

3.3. X-ray diffraction measurements

3.3.1. Wide-angle X-ray diffraction (WAXD)

The wide-angle X-ray diffraction (WAXD) patterns obtained from slices taken within 300 μm of the surface show a single-ring pattern; slices cut at the centre of the moulding exhibit a double-ring WAXD pattern (Fig. 6). The single-ring and two double-ring patterns are superimposed for sections of nylon-6 cut between the surface layer and central core.

The single-ring pattern is characteristic of the pseudo-hexagonal γ phase, a metastable crystalline phase formed at low temperatures in short times. As this pseudo-hexagonal structure becomes more ordered then the sharper becomes the reflection and the smaller is the associated d spacing [13]. The monoclinic α phase, shown by the double-ring pattern, is a stable crystalline phase of nylon-6 which is formed at higher temperatures and in longer times compared with the γ phase. The more ordered the α phase, the larger is the d (200) spacing and the smaller is the d (202 + 002) spacing. The α phase has a higher density than the γ phase.

The γ phase exists in a nylon-6 moulding close to the surface ($\leqslant$ 300 μm) when a mould temperature of 25° C is used. A typical microdensitometer trace of the characteristic single-ring pattern shows an intensity maximum at a 2θ value of 21.3° and a d spacing of 4.16 Å (Fig. 7). A microdensitometer trace of the superimposed single-ring and double-ring patterns in the intermediate zone of a moulding (where the depth from the surface of the moulding is between 300 and 600 μm), shows a shift in the γ phase diffraction peak to a higher 2θ value and the corresponding d spacing becomes 4.13 Å; the α phase diffraction maxima are found at 2θ values of 23.1° and 20.5° corresponding to a d (200) spacing of 4.32 Å and a d (202 + 002) spacing of 3.85 Å, respectively (Fig. 8).

The structure at the centre of the moulding consists almost entirely of the α phase (Fig. 9). The weak intensity maximum reveals the presence of a small amount of γ phase. The d (200) spacing of the monoclinic crystal has increased to 4.35 Å and the d (202 + 002) spacing has decreased to 3.84 Å. Table I summarizes the changes in crystal structure with distance from the surface of a

