Changes in lamellar thickness observed in polyethylene single crystal mats as a result of treatment with chlorosulphonic acid

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The lamellar thickness of polyethylene crystals measured by electron microscopy following chlorosulphonic acid fixation is often lower than the expected value. Experiments indicate that this is the result of insufficient acid treatment: the electron beam interacts with poorly fixed crystals to reduce lamellar thickness. Thickness reduction is not recorded when polymer has been fixed for longer times.

(Keywords: lamellar thickness; polyethylene crystals; electron microscopy; chlorosulphonic acid)

Introduction

In recent years polymer electron microscopists have been greatly aided by the discovery of several techniques which have made it possible to investigate the interior of bulk polymer samples. Two of the techniques commonly used to look at bulk polyethylene are permanganic etching, followed by replication, a technique developed by Olley *et al.*[1] and chlorosulphonation followed by sectioning—the method due to Kanig[2,3]. Both of these experimental techniques can give excellent pictures of the internal morphology of bulk samples; they are, in some ways, complementary. Permanganic etching and replication gives a very good idea of the overall morphology, it is particularly suited to looking at large flat areas, e.g. the surfaces of films. Chlorosulphonation, followed by sectioning, is very useful for looking through the thickness of films, e.g. cutting through single crystal mats to reveal the lamellae edge on. However, sometimes the crystal thicknesses, as measured by the Kanig technique, have been reported as smaller than expected from other experimental techniques[4,5]; although on other occasions good agreement has been found[6,7]. The reason for these low results has not, to our knowledge, been investigated previously. 'Over etching' had been considered a probable cause by the present authors and some co-workers, but without any experimental evidence.

This communication gives an account of experiments to investigate the variation of measured lamellar thickness as a function of chlorosulphonation treatment. We have looked at single crystal mats after cutting at room temperature following treatment in acid for various times at three temperatures. As treatment progresses the sample blackens. The material cannot be cut without serious deformation until it appears black. Cutting when the sample was first black proceeded satisfactorily but gave sections in which the lamellae appeared thinner than expected from small angle X-ray scattering (SAXS) measurements on the same mats. As the treatment time was increased, the measured lamellar thickness increased, until the SAXS value was reached. The measured thickness then remained constant with time until, after long treatment, the material became very fragile and difficult to cut.

We conclude that the reason why low values for lamellar thickness are often recorded following chlorosulphonation is that insufficient acid treatment leaves material in which beam damage can take place; it is well established that beam damage reduces lamellar thickness[8]. Thus the cause of low lamellar thickness measurements is not over treatment, as previously assumed, but under treatment in chlorosulphonic acid.

Experimental

Single crystals of Rigidex 50 were grown at 83°C from 0.01% w/v solutions in xylene after self seeding[9] at 99°C. The crystals were hot filtered to remove low molecular weight polymer which had not crystallized at 83°C. Crystal mats were removed from the filters, pressed lightly at room temperature to make them more compact, and dried in a vacuum oven.

The mats were cut up. Material was taken for SAXS analysis, using a Rigaku-Denki camera. The remaining segments of mat were treated with chlorosulphonic acid.

Safety equipment was always worn and great care taken when handling the acid. The acid was added to tubes containing the samples at room temperature. The stoppered tubes were transferred to water baths at the treatment temperatures.

All samples were removed from the acid during the time when they looked black and still remained intact. Treatment temperatures and times were as follows:

- Samples treated at 16°C for 1, 2, 3, 4 and 5 days
- Samples treated at 34°C for 6, 12, 18 h; 1 and 2 days
- Samples treated at 40°C for 6, 12, 18 h and 1 day

One further sample, treated for 1 day longer, was produced at each temperature, but was found to break up in the acid.

