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# A comparison of methods of specimen preparation for transmission electron microscopy of bulk polyethylene

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Polyethylene samples, crystallized from the melt both by quenching and by isothermal crystallization at each of five different temperatures, have been characterized by small-angle X-ray scattering (SAXS) to monitor the lamellar separation. The same materials were prepared for transmission electron microscopy using two different specimen preparation techniques: fixation with chlorosulfonic acid, followed by sectioning, and permanganic etching, followed by replication. Lamellar spacings were measured from negatives of micrographs obtained following specimen preparation using each of the two techniques. Measurements close to the SAXS spacings were obtained from both techniques if particular experimental procedures were followed. However, too low a value for lamellar separation was recorded when samples were fixed for insufficient time in chlorosulfonic acid, and too high a value for lamellar separation was recorded when samples were shadowed at too low an angle, following permanganic etching, or when polymer adhered to the replicas. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: polyethylene; TEM; specimen preparation)**

## INTRODUCTION

In polymer science transmission electron microscopy (TEM) is a very valuable technique, but one that requires specimens of less than about 100 nm thickness in order that the electrons can pass through. Certain specimen types, for instance polymer lamella single crystals and solution cast thin films, are well suited to TEM, but the technique poses problems of specimen preparation for the investigation of bulk material. For polyethylene, which deforms badly on cutting unless sectioned at liquid nitrogen temperatures, there are two methods of specimen preparation in general use: fixation with chlorosulfonic acid, followed by sectioning, a method developed by Kaning[1,2] and permanganic etching, followed by replication (developed by Olley, Bassett and Hodge[3,4]). Both methods give very satisfactory results and have been widely used, but not often on the same samples.

We use both methods in our laboratory, and, over the years, have formed the view that the two methods give the same qualitative morphological picture, but that the scale is different. Features appear smaller after the chlorosulfonic acid treatment and larger after permanganic etching and replication. A published example of this concerns polyethylene crystallized under pressure into an interlocking shish-kebab morphology. We examined this material using both techniques of specimen preparation (see reference 5 and compare *Figure 2a* and *b*); the morphologies appeared to be the same, but the scale was noticeably different.

Other authors have compared one or other TEM technique with measurements obtained in other ways. Bassett and Hodge[4] showed that permanganic etching gave results that corresponded with those from gel permeation chromatography. Voigt-Martin *et al.* found results from chlorosulfonation and sectioning were in agreement with measurements from small-angle X-ray scattering[6] (SAXS) and from Raman longitudinal acoustic model (LAM)[7]. However, as far as we know, neither group has looked at a single sample type prepared for TEM by both permanganic etching and by chlorosulfonation.

We have previously looked at the chlorosulfonic acid treatment in some detail[8]. We showed that, in mats of polyethylene single crystals, a value for the lamellar spacing, in agreement with that found by SAXS, could be achieved if the fixation time was long enough. Too small a value for crystal spacing was observed when treatment time was short. This is a result of beam damage in insufficiently fixed films. It is well know that polyethylene crystals interact with the electron beam, losing their crystallinity. Grubb *et al.* have shown that during this interaction the crystals become larger laterally (at right angles to the chain direction) whilst the crystal thickness decreases[9]. After chlorosulfonation and sectioning we see lamellae edge-on; the technique picks out the lamellar surfaces, and these appear as dark lines, particularly after staining[1,2,10] (see *Figure 2* below). Flat-on lamellae are not clearly visible in chlorosulfonated samples. Crystals that are not fully fixed by the chlorosulfonic acid suffer beam damage and, since only edge-on crystals are clearly visible, appear to shrink on exposure to electrons. The minimum treatment time to obtain the correct, unshrunk, lamellar spacing depends on the speed

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with which the acid diffuses into the specimen and, therefore, on both the treatment temperature and the sample type. Annealed bulk polymer will require longer treatment than a single crystal mat because it is harder for the acid to penetrate into the sample. (Very impenetrable samples, such as the interlocking shish-kebabs of reference 5, *Figure 2*, will take a very long time to fix fully; indeed, it is possible that the acid will never be able to get into the interior of the samples, so some residual beam damage may be unavoidable.)

