Still another factor that may be involved is molecular weight. The resistance ot fatigue fracture of glassy polymers, whether notched or unnotched, is greatly increased by increase of molecular weight[7,8,11-13]. Hence, a lower matrix molecular weight may be a contributing factor to the observed lower fatigue resistance of HIPS compared with PS.

Although HIPS is inferior to PS when fatigue lifetimes are compared on a basis of absolute stress magnitude, the rubber modified polymer shows up favourably if comparison of fatigue lifetimes is made against relative stress magnitude, based on ratio of the applied stress amplitude to the observed maximum stress in a tensile test. This is because the tensile fracture stress is much higher for PS than HIPS. At an elongation rate of 0.02 in min^{-1}, the tensile strength of HIPS was observed to be 19.5 MPa (2830 p.s.i.) vs. 43.4 MPa (6300 p.s.i.) for PS. Hence the ratio of endurance strength to tensile strength, a parameter of significance to designers, is 0.22 for PS and 0.44 for HIPS.

It has been reported that blends of glassy polymers with a nitrile elastomer lead to a lower fatigue resistance than that of the unmodified polymer[14]. From the present study, it appears that fatigue resistance is also reduced even when the rubber component is grafted to the glassy matrix and rubber phase volume is high. Thus greater toughness, as assessed from tensile data on unnotched specimens or from impact data on notched specimens, does not necessarily imply greater resistance to fatigue fracture when the material is exposed to alternating stresses. Another conclusion is that in rubber modified polymers subject to alternating loads, craze and crack initiation occur sooner than in unmodified polymers and appear to have a greater influence on fatigue life than a possibly reduced fatigue crack propagation rate due to presence of the dispersed rubber phase.

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Annealing of nodular linear polyethylene crystallized from the glass

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Since Yeh and Geil reported the presence of nodular structures of the order of 10 nm in diameter in amorphous polyethylene terephthalate[1], there have been several reports of similar size nodular structures in amorphous samples of polycarbonate[2], isotactic poly(methyl methacrylate)[3] and polypropylene[4]. Smaller nodules have also been reported for atactic polystyrene[5]. Based primarily on dark field diffraction contrast observations of polyethylene terephthalate[1] and polystyrene[5] the nodules were suggested to represent domains of local order. There has, however, been considerable debate as to whether the nodules represent a bulk structural feature, a surface structure or are merely an artifact. For instance, Thomas and Roche recently reported[6] that apparent structures of several nm in diameter could be caused by defocus fringes and/or noise; they showed such size structures even in evaporated carbon film, which is expected to be structureless above the 0.5 nm level.

In this report, we will show the presence of nodular-like crystallites with dimensions of the order of 10 nm in samples of ultraquenched polyethylene warmed to room temperature and their growth with annealing at elevated temperatures; these nodular crystallites can be considered as an extreme morphology for crystalline polymers.

EXPERIMENTAL

The polyethylene used was Marlex 6015. Xylene solutions of 0.5 ~ 0.2% polyethylene were heated to 120°C and a carbon-coated glass slide dipped into the solution and then removed; thin polyethylene films from less than 100 nm to several hundred nanometers in thickness were obtained. The thickness was estimated from the interference colour of the films. The polyethylene–carbon film was floated on a water surface and picked up on an electron microscope grid. The grid with specimen was heated to 175°C for 5 min in an oven flushed with dry nitrogen and ultraquenched into isopentane cooled by

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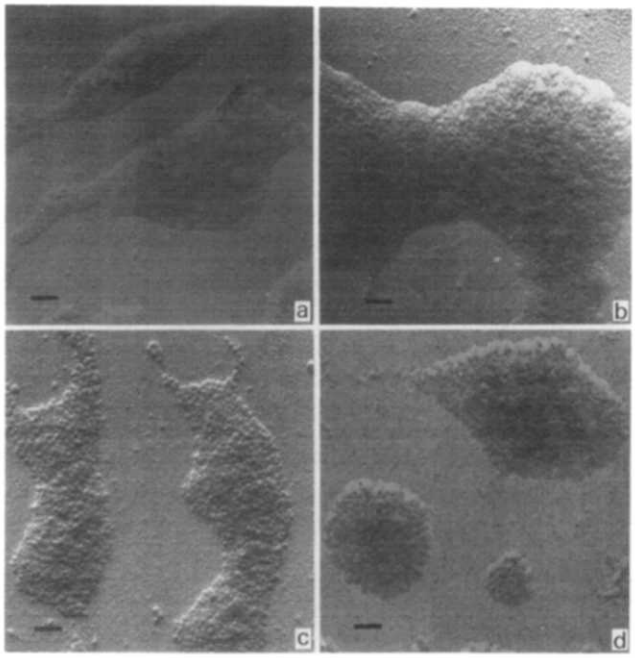

