polymer communications

Morphology of crosslinked polyethylene

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INTRODUCTION

The permanganic etching technique is being successfully used for microstructural studies of extruded crosslinked polyethylene (XLPE). Scanning electron microscope (*SEM*) studies have revealed a variety of morphological features. The results so far are outlined and possible extensions of the technique are discussed.

EXPERIMENTAL

The purpose of the investigation was to determine the morphological properties of dicumyl peroxide cured XLPE. To do this 2 cm diameter extruded samples were prepared from HFDS 4201 supplied by Unifos Kemi AB. Samples were cut in two directions, parallel and perpendicular to the extrusion direction, to see if there were any significant orientation effects.

At first the samples were polished using standard metallurgical techniques[1]. The specimens were saw cut and then smoothed on 600 grit abrasive paper. Final polishing was performed on 7 μm and 1 μm polishing wheels. Great care was taken, during all four stages, not to overheat the specimens. Latterly samples were freeze fractured after cooling them in liquid nitrogen.

Both procedures were followed by etching. The permanganic etching technique used was that described by Olley *et al.*[2]. The polished samples required up to 40 h etching at 70°C before large amounts of detail could be observed. The fractured samples generally required a 1–3 h etch (see *Figures* 1 and 2).

The specimens were coated with 100 Å thick gold film and studied on a JEOL JSM-2 scanning electron microscope. The instrument had been carefully calibrated so that the dimensions of the spherulites could be determined within ±2%.

The method used to determine the average spherulite diameter was an adaptation of the Heyn method used in the determination of grain size in metals[3] and

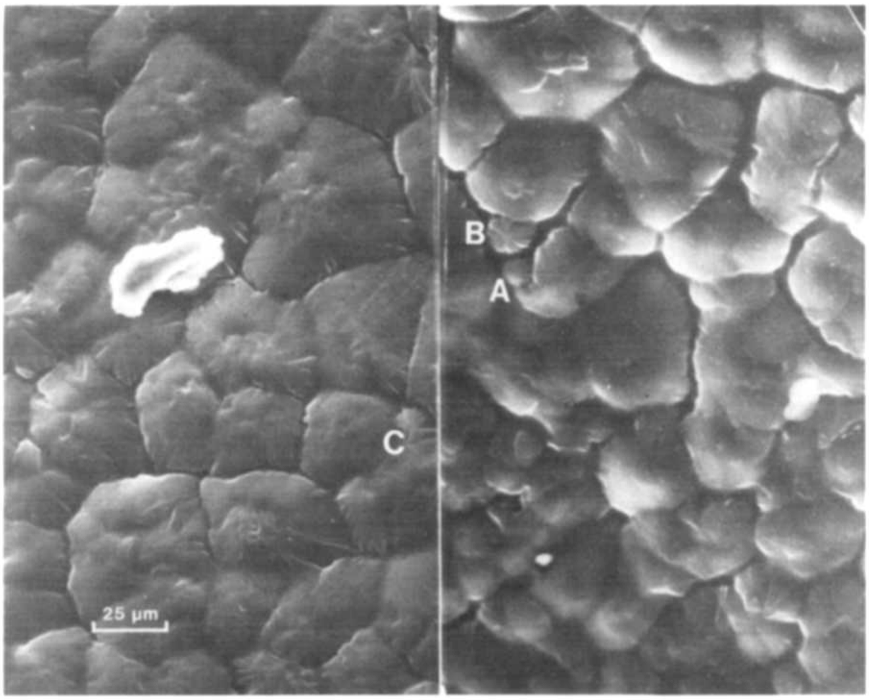

Figure 1 Two well crosslinked regions that were etched for 3 h at 70°C. Smaller spherulites which are located in the interstices of the larger variety are labelled A, B and C. The greater detail in these spherulites is ascribed to crosslinking