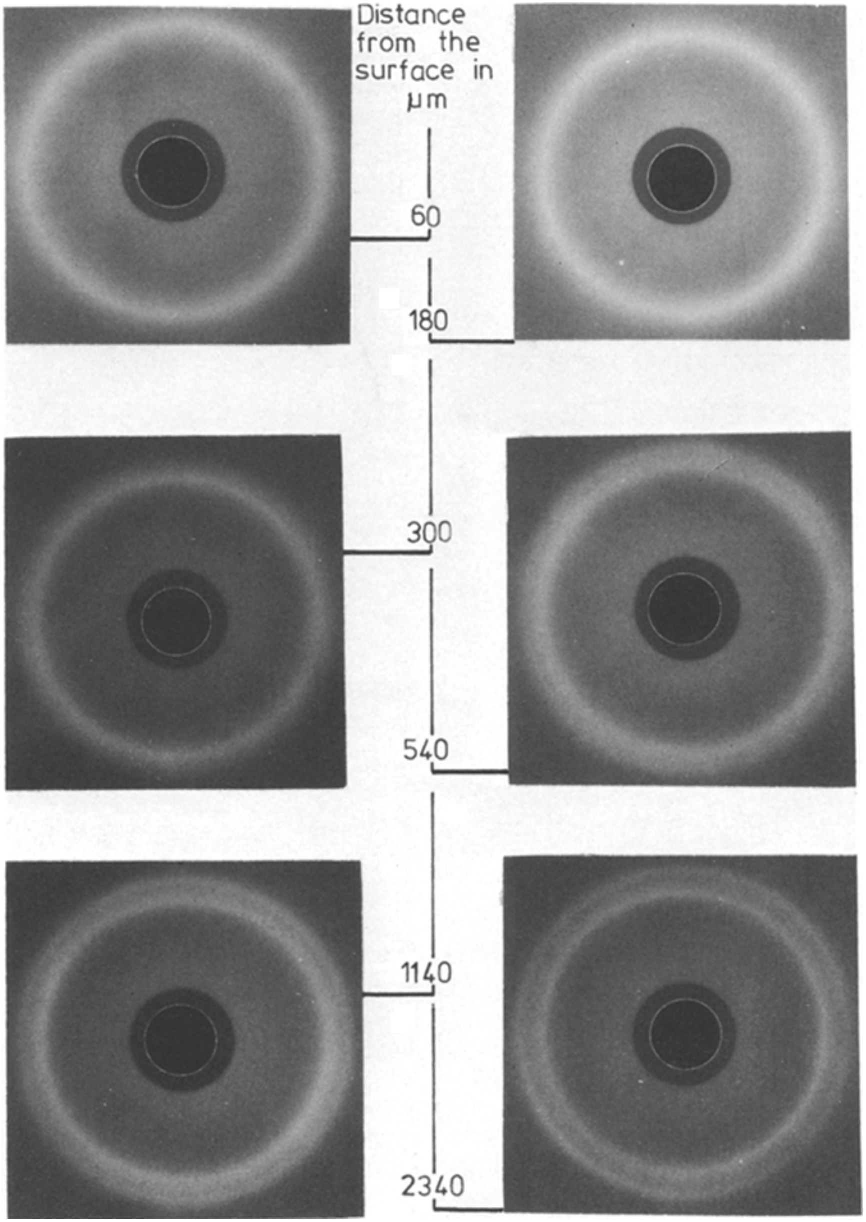


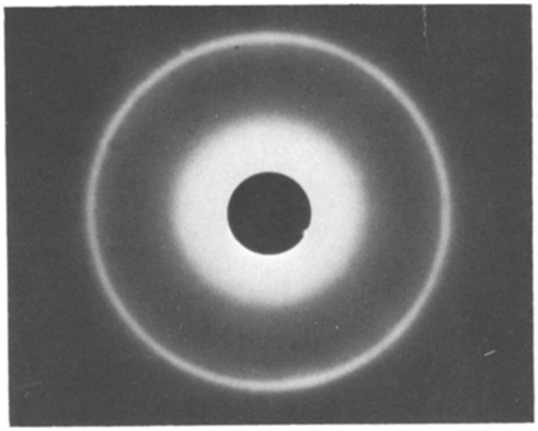
Figure 6 WAXD patterns obtained from slices cut at various depths from the surface of nylon-6. The mould temperature was 25° C.

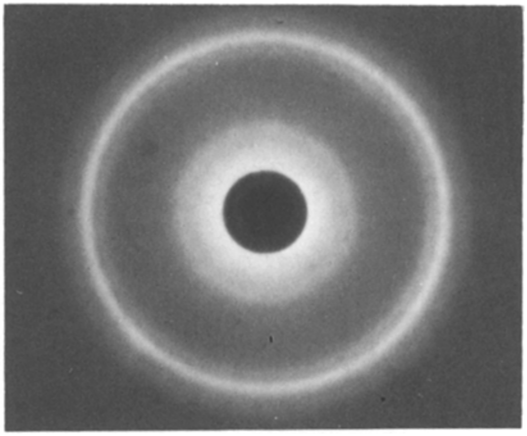
nylon-6 moulding using a mould temperature of 25° C.

Similar observations were made for mouldings using a mould temperature of 85° C but the α phase and the γ phase disappears at smaller distances below the surface. This is a direct consequence of the differences in cooling-rates for the two mouldings; the slower the cooling rate the greater is the volume fraction of α phase compared to the γ phase. The low density of nylon-6 in the surface layer is associated with the pseudo-hexagonal γ phase while the maximum density in the centre of the moulding is connected with the monoclinic α phase.