In the present paper we describe experiments in which we have examined six samples of the same linear polyethylene, one quenched and the remainder isothermally crystallized from the melt at a series of different temperatures. We have compared the results for lamellar spacing obtained following specimen preparation by the two TEM methods, chlorosulfonation and sectioning and permanganic etching and replication, with data obtained using SAXS. We believe that the SAXS results are the most accurate because the SAXS technique averages over many crystals, the samples do not require elaborate preparation and are not damaged during observation. We have found that both methods of sample preparation for TEM show the same morphology and that if the specimen preparation methods are correctly applied, the results for lamellar thickness are close to each other and to the value obtained for lamellar spacing from SAXS. However, we find that the permanganic etching and replication method, if not applied correctly, can give too high a lamellar spacing, whilst, as established previously with single crystal mats, samples give too low a spacing if the chlorosulfonic acid treatment is not completed.

## EXPERIMENTAL

### *Materials*

The linear polyethylene (LPE) used was Sclair 2907 ($M_w$ $10^5$, $M_w/M_n$ 3.5). We used material crystallized in 1985 for different study. At that time the polymer was sealed into glass tubes under argon. The tubes were placed in an oil bath and melted by holding at 150°C for 1 h. Each LPE sample was then crystallized isothermally by holding at the chosen crystallization temperature for 167 h. The tubes were then quenched into acetone at freezing point, broken and the polymer removed.

Other specimens were blends containing 1% LPE (Sclair 2907) with 99% branched polyethylene (BPE; BP PN220, $M_w$ $2 \times 10^5$, $M_w/M_n$ 10, branch content 26 branches per 1000 backbone carbon atoms). Such blends have been the focus of extensive work in our laboratory[11–16]. The materials were blended in solution[11,12]. The blends were dried, mounted between cover slips, melted in an oil bath and then held for two days at 122°C, a process which, we have established, will give a morphology of LPE-rich lamellae in a matrix of quenched BPE lamellae[11–14].

### *Chlorosulfonation*

Some isothermally crystallized LPE samples and some blend samples were placed in glass tubes (two or three samples, of dimensions 3 mm × 3 mm × 0.5 mm, per tube) and 15 ml of chlorosulfonic acid added. Some of the tubes were held at room temperature for times between 10 and 21 days; others were placed in a water bath at 40°C for two days. After this treatment the polymer was removed from the acid, washed and cut at room temperature using an LKB microtome. Sections were stained with uranyl acetate for 1 h to enhance contrast[10]. Micrographs of the sections were taken using a Philips 301 TEM operating at 80 kV. Care was taken to see that the samples were held at eucentric height and the magnification of the microscope was checked using standard diffraction gratings. Some micrographs were taken after careful focusing on the area to be recorded, but others were taken immediately on exposure to the beam (after focusing in an adjacent region of film) so as to minimize beam damage[8,9].

### *Etching by permanganic acid*

Isothermally crystallized LPE samples and blend samples were etched with permanganic acid solution. The standard process carried out in our laboratory is, presently, as follows.

1. Etching solution is prepared from 10 ml of concentrated sulfuric acid added to 10 ml orthophosphoric acid in a strong boiling tube fitted with a quick-fit glass stopper. Potassium permanganate crystals (0.35 g) are added to the acid mixture. The tube is placed in an ultrasonic bath and agitated for 1 h to mix; a dark green solution results.
2. Up to six clean, dry polymer samples of approximately 0.3 cm diameter and 0.5 to 1 mm thickness are carefully placed in the solution. If samples have been washed in acetone, care is taken to avoid traces of solvent remaining in cracks—*acetone will cause an explosion or catch fire on contact with the acid solution.* PE floats, so we have to note which surface is down; this is the surface to be replicated. The tube is replaced in the ultrasonic bath and agitated for 2 h. (For many sample types we believe that it is difficult to over-etch, the solution lasts for 2 h and we usually etch for the whole life of the solution; 0.5 h is a minimum etch time for the conditions that we use. In the present work we found that a short etch time may be an advantage for some sample types, see below.)
3. Each sample is carefully removed and washed in four washing baths as follows:
   (a) 7:2 solution of distilled water and $H_2SO_4$, from the fridge;
   (b) $H_2O_2$, from the fridge;
   (c) distilled water at room temperature;
   (d) acetone at room temperature.
   Washing in each bath is for at least 30 s.