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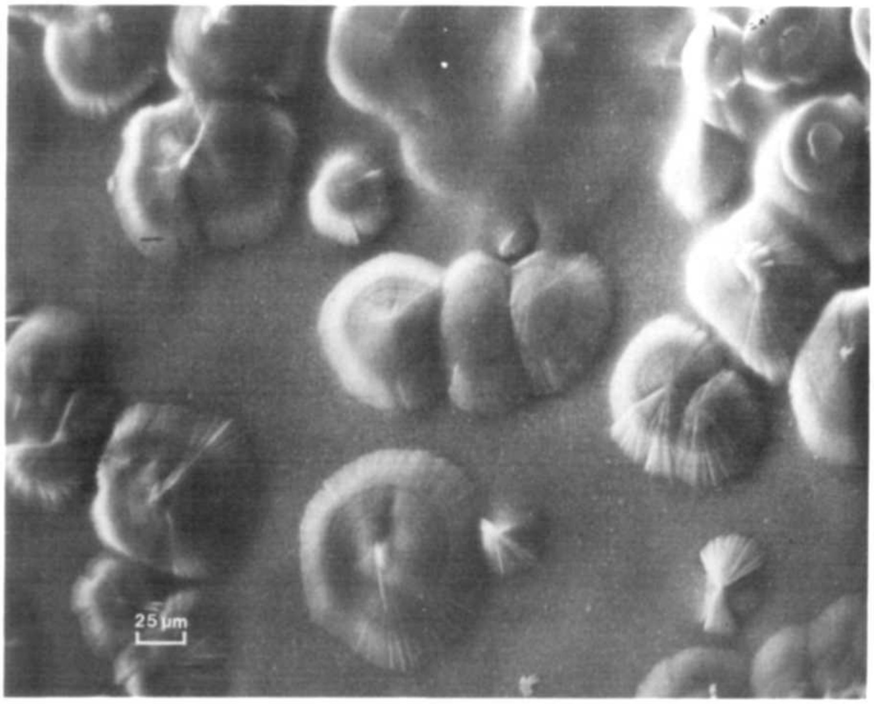

Figure 2 Micrograph of a region etched for 2 h at 70°C which shows areas ascribed to lower crosslinking

subsequently used by Phillips[4] for determining the spherulite size in polyolefinic cable insulations.

DISCUSSION

For the three polyolefins studied by Olley *et al.*[2] it was concluded that the etching technique removes defective crystalline and possibly disordered material preferentially. With XLPE three different etch rates would be expected: (i) the uncrosslinked amorphous; (ii) the crosslinked amorphous; and (iii) the crystalline material. As there is little detail to be seen in the majority of spherulites and most of the material contains some crosslinks (gel content 78–80%) it can be concluded that rates (ii) and (iii) are more or less identical. The only fine detail seen must therefore be due to the etching away of the uncrosslinked amorphous material.

Polished samples were used initially since these were used in etching/morphological work on XLPE[1,4,5] and it was thought that comparison with previous work would be a good way of assessing the etching technique. However, the quantitative measurements of the spherulite size and the quality of the micrographs obtained are such as to cast doubts on the findings of the previous work rather than to question the etching technique. The spherulites were measured at the edge and in the centre of the extrudate. Those at the edge tended to be smaller than those in the centre (16.0 ± 2.0 μm compared with 27.0 ± 9.0 μm). This would be expected from the higher rates of nucleation at the faster cooled extrudate edge. The poor thermal conductivity would, as Phillips[1] suggests, result in a lower rate of nucleation in the slower cooled centre. The large scatter in spherulite sizes, however, indicates some heterogeneity in the nucleation and this could be seen in clusters of larger and smaller spherulites adjacent to one another. If one assumes that two such areas have been subjected to similar thermal regimes and similar levels of contaminants, which is a reasonable assumption with extruded materials, then something other than temperature is affecting the nucleation rates. As the spherulites in the uncrosslinked material tend to be larger than in the crosslinked (see *Figures* 1 and 2) it may be possible that the crosslinks, or by-products of the crosslinking reaction, act as nucleation sites in some way. Hot stage work on the base polymer with the dicumyl peroxide but without the antioxidant will probably throw some light on the matter.

Little distortion or orientation can be seen in the samples cut parallel and perpendicular to the extrusion directions and one can only assume that the slow line speeds resulted in little residual strain and hence little distortion of the spherulites.