3.3.2. Small-angle X-ray diffraction (SAXD)

A typical SAXD pattern corresponding to the centre of a moulding for a mould temperature of 25° C is shown in Fig. 10. The long spacing





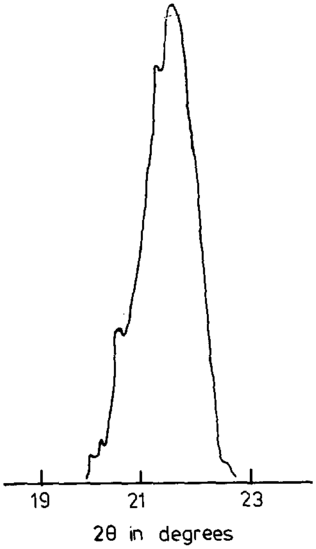


Figure 7 A microdensitometer trace of a WAXD pattern obtained from a slice taken at the surface of a moulding.

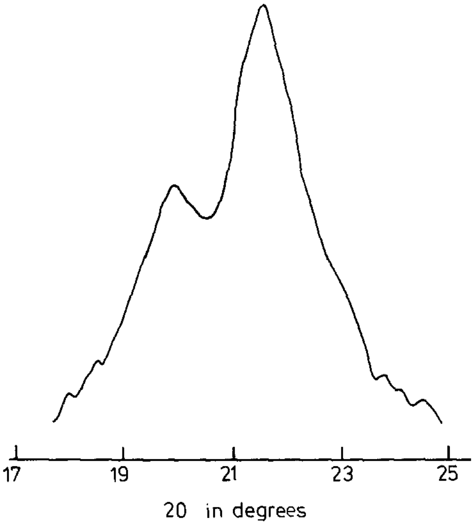


Figure 8 A microdensitometer trace of a WAXD pattern obtained from a slice taken in a transition zone of the moulding.

between centres of gravity of adjacent α crystals is 85(± 5) Å. Young [17] obtained a value of 87 Å and Sakurai *et al.* [18] measured 105 Å for nylon-6 fibres.

3.4. Molecular orientation

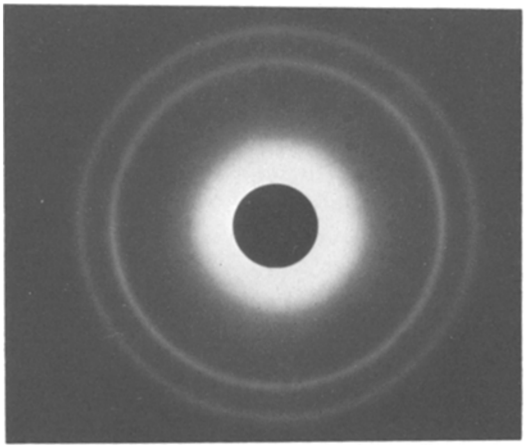
All of the diffraction patterns obtained for various positions in the mouldings have uniform intensity around the circumference of each ring and there is no evidence of any molecular orientation. WAXD patterns from slices in the *YZ* plane provide no evidence of molecular orientation. The melt viscosity of nylon-6 is low; elongational and shear forces in the melt during injection mouldings are correspondingly low and therefore little molecular orientation is formed. Any molecular orientation that may occur during moulding quickly disappears owing to the short relaxation time for the polymer.

3.5. Degree of crystallinity

The degree of crystallinity in nylon-6 can be estimated using an X-ray technique [19, 20]. The crystallinity content is given by

$$X_c = \frac{I_c}{I_c + I_a},$$

where I_c and I_a are the X-ray intensities due to the crystalline and amorphous phases, respectively. A WAXD pattern for amorphous nylon-6 is shown in Fig. 11 and was obtained from splat-quenched nylon-6. The intensity of trace due to the crystalline phase is calculated by subtracting the intensity of trace due to the amorphous phase from the