Replicas are then made. Dry samples are mounted, etched side up, on Sellotape on a microscope slide. They are lightly shadowed with Pt/Pd at about 40° (higher angles were also used in the present work, see below). The shadowed samples are then coated with carbon at normal incidence. (We have found that over 90% of our replicas are successful if 'rope' is used for carbon evaporation; however, only 40% of replicas from carbon rods are successful.) After coating with carbon, a blob of polyacrylic acid glue is placed on the etched surface of each sample. Samples are left in a desiccator for two or three days until the glue is dry. The glue (plus replica) is then prised off and floated in distilled water for 2 h. The glue dissolves, leaving the floating replicas, which are picked up on TEM grids for examination.

**Table 1** Comparison of measured lamellar spacings

| Sample | SAXS (1995) (nm ± 2) | SAXS (1985) (nm ± 2) | Chlorosulfonation (nm ± 3) & ratio to SAXS | | Permanganic etching 40° (shadow nm ± 5) & ratio to SAXS | |
|---|---|---|---|---|---|---|
| Quenched | 18 | | 17 | 0.9 | 40 | 2.2 |
| Isoth. 119°C | 31 | 30 | 27 | 0.9 | 53 | 1.7 |
| Isoth. 122°C | 31 | 30 | 28 | 0.9 | 54 | 1.7 |
| Isoth. 126°C | 38 | 41 | 34 | 0.9 | 58 | 1.5 |
| Isoth. 128°C | 41 | | 41 | 1.0 | 65 | 1.6 |
| Isoth. 130°C | 53 | 56 | 45 | 0.9 | 71 | 1.3 |
| LPE in blend | | | 23 | | 33 | |
| BPE in blend | | | 12 | | 17 | |

Note that the ratio of thickness as measured by the two TEM methods is greater for all the isothermally crystallized LPE samples (average permanganic thickness/chlorosulfonic 1.85:1) than for the blend samples (ratio 1.45:1). Note also that values for lamellar spacing, measured by all three methods, are very close for samples crystallized at 119 and at 122°C. This indicates that crystallization is very fast at these temperatures. The samples nominally crystallized at 119°C probably actually crystallized at just below 122°C whilst cooling. The quenched samples must have crystallized at a considerably lower temperature

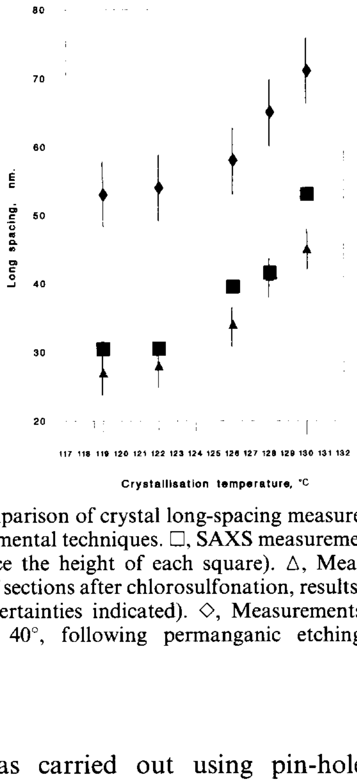

**Figure 1** Comparison of crystal long-spacing measurements obtained by three experimental techniques. □, SAXS measurements (uncertainty in spacing twice the height of each square). △, Measurements from micrographs of sections after chlorosulfonation, results uncorrected for shrinkage (uncertainties indicated). ◇, Measurements from replicas, shadowing at 40°, following permanganic etching (uncertainties indicated)

### *SAXS*

SAXS was carried out using pin-hole collimated copper K$\alpha$ radiation from an Eliot Marconi GX21 rotating anode generator running at 40 kV and 40 mA, fitted with a Rugaku Denki camera holding flat-plate film at a specimen to film distance of 35 cm. Calibration was carried out using a collagen standard.