The technique appears to be useful for locating regions in the extrudate where the peroxide has been poorly distributed. These areas, where the crosslinking is low, can be identified as regions of greater detail (see *Figure* 2). The spherulites on average are about twice the size of those with crosslinks (i.e. those which show no internal detail). These areas are even more apparent in the polished and etched samples where it is possible to etch up the uncrosslinked spherulites and no other detail. At the moment we are relating the gel content[6] to the percentage of 'non-detail' with varying degrees of success.

We have also identified smaller spherulites which are located in the interstices of the larger variety (see *Figure* 1). Smaller spherulites of similar dimensions have been previously created by heat treating voids in steam cured XLPE[7] and have not been previously observed in bulk. According to Keller[8], who occasionally found such regions in high density polyethylene, these spherulites are composed of lower molecular weight species which behave as uncrystallizable impurities at low supercooling. Of particular interest to the design engineer is the temperature at which these spherulites melt, particularly if the service temperature of the extrudate is high, such as in hot water tubing etc. It is hoped to observe the growth and behaviour of these spherulites in detail using an optical microscope with hot stage attachment.

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Time–stress supersition in some creep experiments

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Elastomer-modified thermoplastics have gained acceptance by automotive producers as a result of a combination of good processability, moderate prices and adequate performance. Examples are the adoption of rubber-modified polypropylenes, like Moplen SP 25 and others, in the dashboards and bumpers of some cars, where they exhibit high impact resistance. In this context we are presently engaged in a program aimed at comparing the creep resistance of various polypropylene-based materials, differing in both rubber and filler content and from different producer. We are thus conducting conventional measurements of elongation *versus* time in tensile creep apparatus.

From a practical point of view, it would be highly desirable to be able to hasten the test, for instance by enhancing the stress to which samples are subjected, or temperature, or both. A fundamental prerequisite to any kind of acceleration must be, of course, the previous demonstration that the mechanisms operating in the "accelerated situation" are the same which are active in the "actual situation" (in our case, creep at a low to moderate temperature, and low applied stresses). As for "stress acceleration", a positive clue would be the existence of a master curve for time–stress superposition, analogous to the time–temperature superposition in amorphous linear polymers above the glass transition[1,2].

Recent reports hint at such curves in particular cases[3–6], but we have been unable to find explicit reference which would warrant such a procedure, especially in the case of a crystalline thermoplastic like polypropylene, eventually rubber-modified.

As a consequence, we have empirically probed the existence of master curves in the case of two propylene–ethylene copolymers, tested at different tensile stress levels, and at a constant temperature of 32°C. *Figures* 1 and 2 show the experimental data: the materials are, respectively, a copolymer (Moplen EPT 30R, from Montedison) and an elastomer-modified copolymer (Moplen SP 25).

The data were successfully reduced to single master curves (*Figures* 3 and 4) by shifting along the time axis (a small vertical shift makes the coincidence better, although its physical significance is not yet clear). As reference stresses we chose those corresponding to 40% of the tensile yield stress (13.1 MPa for Moplen EPT 30R; 10.8 MPa for Moplen SP 25). The two master curves are exactly superposable. Both shift factors are collected in *Table* 1.

We tentatively suggest a possible connection be-

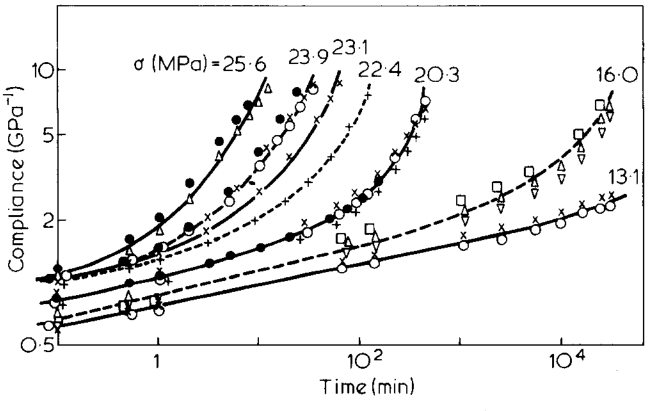

Figure 1 Creep curves for Moplen EPT 30 R at 32°C

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