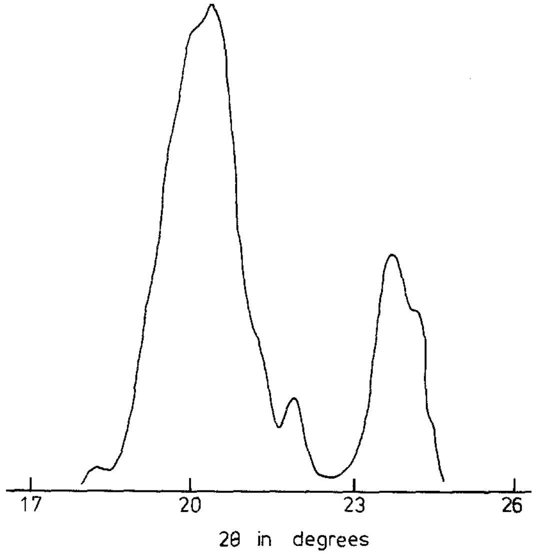


Figure 9 A microdensitometer trace of a WAXD pattern obtained from a slice taken at the centre of a moulding.

intensity of the diffraction pattern for the sample. A comparison is made between the crystallinity content determined using density measurements and the X-ray diffraction method (Table II). Reasonable agreement is found except for the degree of crystallinity in the surface layer of the moulding.

TABLE I Crystal structure of nylon-6 injection mouldings

Position in moulding	Crystal structure	Characteristic d spacing (Å)
Close to surface	γ	4.16
Intermediate position	$\gamma + \alpha$	$\gamma/d = 4.13$ $\alpha/d\ (200) = 4.32$ $d\ (202 + 002) = 3.85$
Centre	α	$\alpha/d\ (200) = 4.35$ $d\ (202 + 002) = 3.84$

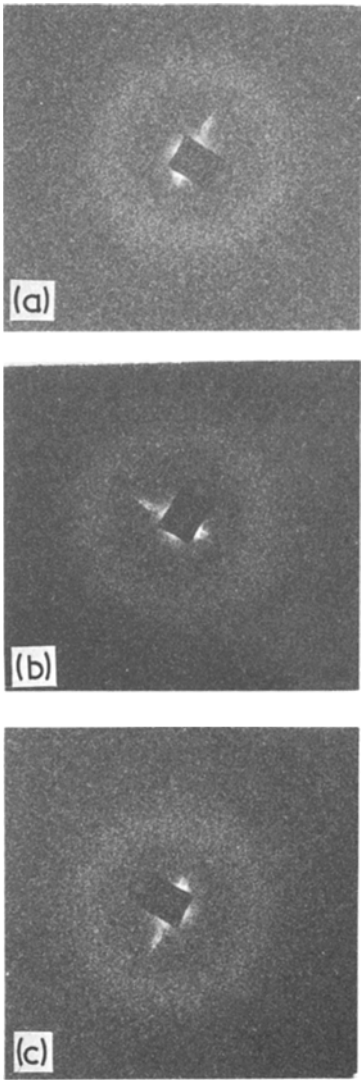


Figure 10 SAXD patterns obtained from a slice taken at (a) the centre of a moulding, (b) the surface of a wet moulding, and (c) the centre of a wet moulding.

4. Exposure to water

Nylon-6 is hygroscopic and absorbs water from the atmosphere. Some of the mouldings were boiled in distilled water for up to 8 h and increased in weight by 10%, approximately. The variation of density with distance from the surface of the moulding is shown in Fig. 2. After exposure to water the density of nylon-6 is increased with the density of the surface layer higher than the centre of the moulding, the inverse of the density–distance relationship observed for dry mouldings. The density of the surface layer increased by about 2.5% compared to a value of only 0.6% for the central core.