## RESULTS AND DISCUSSION

### *SAXS*

The SAXS spacings are listed in *Table 1*. As observed in much previous research, higher values for lamellar spacing are recorded as the crystallization temperature is raised[17,18]. Our SAXS spacings (which are in line with the literature values[17,18]) are plotted in *Figure 1*.

It is interesting to note that several of these same samples were examined by SAXS after the original crystallization in 1985; the results obtained at that time are also shown in *Table 1*. The SAXS spacings of these samples have remained the same, within experimental error, over ten years.

### *Chlorosulfonic acid fixation and sectioning*

*Figure 2* shows typical micrographs of sections of various types of sample: (a) LPE crystallized at 122°C; (b) LPE crystallized at 130°C; (c) the 1% blend crystallized at 122°C. In all micrographs the edge-on crystals are clearly seen, with the lamellar surfaces appearing dark because the heavy atoms in the stain scatter electrons. In the blend (*Figure 2c*) there are thicker crystals (LPE-rich material isothermally crystallized at 122°C) dispersed in a matrix of thinner crystals (BPE-rich material, unable to crystallize at 122°C, but later crystallized on quenching). In *Figure 2b*, the micrograph of LPE isothermally crystallized at 130°C, small groups of thin crystals can also be seen. These crystals are of low molecular weight polymer which was unable to crystallize at the isothermal temperature. (Note that the LPE-rich crystals in the blend (*Figure 2c*) are visibly thinner than those in the pure LPE sample crystallized at the same temperature, 122°C, (*Figure 2a*). This difference in crystal thickness was previously recorded by Puig *et al.*[19] who showed that crystals initially form at the same thickness in both sample types, but those in the blend fail to thicken on annealing).

The lamellar spacings were measured, from negatives, by counting the number of crystals in 100 1 cm stacks. The average separation so measured should correspond to the SAXS spacing, each dark/bright line pair giving one crystal/amorphous repeat distance. For short fixation times the crystals were seen to thin by a factor of up to 1:0.64 on exposure to the beam, as found previously for single-crystal mats[8]. We found that thinning as a result of beam damage could not be completely eliminated for melt-crystallized Sclair 2907. For treatment times of between 10 and 21 days at room temperature a reduction in measured lamella spacing of about 5% was consistently observed. The sample broke up if left in acid for more than 21 days.

The spacings measured after chlorosulfonic acid treatment (after long treatment times and uncorrected for shrinkage in the beam) are listed in *Table 1* (expressed both in nanometres and as a ratio to the SAXS spacing, taken as one); the results are plotted as a function crystallization temperature in *Figure 1.* These lamellar spacings are close to, but consistently about 10% less than, those obtained by SAXS; residual shrinkage in the beam can account for about half this difference. Lamellar spacings following chlorosulfonation, corrected for shrinkage, would be within the experimental errors of the SAXS measurement, but consistently a little low.

*Permanganic etching and replication*

*Figure 3* shows typical micrographs of replicas of various types: (a) LPE crystallized at 122°C; (b) LPE crystallized at 130°C; (c) blend crystallized at 122°C. These micrographs, obtained from specimens after permanganic etching and replication, clearly show the same overall morphology as do those after chlorosulfonation (*Figure 2*). In *Figure 3*, especially (c), lamellae are sometimes visible flat-on, but more often we seen them edge-on. There is a certain amount of detached polymer (visible as irregular dark patches, particularly clear at the edges of the large, LPE-rich crystals in the blend sample in *Figure 3c* and as the very dark material seen on the lamellae at the top left of *Figure 3b*).