Figure 1 Morphologies of ultraquenched polyethylene, (a) as-crystallized (shadowed at room temperature); and annealed at (b) 75°C for 2 h; (c) 100°C for 2 h and (d) 125°C for 2 h. In all Figures the scale bar represents 100 nm

liquid nitrogen. The detailed quenching technique has been described elsewhere[7]. The quenched specimen was removed from the quenchant (isopentane) and allowed to warm up to room temperature on a glass slide in air. For the observation of surface morphology, half of the specimen on the grid was shadowed with platinum/carbon at room temperature. The grid was then annealed in an oven at the chosen annealing temperature for 2 h and finally the other half of the grid was shadowed from the opposite direction to the first shadowing so that we could compare the morphologies before annealing with that after annealing on one grid.

Samples were examined in a JEOL 100 C electron microscope. Dark field images were obtained from shadowed samples at 5000x magnification with both the 110 and 200 reflections, which are part of continuous Debye–Scherrer rings, using beam tilt and a 40 μm diameter objective aperture. Bright field diffraction contrast images were obtained at a magnification of 10 000x using the 40 μm aperture. For both types of diffraction contrast, exposure conditions were such that these were the maximum magnifications that could be used to obtain a recordable image on Kodak 4463 Electron Image Film within the lifetime of the diffraction pattern.

RESULTS AND DISCUSSION

Figure 1 shows the morphology of ultraquenched polyethylene as crystallized by warming to room temperature and after annealing at 75°, 100° and 125°C for 2 h. With increasing annealing temperature, the size of the nodules increases; at room temperature their size is around 10 nm and they increase up to 20 nm after annealing at 100°C for 2 h.

Figure 2 shows bright field and dark field diffraction contrast images for unannealed and annealed specimens. The dark field images show small bright spots of ~10 nm diameter in the room temperature sample, whereas the bright spots in the sample annealed at 100°C are larger, being 20 nm in diameter. In bright field diffraction contrast all crystallites through the thickness of the film which are in a diffracting position, i.e. low index planes properly oriented with respect to the incident beam, will appear as dark spots. The dark field image selects some of these (depending on the position and size of the aperture) as the bright spots. It is noted that weakly reflecting crystallites can be observed in dark field, whereas their contrast is obscured in the shadowed bright field micrograph. The bright field micrograph in *Figure 2* shows that a number (~10%) of the dark spots correspond to the