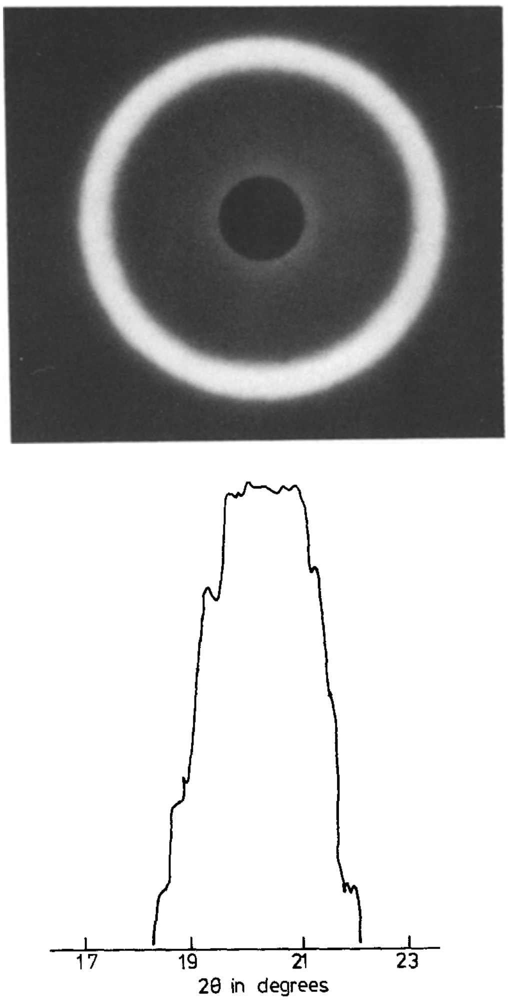


Figure 11 WAXD pattern and its microdensitometer trace obtained from splat-quenched nylon-6.

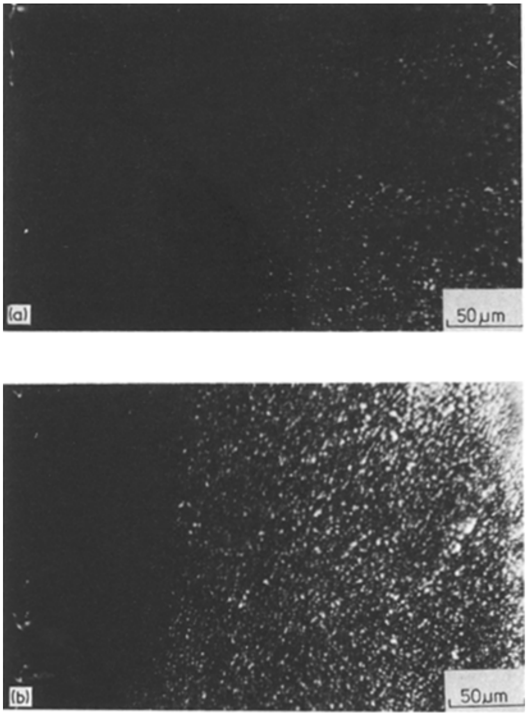


Figure 12 Optical micrographs of the surface of nylon-6 after boiling in water for 8 h. The mould temperature was (a) 25° C, and (b) 85° C.

This difference in the increase in density through the thickness of the moulding on wetting has important effects on the residual stress distribution (Part 2).

An increase in water content of nylon-6 lowers the glass transition temperature below 0° C and plasticizes the polymer at room temperature, molecular mobility increases and secondary recrystallization can occur – the amorphous phase can transform to a crystalline state which results in an increase in density [6, 10].

Photomicrographs of the surface of nylon-6 after exposure to water are shown in Fig. 12. The morphological features of the dry mouldings are retained, a non-spherulitic surface layer, a spherulitic central core and a transition zone in which isolated spherulites appear, and the extent of these portions is essentially unaffected. Water absorption allows some reorganization of the molecules into a more ordered structure; however, large scale reorganization of the molecular chains needed to produce changes in the spherulitic

TABLE II The crystallinity of nylon-6 injection mouldings determined using X-ray diffraction and density measurement techniques

Position	Density ($g\,cm^{-3}$)	% crystallinity	
		density measurement	X-ray diffraction
Surface	1.120	27	11
Transition	1.129	34	27
Centre (dry)	1.134	37	34
Centre (wet)	1.140	41	45