The intact samples were cut using an LKB microtome at room temperature. Some of the samples could be cut without further treatment, others were too fragile and

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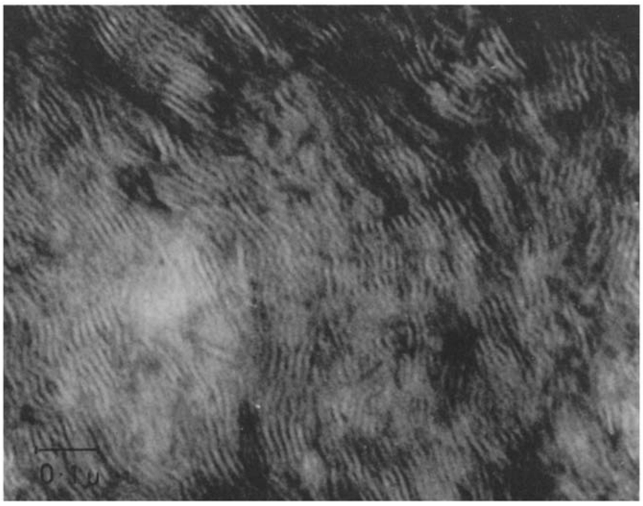

Figure 1 Transmission electron micrograph of a typical area of a lightly pressed mat of single crystals grown at 83°C. The sample was chlorosulphonated for 1 day at 34°C and cut at room temperature, after which this section was stained for 2 h in 1% aqueous uranyl acetate solution

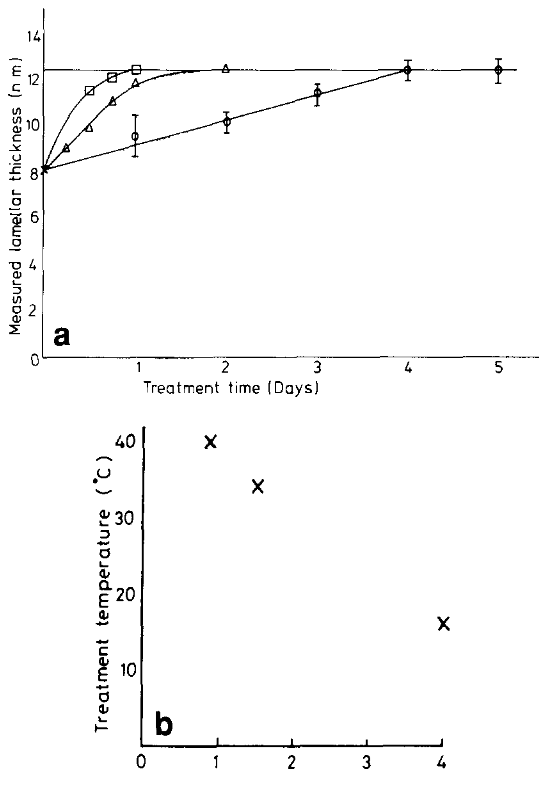

Figure 2 (a) Variation of measured lamellar thickness as a function of treatment time at 16°C (○), 34°C (△) and 40°C (□). (b) The variation, with temperature, of the minimum treatment time to achieve a measured lamellar thickness (after chlorosulphonation) which is equal to the SAXS lamellar thickness value

required embedding. Spurr's Resin was used as the embedding medium.

From each preparation some sections were stained with uranyl acetate and others left unstained. Sections were viewed in a Phillips 301 electron microscope operating at 80 kV. Pictures were taken of several different sections from each preparation, lamellar spacings were measured from the negatives and the measurements averaged.

Some of the sections moved when initially subjected to a strong beam (suitable for normal imaging). Focusing was usually carried out, and photographs taken, after the sample became stable. However, in one set of experiments fast film was used and pictures taken immediately on exposure to the low intensity beam, after focusing on an adjacent area.

Results

SAXS indicated that the average thickness of the crystals grown at 83°C was 12.5 ± 0.5 nm. This agrees well with literature values[10,11].

Figure 1 shows an area of a section from the sample treated for 1 day at 34°C and then stained. In this sample the lamellae are clearly visible and the average lamellar thickness can be easily measured. It was observed that the edges of lamellae appeared somewhat clearer after staining, especially when the samples had not been treated in the acid for long. However, in all preparations measurements could be made from stained and unstained sections without difficulty and the average measured spacing was the same for both.