The lamellar spacings were again measured, from negatives, by counting the number of crystals in 100 1 cm stacks. The initial results, from isothermally crystallized samples shadowed at 40° during replication, are shown in *Table 1* (both expressed in nanometres and compared to the SAXS spacing). Although this method of specimen preparation gives particularly clear micrographs, the measured lamellar spacing is considerably greater than that found by SAXS or after chlorosulfonation and sectioning. Taken at face value, this seems to imply that chlorosulfonation should be preferred for specimen preparation when crystal thicknesses are being assessed.

## FURTHER INVESTIGATIONS INTO PERMANGANIC ETCHING AND REPLICATION

### *Detached polymer*

We initially suspected that the detached polymer, adhering to the replicas, might obscure some crystals to give a high overall average crystal thickness. Selected-area electron diffraction and dark-field imaging on blend samples confirmed that there was indeed polymer attached to the replicas. In blend samples it was attached to replica corresponding to both the large LPE-rich crystals and the smaller BPE-rich crystals. However, material from the LPE-rich crystals was more obvious: lumps of deformed polymer were seen attached to some replicated LPE-rich crystals. This polymer must have been ripped off the shadowed and carbon-coated sample,

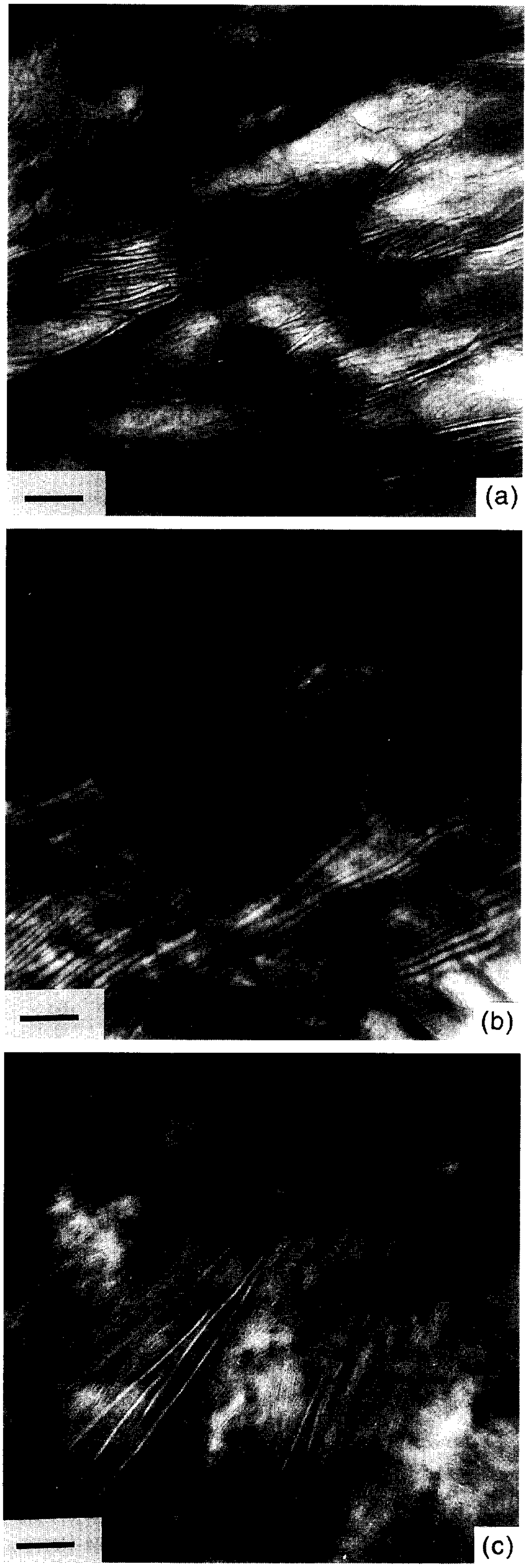

**Figure 2** Micrographs of LPE samples obtained following chlorosulfonation, sectioning and staining. The prints are all to the same magnification; the scale bar represents 0.25 $\mu$m. (a) LPE crystallized at 122°C. (b) LPE crystallized at 130°C. Note the groups of thinner lamellae; there are several groups to the right of the picture. (c) The 1% blend crystallized at 122°C. The white lines are the (unstained) crystal interiors and the dark lines the stained crystal surfaces. Note that only edge-on crystals can be seen clearly, where the crystals twist to become flat-on they are indistinct because the stained edges do not stand out