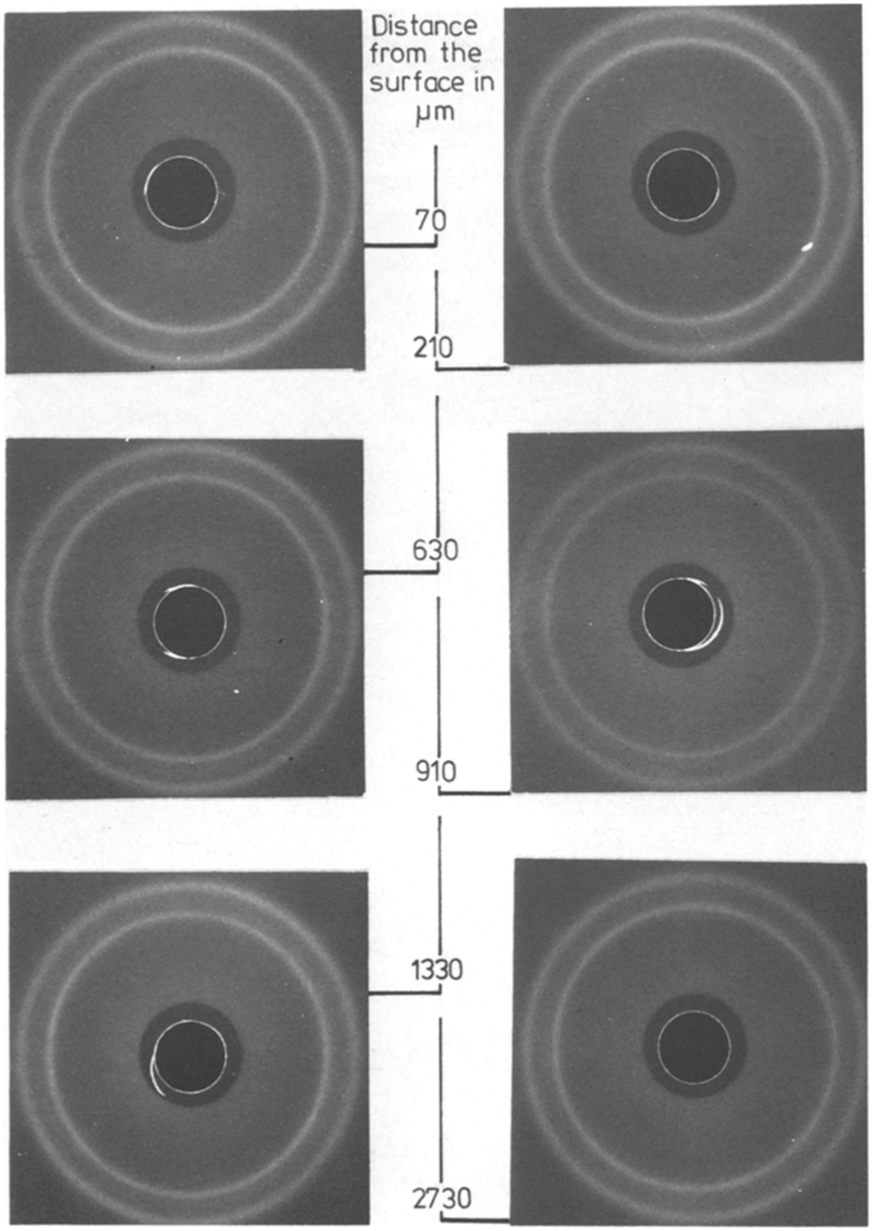
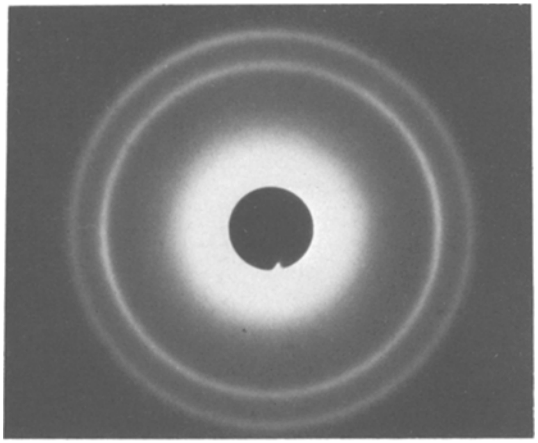


Figure 13 WAXD patterns obtained from slices cut at various depths from the surface of nylon-6 after boiling in water for 8 h. The mould temperature was 25° C.

morphology of a moulding cannot be realized simply by wetting the mouldings.

