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On the morphology of oriented nylon-12*)

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Abstract: The morphology of drawn and annealed sheets of nylon-12 was investigated by transmission electron microscopy of stained sections, and the results compared with equivalent small-angle X-ray scattering (SAXS) patterns. A three-component structure was observed, consisting of crystalline (C) and amorphous (A) regions in the microfibrils and an interfibrillar component whose density was deduced to be intermediate between that of the C and A regions. The crystallite width was given satisfactorily by a Guinier analysis of the SAXS profile.

Key words: Electron microscopy, staining, morphology, nylon-12, orientation.

Introduction

A detailed knowledge of the arrangement of crystalline and amorphous regions in aliphatic polyamides (nylons) is desirable from the point of view of understanding their mechanical properties. However, the morphology is difficult to image satisfactorily by electron microscopy, so that there have been relatively few reports on the structure of nylons in the scientific literature using this method. Staining electron microscope specimens with chlorosulphonic acid, which has been applied successfully to polyolefines (e. g. 1, 2) is inapplicable for the polyamides, due to the strong polar nature of the molecules. In this work we have adopted a staining method using OsO_4 and formaldehyde, as proposed by Weber and coworkers [3].

In this paper, transmission electron microscope results are presented for drawn and annealed nylon-12 sheets, and the results compared with the corresponding small-angle X-ray scattering pattern.

Experimental

Starting material was "Vestamid L 2102 F" nylon-12 granules supplied by the firm Hüls AG, Marl, W. Germany. The granules were dried at 80 °C before being compression moulded at 220 °C into sheets of 1 mm thickness. The sheets were quenched into cold water. 6 cm wide strips were then drawn at 20 °C at a rate of 10 mm/min to a draw ratio of 3 : 1. Subsequently the cold-drawn sheets were annealed with free ends in a silicone oil bath at 170 °C for 17 hours. The final density of the drawn and annealed sheets was 1.0296 g/cm^3.

Specimens were prepared for transmission electron microscopy as follows: strips 8 mm long and 3 mm wide were stored at room temperature in an equal mixture of 1% aqueous solution of osmium-(VIII)-oxide and 40% aqueous solution of formalin for times between 80 and 200 hours. The staining reaction could be observed through a gradual darkening of the samples. Subsequently they were stored for several hours in distilled water and dried in air. The OsO_4 is thought to be reduced by formaldehyde and to react selectively with the carbonamide groups [3] in the amorphous regions of the polymer.

The contrasted strips were cut into sections suitable for transmission electron microscopy (TEM) by means of an ultra-microtome with the glass knife cooled to − 20 °C. A JEOL JEM T7 TEM was used for the investigation (60 kV operating voltage). For this work, all the sections were cut parallel to the draw direction and perpendicular to the plane of the sheet.

Comparative small-angle X-ray scattering (SAXS) measurements were made using point collimation and monochromatic CuKα radiation. The beam direction was normal to the plane of the corresponding electron microscope sections. SAXS measurements were made on uncontrasted specimens prior to sectioning.

Results and Discussion

Electron microscopy

Figure 1 shows a transmission electron micrograph of the morphological structure of oriented and annealed nylon-12 sheet. By means of optical diffraction patterns of the TEM negatives, we deduced that

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*) Dedicated to Prof. Dr. R. Bonart on the occasion of his 60th birthday.

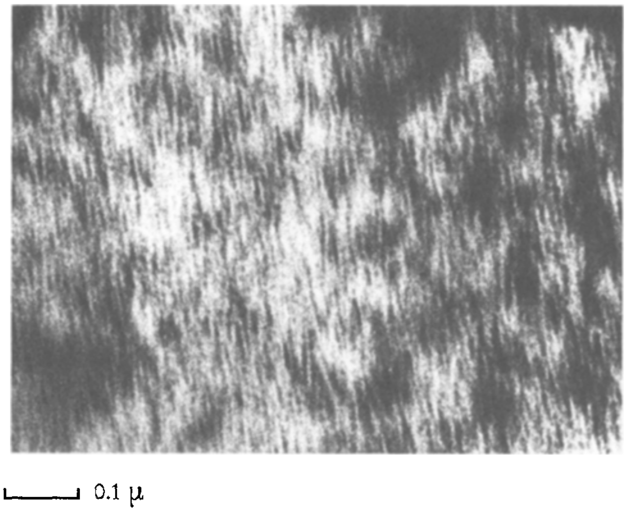

Fig. 1. Electron micrograph of drawn and annealed nylon-12 (draw direction vertical)