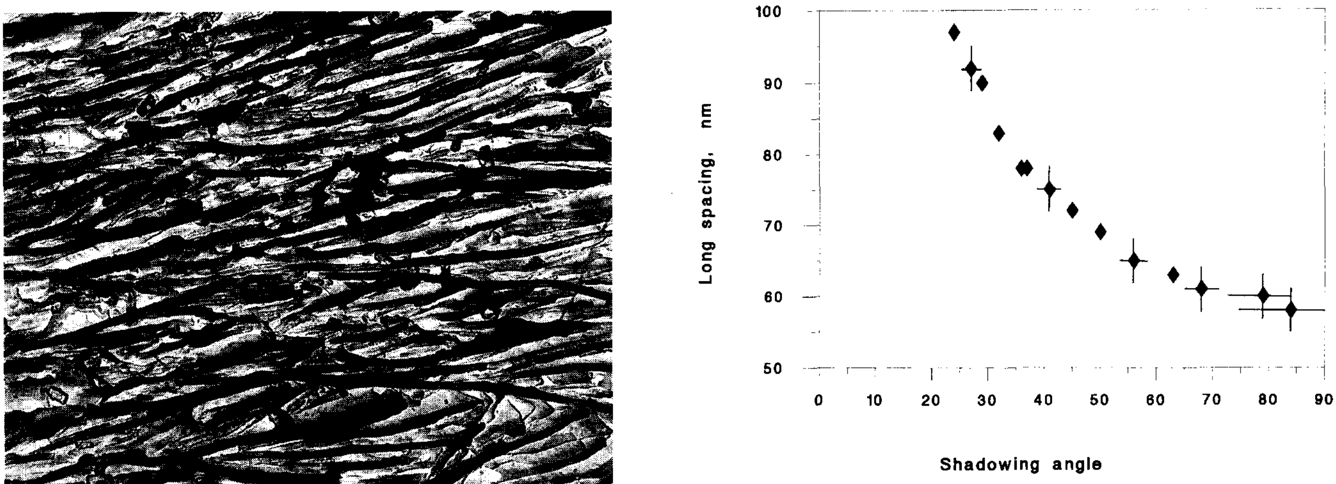

**Figure 4** The variation in measured long-spacing with shadowing angle for samples prepared for TEM by the permanganic etching and replication technique. These samples were originally crystallized isothermally at 130°C. Uncertainties are marked on representative points. Note that the uncertainty in the spacing is the same on all points, but the uncertainty in the angle increases rapidly as the angle nears 90°. This is because the angle was estimated from the measurement of the cosine, and one of the distances to be measured becomes very short as the angle nears 90°

sticking to the replica when it was prised off. Quantitative measurements showed that in the blends the LPE-rich crystals, with their detached material, were thicker than similar crystals measured from sections of chlorosulfonated samples in the ratio 1:1.45 (SAXS requires stacked crystals and so cannot be used to measure the thickness of these isolated LPE-rich crystals in isothermally crystallized blends.) We know that thicker crystals etch more slowly than thinner crystals in the permanganic acid solution[20]. As a result, the LPE-rich crystals in the etched blend will stand well clear of the surface and, consequently, will become embedded in the glue during replication. Parts of isolated embedded crystals will be inclined to tear off with the replica.

Selected-area electron diffraction and dark-field imaging confirmed that there was also detached material adhering to the isothermally crystallized LPE samples. Detached polymer may account for the factor of 1.45:1 difference in lamellar thickness recorded in blend samples prepared by the two TEM methods, but it cannot account for the entire difference (1.85:1) in lamellar spacing recorded for isothermally crystallized LPE samples.

