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Comparison of different techniques for the observation of the lamellar texture of isotactic polypropylene: TEM of surface replicas, TEM after staining, and SFM

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Summary

In the present study three different techniques have been employed to observe the lamellar texture of isotactic polypropylene (iPP) crystallized from the melt under the influence of shearing: (a) Transmission electron microscopy (TEM) of surface replicas of permanganically etched samples (b) TEM of thin sections of Ruthenium-oxide stained samples and (c) Scanning force microscopy (SFM) in contact mode of permanganically etched samples. The aim was to assess their relative merits in terms of practicability, resolution and type of information.

Introduction

It is well known that the lamellar texture of semicrystalline polymers is strongly influenced by the processing conditions and that its detailed characterization can provide valuable insights into the process of solidification as well as the ensuing thermal and mechanical properties of the polymer. Hence methods for the direct observation of lamellae have been developed over the past 40 years.

The lamellar structure of solution-crystallized aggregates of iPP was first investigated by Khoury in 1966 (1), who prepared surface replicas for electron microscopic examination. The direct observation of the lamellar texture of melt-crystallized iPP, however, has only been possible since the adaptation by Norton and Keller in 1983 (2) of the method of permanganic etching and subsequent surface replication originally developed for polyethylene. This method has been applied in several laboratories and has provided excellent images. Not much later a second method was developed (3) which is based on staining the samples with Ruthenium-oxide. More recently, direct imageing of iPP structures by means of the scanning force microscope has been reported, first of epitaxially crystallized material (4,5), and subsequently also of 'bulk' crystallized polymer, oriented by uniaxial stretching (6,7). In the present comparative study all three methods have been applied to the same shear-crystallized sample.

Materials

Samples were kindly provided by CEMEF (8). Isotactic polypropylene (M_w = 377000,

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supplied by Borealis AS, Norway) was crystallized isothermally from the melt under shear between two moving glass plates ($T_c = 125°C$, shear rate $\dot{\gamma} = 6.2sec^{-1}$) yielding sheets of about $300\mu m$ thickness.

Results and discussion

Method 1: TEM of surface replicas
The surface replica method offers the possibility of producing rather striking, very well defined images of lamellar structures larger than about $10nm$ (*Figure* 1). The resolution is eventually limited by the grain-size of the Pt/Pd shadowing which lies at around $5nm$. However, it is in most cases also the most time-consuming method. The preparation of a set of replicas takes one day, then follows a waiting time of at least two days during which the polyacrylic acid glue (which serves to hold the replica during removal from the sample) dries, followed by another day of final preparation and eventually observation in TEM. Furthermore, the replica preparation requires some experience, in particular in the case of polypropylene where the lamellar texture tends to be fine because of cross-hatching. Finally, by its very nature, the method can only be applied to surfaces, and hence the structure through fairly thin samples like e.g. injection moulded parts, cannot readily be observed. Nevertheless, the excellent visualization of the texture can still make the method worthwhile in many cases.

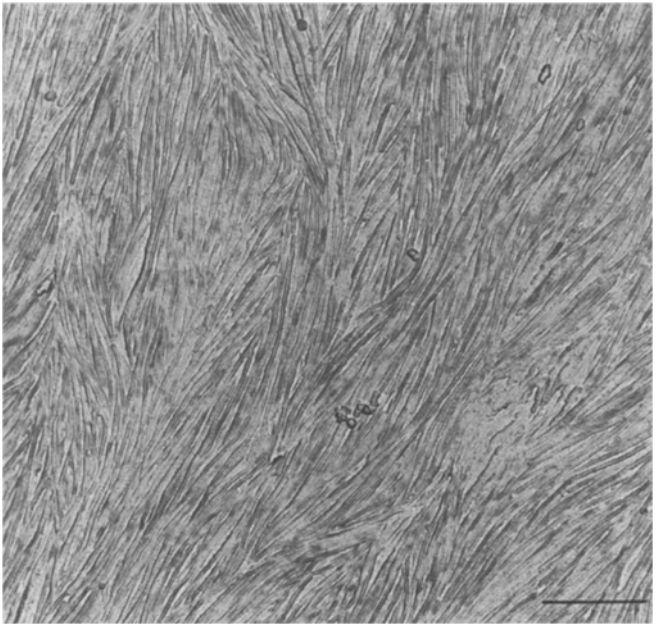

Figure 1:
TEM micrograph of a surface replica of shear crystallized polypropylene. The top surface, parallel to the deformation field, is viewed. The bar is $1\mu m$ long.

Method 2: TEM of stained samples
TEM of stained samples is in principle a much simpler and faster method since it requires only the simple preparation of the Ruthenium-oxide staining solution as described in Reference (3), the immersion of the samples for about 16 hours and subsequent cutting on an ultramicrotome with a diamond knife. This last step requires some experience in cutting samples thin enough ($50 - 80nm$) for transmission elec-

tron microscopy. Two problems can arise during observation. Firstly, beam damage leads to shrinking of the sample. Hence the lamellae appear much thinner than in the replica method (compare the length scales in Figures 1 and 2). Secondly, lack of contrast in large regions of the sample. In the present case, both difficulties may be related to the dense texture of shear-crystallized polypropylene which prevents the staining agent to diffuse into the sample, and hence provide both contrast as well as fix the material. Although roughly the same resolution can be obtained as with the replica method (i.e. individual lamellae), the images appear much less sharp (*Figure 2*), and it is more difficult to visualize large regions. The advantage of the method is that it is possible to cut slices in different directions and, if in addition embedding in resin is used, the structural profile of even very thin samples can in principle be observed.