Table 1. Drawn and annealed nylon-12

Drawn and annealed nylon-12		(values in nm)
Electron microscopy		
Crystal-amorphous periodicity	L	14 ± 2
Width of microfibrils	D	9 ± 3
Est. thickness of interfibrillar regions		5
Small-angle X-ray scattering		
SAXS long period		16.4 ± 3
Ave. radius of gyration of scatterers		1.87
Calculated microfibril diameter		7.4

the draw direction lies vertically in the diagram. This means that the vertical stripes are of a fibrillar, rather than a lamellar, nature. On the positive, the crystalline regions are light and the amorphous regions dark. Microfibrils can be seen consisting of alternating blocks of crystalline and amorphous regions. Between the microfibrils lie essentially continuous interfibrillar regions of noncrystalline material. From the electron micrographs, the schematic structural model shown in figure 2 is suggested for the morphology of oriented nylon-12. This is similar to that proposed by Prevorsek and coworkers for nylon-6 fibres [4].

The dimensions of the various regions as viewed in the electron microscope are given in table 1. The errors are relatively large, since it was difficult to judge exactly where the boundary between regions lay, i. e. the image is smeared both by the resolution capability of the microscope (ca. 1 nm) and by the likelihood that the phase boundaries themselves are diffuse. The values given are average values for the specimen as a whole.

Small-angle X-ray scattering

The corresponding SAXS pattern is shown in figure 3. This is a two-point meridional pattern with no equatorial scattering. The spacing of the reflections gives a long period of 16.4 ± 3 nm (table 1), which agrees well with the crystal-amorphous periodicity seen in the microfibrils, i. e. the microfibrils do not appear to have been swollen by staining.

The absence of equatorial streaking in the SAXS diagram is at first surprising, since the TEM images show distinct fibrillar structures. This can be understood as follows: in the TEM specimens (e. g. fig. 1), the staining material has diffused into the interfibrillar regions and produced strong contrast between microfibrillar and interfibrillar regions, which leads to equatorial scattering, as is indeed found in the optical diffraction pattern of the TEM negative (not shown here). In the SAXS pattern of uncontrasted material, on the

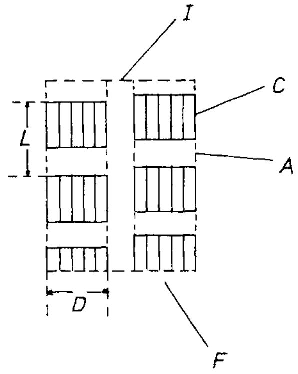

Fig. 2. Schematic model of the structure of oriented nylon-12 (interfibrillar region I; crystal C; amorphous A; microfibril F)

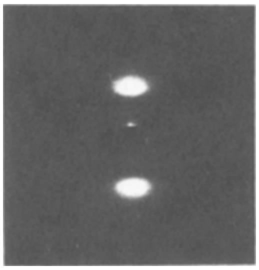

Fig. 3. Small-angle X-ray scattering pattern for oriented nylon-12 (corresponding to TEM image of fig. 1)

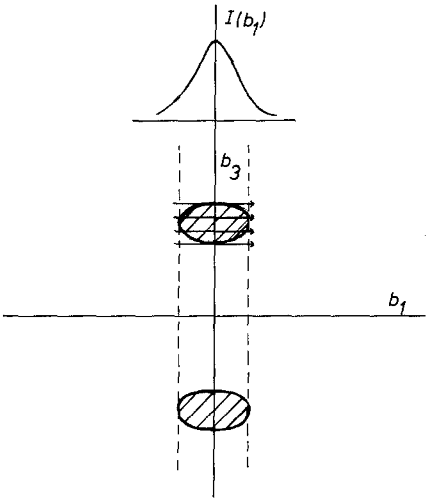

Fig. 4. SAXS pattern (schematic) showing b_1 and b_3 where $b(b_1, b_2, b_3)$ is the scattering vector

other hand, the absence of equatorial scattering suggests that the projection of the electron density on the equator is constant. In other words, the average density of the microfibrils is approximately the same as that of the (uncontrasted) interfibrillar regions.