### *Shadowing angle*

When isothermally crystallized LPE samples are etched the acid solution penetrates between individual crystals, leaving some standing out from the polymer surface. Although we do not have crystals that etch slowly in a fast-etching matrix (as in the blend) some LPE crystals will stand out from the surface more than others. It occurred to us that shadowing, as we did, at

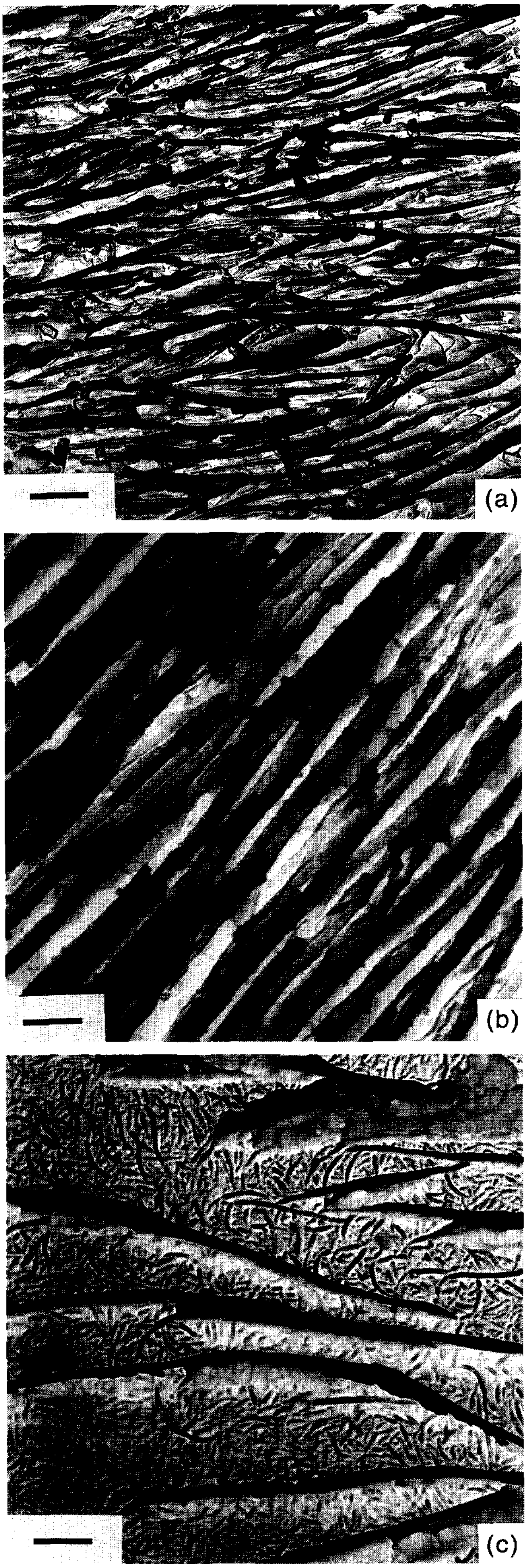

**Figure 3** Micrographs of LPE samples obtained following permanganic etching and replication. The prints are all to the same magnification; the scale bar represents 0.25 $\mu$m. (a) LPE crystallized at 122°C. (b) LPE crystallized at 130°C. (c) Blend crystallized at 122°C. Note the flat-on crystals (with some detached polymer adhering) at the top right. Detached polymer is present where the crystal edges appear very dark

a relatively shallow angle of 40°, some of the crystals that protruded less might be shielded by higher neighbours from the shadowing metal and so not be seen clearly in the micrograph of the replica.

We shadowed two of the isothermally crystallized samples (those crystallized at 122°C and 130°C) at a range of increasing angles, and measured the lamellar spacings obtained. The results for the 130°C samples are plotted in *Figure 4*. The measured lamellar spacing decreases as the shadowing angle increases, and the extrapolated value for a shadowing angle of 90° is close to, but still greater than, the value obtained from SAXS. Thus it appears that the measured lamellar spacing for a shadowing angle of 40° was larger than that obtained from other methods, at least in part because the crystals standing out from the etched sample surface were of uneven height. Some of the lamellae were not shadowed and were missed when measuring up the photographs. Increasing the shadowing angle revealed more and more of these crystals. The residual increase in spacing recorded after permanganic etching and replication, even after extrapolation to 90°, probably results from detached polymer, adhering to some of the more prominent crystals in these replicas, obscuring less prominent crystals. It is possible that shorter etching times would give rise to less difference between lamellar heights, and so in less shielding of low lamellae. It may also lead to less polymer detachment because crystals may protrude less far into the glue and so be less prone to detachment.