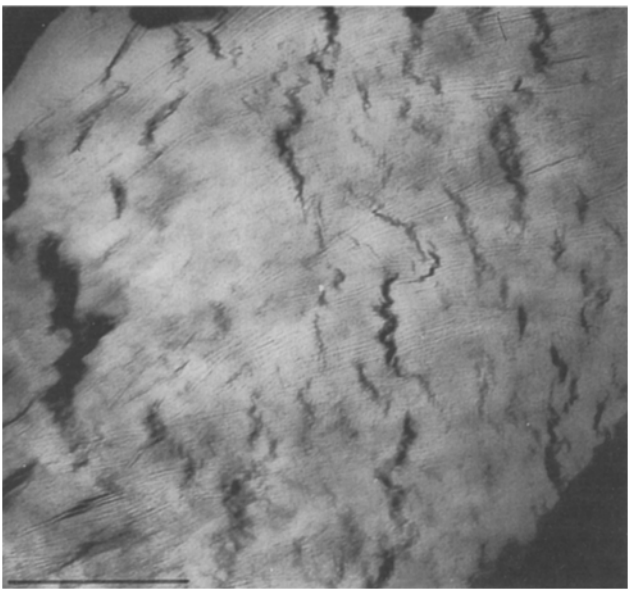

Figure 2:
TEM micrograph of a stained sample, cut normal to the top surface, hence the internal structure is revealed. The sample has shrunk in the beam, so the lamellae appear to be thinner than in *Figure 1*. The bar is $1\mu m$ long.

Method 3: SFM of etched surfaces
SFM experiments were carried out with a "Nanoscope III" (Digital Instruments Inc.) in contact mode, recording height images. This proved to be a fast and relatively easy method to visualize morphologies with a resolution comparable to that of the TEM methods, i.e. of structures of the order of $10 - 50nm$ (*Figure 3*). It requires basically only one relatively simple step of sample preparation prior to observation, i.e. permanganic etching. A coarse picture can then be obtained relatively easily. The similarity with the TEM micrograph shown in *Figure* 1 is obvious.

Furthermore the method offers the potential to achieve a much higher resolution with the same instrument, if e.g. experiments are conducted under water (7). Since it is a method of direct observation on the sample surface SFM offers the possibility to record the location of particular morphologies across a sample surface. This at least much more difficult with the TEM methods since in method 1 the exact origin of the surface replicas is often known and in method 2 ultramicrotomed sections of the lateral face are taken.

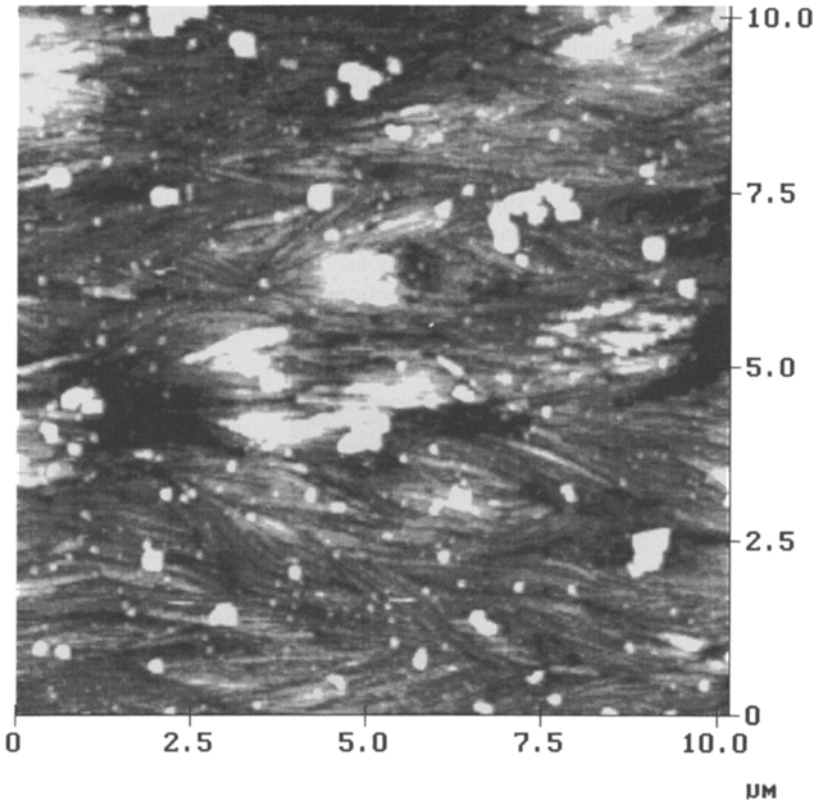

Figure 3: SFM image of the same surface as in *Figure* 1.

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