Figure 2a shows the most important data. The variation of measured lamellar thickness is plotted against treatment time for all three temperatures. Note that the shape of the graph is the same in each case—the spacing starts at a low value and then rises with treatment time to within experimental error of the SAXS value. The standard deviations of 20 thickness measurements (each measured over a group of eight lamellae) are shown as error bars. The dependence of the time to achieve lamellar thickness equivalent to the SAXS value is indicated in *Figure 2b*.

The appearance of sections cut after chlorosulphonation at different temperatures was generally similar, but there were differences in detail. Our sections showed clear lamellae and gave reproducible spacing measurements after treatment at 16°C, as they did at 34 and 40°C, but the sections did not cut as evenly after treatment at the lower temperature; considerable thickness differences were observed in the sections themselves.

Micrographs of sections which had been irradiated only during the minimum exposure time (see Experimental) were compared with those of the same areas photographed after long exposure to the beam. Two preparations were examined, sections cut from a 5-day 16°C sample and sections from a 2-day 16°C sample. The sample which had had the longer treatment showed no change in measured spacing as a result of irradiation, the spacing was 12.5 nm in both cases. However, the sample which had had a lighter acid treatment showed a larger spacing (again 12.5 nm) when the irradiation was minimal; the spacing reduced to 10.1 nm after long irradiation. Thus the effect of irradiation on the 2-day 16°C sample was to decrease the lamella thickness from 12.5 to 10.1 nm.

Discussion

We have shown that the lamellar thickness of single crystal mats treated with chlorosulphonic acid increases with treatment time to a maximum which is, within experimental error, the crystal thickness obtained by SAXS measurements on the same mat. This is the same thickness as expected from the literature[10,11]. The shape of the lamellar thickness *versus* treatment time curve

(*Figure 2a*) is the same for each temperature but the SAXS thickness value is achieved more rapidly if the treatment temperature is higher, as would be expected since the acid should be able to penetrate more quickly at higher temperature. The temperature range which we have used here is too small to allow us to determine the relationship between penetration time and treatment temperature.

A second factor influencing treatment times is the packing of the lamellae. Our experiments were carried out on lightly pressed mats; we know, from experience, that treatment times are longer for hard pressed mats, longer still for bulk material and longest of all for certain special samples: polyethylene of the interlocking shish-kebab type had to be treated for 2 weeks at 70°C before the polymer blackened and could be cut at all[5]. Even then the lamellar thicknesses recorded were lower than expected which, in the light of this present work, indicates that 2 weeks was insufficient treatment time. The treatment time is clearly dependent on the ability of the acid to penetrate the polymer. It is not usually possible to change the state of packing of the lamellae in a given experimental specimen. However, treatment times can be reduced by treating at higher temperature.

Two pieces of experimental evidence lead us to an understanding of why the variation in measured lamellar thickness is observed: (1) In lightly treated samples, the initial lamellar spacing, measured during brief irradiation, is the same as that obtained by SAXS or from samples which have experienced longer acid treatment. It is on exposure to the beam that the spacing reduces; (2) Extrapolating the curves in *Figure 2* back to zero treatment time gives just the lamellar thickness to be expected from an application of Grubb's shrinkage ratio[8] to crystals originally 12.5 nm thick.

Hence we believe that the reason for observations of unexpectedly low lamellar spacings sometimes reported following chlorosulphonic acid treatment[4,5] is now quite clear. The actual lamellar spacing is the same and in agreement with the value from SAXS for all treatment times, but when the treatment time is short, beam damage takes place in the electron microscope, and this is the reason for the unexpectedly low spacings sometimes recorded.

Conclusions

We have clear instructions for experimentalists embarking on chlorosulphonic acid treatment of polyethylene—to obtain correct values for lamellar thickness (in agreement with values obtained from other techniques and with the expected literature values) treat the polyethylene in the acid for as long as possible. This will eliminate the crystal shrinkage along the chain direction which can occur as a result of interaction with the beam. If, in an experiment, the lamellar thickness measured is lower than expected, it is probable that the sample is insufficiently fixed; the acid treatment should be prolonged or another sample treated at a higher temperature.

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