## COMPARISON OF FINAL RESULTS

Comparing SAXS results with those from sections after full chlorosulfonation (taking values for undamaged samples) and those from replicas shadowed at angles approaching 90° we see much closer agreement (*Table 2*).

TEM results for these isothermally crystallized LPE samples from the chlorosulfonation technique, operated under optimum conditions (i.e. long treatment times), show lamellar spacings that are consistently slightly lower than the SAXS values. Some shrinkage in the beam seems unavoidable for melt-crystallized material. In contrast, no difference in spacing was found when comparing results from SAXS and chlorosulfonation with the single-crystal mat specimens used in our previous work[8]. Shrinkage could be eliminated, for single-crystal mats, by long exposure to acid. We can only think that this difference is a result of variation in ease of acid penetration. The acid can penetrate single-crystal mats quite easily, allowing all chemical reactions to proceed to completion. It is possible that the acid cannot penetrate throughout isothermally crystallized melt samples, where the crystals are molecularly connected. Thus some shrinkage in the beam could have been expected. (Acid penetration will be much more difficult in the very compact interlocking shish-kebab morphology[5]. Considerable shrinkage, due to interaction with the beam, is probably unavoidable for that morphology.)

We have now shown that permanganic etching and replication, involving shadowing at 40°, leads to measurements giving lamellar spacings nearly double those measured by the other two techniques. However, if the replication involves shadowing at steep angles the measured lamellar spacing is only greater than that assessed by SAXS in the ratio 1.1:1. We believe that the residual difference is a result of polymer detached from the sample and adhering to the replica and shielding adjacent lamellae from the shadowing metal.

## CONCLUSIONS

The same morphologies are revealed for any sample type following the two specimen preparation methods for TEM. The permanganic etching and replication method may be considered preferable in morphological studies because flat-on, as well as edge-on crystals can be seen clearly.

For LPE samples isothermally crystallized from the melt, there is near-agreement between the measured SAXS spacing and lamellar spacing values measured from samples prepared by the two TEM methods when the experimental conditions are correct, i.e.

(i) for chlorosulfonation, the treatment time must be greater than some critical value (which varies with sample type and treatment temperature);
(ii) for permanganic etching and replication the shadowing angle, during the replication stage, must be as high as possible

Even so, the chlorosulfonation and sectioning method can still give a value for lamellar spacing a little lower than the SAXS figure for some sample types. Imperfect acid penetration, leading to incomplete fixation and consequent interaction between beam and specimen to give specimen shrinkage is (at least partly) responsible for this.

Where detached polymer adheres to replicas, after permanganic etching (as it often does), the lamellar spacing measured from replicas is a little higher than the SAXS value, even for steep shadowing angles.

As we have shown, both techniques for TEM specimen preparation can give very good results. However, in our view, it is easier to get close to the correct long-period value using the chlorosulfonation and sectioning method but slightly clearer morphological pictures can be obtained using permanganic etching and replication.

**Table 2** Comparison of measured lamellar spacings – optimum experimental conditions

| Sample | SAXS 1995 results (nm ± 2) | Chlorosulfonation (nm ± 3) (undamaged) & ratio to SAXS | | Permanganic etching 90° (nm ± 5) & ratio to SAXS | |
|---|---|---|---|---|---|
| Isoth. 122°C | 31 | 29.5 | 0.97 | 35 | 1.15 |
| Isoth. 130°C | 53 | 47.5 | 0.90 | 56 | 1.06 |

Finally, note that there has been no change in SAXS spacing for our isothermally crystallized LPE samples over 10 years.

## ACKNOWLEDGEMENTS

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