WAXD patterns for nylon-6 at various distances from the surface of a moulding are shown in Fig. 13. The double-ring pattern characteristic of the monoclinic α phase is found even close to the surface of the moulding. Unlike the corresponding patterns for dry mouldings, the single-ring pattern characteristic of the γ phase does not appear. A microdensitometer trace of the pattern is shown in Fig. 14. The two maxima in the diffraction intensity correspond to a d (200) spacing of 4.36 Å and a d (202 + 002) spacing of 3.75 Å. The larger d (200) spacing and smaller d (202 + 002) spacing of the monoclinic phase in the wet moulding compared to the dry moulding indicates a more ordered monoclinic lattice after exposure to water. In nylon-6, the stable crystal structure is the



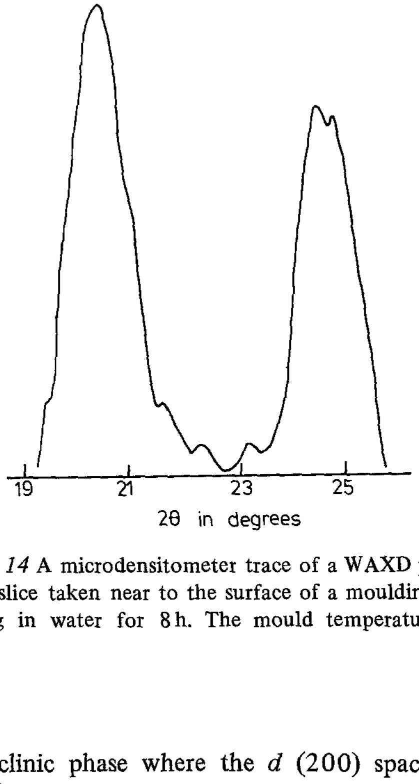


Figure 14 A microdensitometer trace of a WAXD pattern for a slice taken near to the surface of a moulding after boiling in water for 8 h. The mould temperature was 25° C.

monoclinic phase where the *d* (200) spacing is 4.50 Å and the *d* (202 + 002) spacing is 3.70 Å [13].

SAXD patterns obtained from dry and wet mouldings using a mould temperature of 25° C are shown in Fig. 10. The long spacing of the crystals in the surface layer and centre of the wet moulding is 84 (± 5) Å and 83 (± 5) Å, respectively, which are similar to the long spacing of 85 (± 5) Å found in the centre of a dry moulding.

Young and Bowden [21] suggest that the long spacing depends upon the thickness of the lamella. In the case of wet and dry mouldings, the lamella separation, therefore, is the same.

5. Conclusions

No molecular orientation was found in the mouldings. The crystallinity of nylon-6 mouldings varies with distance from the surface; the crystallinity content is lowest at the surface of the moulding and increases with distance eventually reaching a constant value. Increasing the mould temperature results in an increase in the average crystallinity content of the moulding. The size of the spherulite in prenucleated nylon-6 is 7 μm, approximately, and is independent of mould temperature. A non-spherulitic surface layer is found in the mouldings and the thickness is inversely dependent upon mould temperature. Exposure to water of nylon-6 increases the crystallinity but does not affect the structure and morphology of the spherulite.

Appendix 1. Variation of temperature with time of a nylon-6 melt cooled in a mould

The approach is one taken by Carshaw and Jaeger [15]. The temperature, T, at a point some distance, y, from the centre of the moulding after time, t, is given by

$$\frac{T-T_\infty}{T_0-T_\infty} = 2\sum_{n=0}^{\infty}\frac{(-1)^n}{\pi(n+\frac{1}{2})}\left[\cos\,(n+\tfrac{1}{2})\,\frac{\pi y}{6}\right] X$$

$$\exp - \left[(n+\tfrac{1}{2})^2\pi^2\,\frac{\alpha t}{b^2}\right]$$

where T_∞ = mould temperature (25 and 85° C), T_0 = melt temperature (250° C), $2b$ = thickness of moulding (1.5 mm), α = thermal diffusivity of the nylon-6 melt ($5 \times 10^{-4}\,\text{cm}^2\,\text{sec}^{-1}$).

Acknowledgements

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