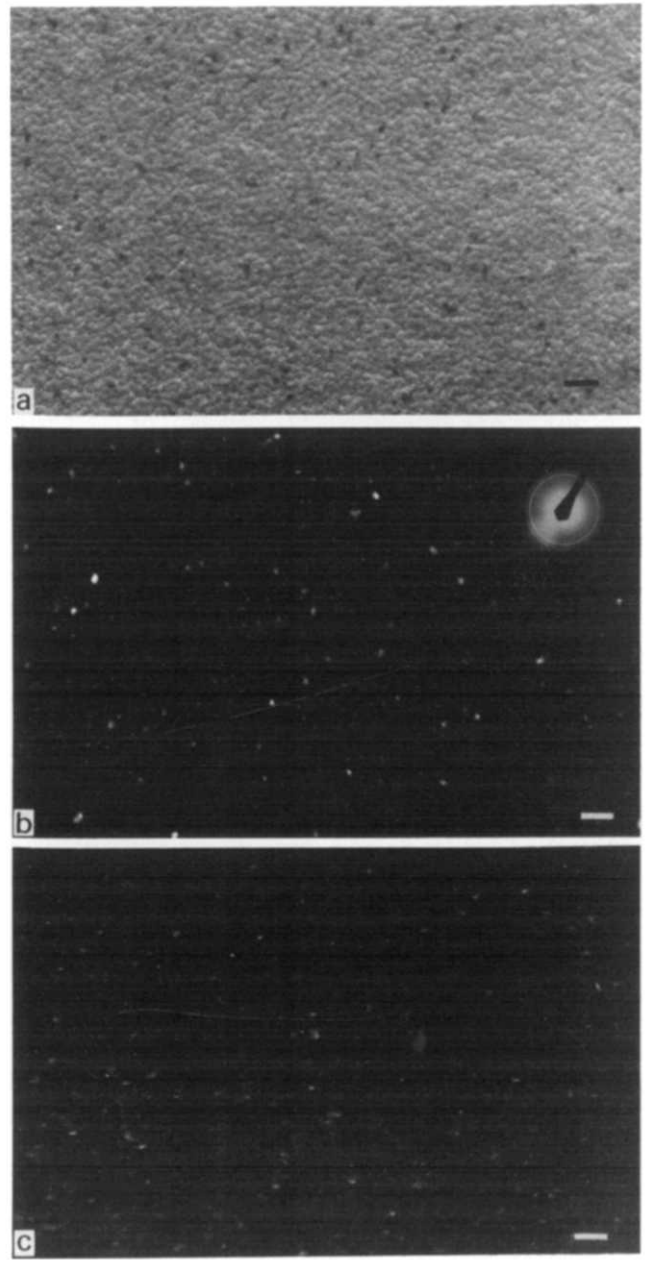

Figure 2 (a) Bright field diffraction contrast image of polyethylene ultraquenched and annealed at 100°C for 2 h. The specimen was shadowed so that it was possible to compare the surface morphology with the position of the crystallites giving the diffraction contrast; (b) dark field image for the same specimen as in (a); insert is the diffraction pattern showing the position of the objective aperture; (c) dark field image for an as-crystallized polyethylene film, ultraquenched and then rapidly warmed to room temperature

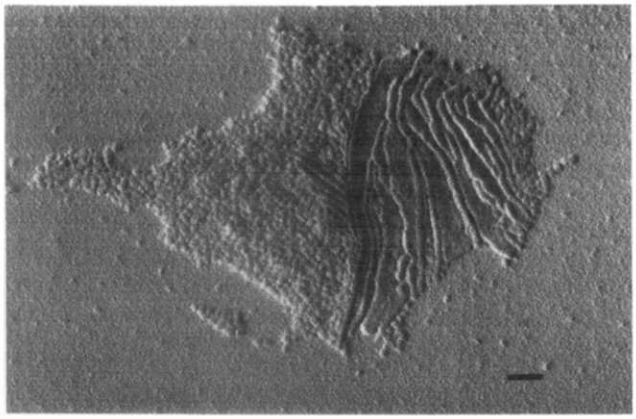

Figure 3 Morphology of a polyethylene sample ultraquenched and then annealed at 100°C for 2 h. The lamellar structures are believed to have been formed during the original quenching

surface nodules revealed by the shadowing. An additional ~20% are located at the positions of the surface nodules, but are smaller in size. This effect may be due either to incomplete merger of smaller crystallites, with a residual disorientation, or the fact that all crystallites beneath the surface will not correspond to surface nodules. Observation of these and related figures, however, leaves little, if any, question that the surface nodules correspond to individual crystallites in these crystallized ultraquenched films: i.e. that these samples are microcrystalline, and are not lamellar. It is noted that the diffraction contrast effects disappear as the LPE diffraction pattern disappears due to beam damage.

The mechanism of growth of the nodules has not yet been clarified. Neighbouring nodules with similar molecular orientation might be able to coalesce with each other in the solid state or, possibly, melting (due to their small volume) and recrystallization occur during annealing. The fact that nodular structures are still observed even in the specimen annealed at 125°C suggests that the former explanation is more likely; crystallization from the melt at 125°C results in the growth of lamellae.

Figure 3 shows an example of the morphology of a thin region in a polyethylene sample ultraquenched and then annealed at 100°C for 2 h; both nodular structures and lamellar structures coexist. Although this lamellar structure might have formed during annealing, it is believed that it represents the effect of annealing a poorly quenched (lamellar) region. Annealing has resulted in a substantial improvement in perfection over that of the lamellae observed in poorly quenched films[8].

In the samples shown in *Figures 1* and *2*, which are crystalline, there can be no question of the nodules being real and representing crystallites. As such they represent one extreme of the possible morphologies for crystalline polyethylene. However, there still remains the problem of the nature of the similar appearing nodules (in shadowed samples) observed in the amorphous, crystallizable polymers.

Further dark field studies of glassy polyethylene and other crystallizable polymers for which the 10 nm nodule size is representative are needed; in these samples their observation is not due to microscope noise or shadowing artifact. It is possible, however, that nodular structures previously observed on the surface of the cold shadowed, glassy, linear polyethylene[8] and amorphous poly(ethylene terephthalate)[1] shadowed at room temperature may be tiny crystallites; so small and/or imperfect that only diffuse diffraction is obtained. Glassy polyethylene and poly(ethylene terephthalate) may really be aggregates of such small crystallites. In the case of polyethylene a concern is whether the shadowing process may have caused the sample to warm up sufficiently to crystallize during shadowing; however, that cannot explain the poly(ethylene terephthalate) results. Further study of the cold shadowed linear polyethylene is in progress, including dark field contrast observations.

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