The horizontal intensity profile of the SAXS meridional reflection (in the b_1 direction of fig. 4) was determined for several values of b_3 using a position sensitive detector. The half-width of the scattering profile was approximately independent of b_3, which suggests that the reflection profile is caused chiefly by crystal width effects. This finding is in direct contrast to the case of polyethylene, where the reflection profile increases in width with increasing b_3 and is related to inclination of the crystal/amorphous interfaces [2].

For nylon-12 it therefore seems appropriate to apply Guinier's equation [5]

$$I(b_1) \approx I_O \cdot \exp\left(-4\pi^2 R_G^2 b_1^2\right)$$

where $I(b_1)$ is the intensity profile in the b_1 direction in the scattering diagram, I_O is the maximum intensity and R_G is the average inertial distance [5] or radius of gyration of the scattering units from their centre of gravity. Here, it has been assumed that all the microfibrils are aligned perfectly in the draw direction. The equation takes no account of interparticle scattering effects.

From the slope of a Guinier plot of ln I versus b_1^2, R_G was estimated to be 1.86 nm. R_G is the fundamental quantity determined here from the scattering profile. The above analysis is equivalent to the method of Bolduan and Bear [6], if it is assumed that the diffracting elements are of cylindrical cross section. In that case, the effective radius (R) of the scattering cylinders is given by $R = 2\,R_G$, and their average width $D = 2\,R = 4\,R_G = 7.4$ nm.

If, on the other hand, the diffracting elements were ribbonshaped and aligned parallel to the plane of the specimen sheet, then the thickness of the ribbons D would be slightly different and given by $D = 2\sqrt{3}\,R_G = 6.4$ nm.

Other microfibrillar cross-sectional shapes and alignments about the draw direction could in principle act as equivalent scattering centres and cause the same SAXS pattern. However, without additional measurements of the SAXS pattern in different directions it was not possible here to decide which cross-sectional shape for the microfibrils would be most appropriate. The good general agreement within experimental error with the average microfibrillar width as seen by electron microscopy (see table 1) shows us clearly however that the microfibrils as scatterers are responsible for the horizontal spread in the meridional SAXS reflection, and that the Guinier equation gives a good estimate of the width.

Finally, it should be mentioned that the slope of the Guinier plot was not quite constant; on the basis of the microfibrillar model this could be caused by a spread in microfibrillar thicknesses. We have in fact above calculated an average R_G from the average slope of the Guinier plot. If the data are analysed in an alternative way using Bonart's theory of paracrystalline layer lattices [7], the measured intensity profile can be understood in terms of directional fluctuations of the neighbouring crystals and the smoothing region over which the lateral structure is fairly continuous. The smoothing region is related to the width of the microfibrils observed in nylon-12. A detailed account of this latter analysis is to be presented in the future.

Conclusion

The conclusions to be drawn from this work are firstly that the morphology of oriented nylon-12 contains essentially three components, as proposed by Prevorsek for nylon-6 [4]. In this "three-phase" model, the density of the interfibrillar material (I) is intermediate between that of the crystal (C) and amorphous (A) regions in the microfibrils (F). The nature of the A material is therefore different from that of the I material, i. e. the regions have different density, are probably differently oriented, and they probably contain different defects (such as proportion of chain ends, chain folds etc.), although they are both noncrystalline. The morphology of nylon-12 is thus different from that of, for example, polyethylene, in that there is a continous amorphous phase in the draw direction for nylon, whereas polyethylene contains crystal continuity [8, 9]. This has already been shown to be the case for nylon-6 as a result of mechanical modelling by Lewis and Ward [10] and by Owen [11]. Furthermore, we should like to emphasise that a meridional SAXS reflection without equatorial streaking does not automatically imply the presence of an extended lamellar structure; only the projection of the structure on the equator is constant. This has possible implications for other morphological investigations of semicrystalline polymers which have been made solely using SAXS. It is desirable to complement SAXS measurements where possible with equivalent electron microscope images. Finally, we have shown that for nylon-12 use of Guinier's equation gives a reasonable estimate of the average microfibrillar width.

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