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Scanning electron micrographs of high density polyethylene fracture surfaces

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Abstract

Three high density polythylenes with widely differing molecular weights have been subjected to a fast fracture process and studied by scanning electron micrography. Two polymers in the low to medium molecular weight range show evidence of substantial melting during facture, in support of some previous work. On the other hand the ultra high molecular weight material seems to deform on a more massive scale without recognisable relics of a melting process.

Keywords: Micrographs; Fracture surfaces; Fracture process

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1. Introduction

The energy required for the propagation of a crack in hard polymeric materials is controlled by the amount absorbed by deformed polymer which spans the initiation area at the head of the crack. In this way material in a craze or deformation zone may absorb a relatively large amount of energy. In order to understand this process a detailed theory of crazing has been worked out for glassy polymers [1,2] according to which the material has a limited extensibility controlled by the entanglement of the polymer chains. At the maximum extension the stress rises and more polymer can be dragged into the deformation zone.

In tough materials this requires a large amount of energy to be absorbed by a small quantity of polymer which, in a fast fracture, should generate increases in temperature. With glassy polymers, Fuller, Fox and Field [3] have estimated rises of 400–450 K during fast cracking, other high values have been reported by Dickenson et al. [4] and Doll [5]. These results are also supported by studies of fracture surfaces. Already in 1963 Preuss [6] made replica electron micrographs from fracture surfaces of 'low pressure' (i.e. medium to high density) polyethylene broken both at room temperature and in liquid nitrogen. In each case he observed long microfibrils and other features suggestive of high temperatures and even melting. Since that time similar fibrils have been described with several different polymers [4,7,8].

More recently interest in this work has been promoted by the use of a model on which a craze or deformation zone is treated as a constant load system where strain hardening and thermal softening compete to increase or diminish the load carrying capacity of the deformed polymer [9]. The publication of true stress strain relations for polythylenes [10,11] now makes it possible to estimate the tensile stresses over a wide range of conditions and to treat this problem in a semi-quantitative way. Where thermal softening is dominant highly deformed polymer at the centre of a deformation zone may be unable to transfer the load from one matrix surface to another which would lead to fracture as proposed by Vincent [12] for PVC. It was therefore decided to repeat Preuss's work using better defined materials while taking advantage of technical advances in scanning electron micrography. In this note we show scanning electron micrographs taken as part of a programme which unfortunately had to be terminated in unforeseen circumstances.

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2. Methods and materials

2.1. Low molecular weight polyethylene (LMW)

Grade 6070 was supplied by BP Chemicals Ltd. Weight average molecular weight 69,500, number average molecular weight 13,100. Density 960 Kg m^{-3}, melt flow rate 7.6 g/600 s. Yield stress 31 MPa.

2.2. Medium molecular weight polyethylene (MMW)

Grade 6007 BP Chemicals Ltd. Weight average molecular weight 129,900, number average molecular weight

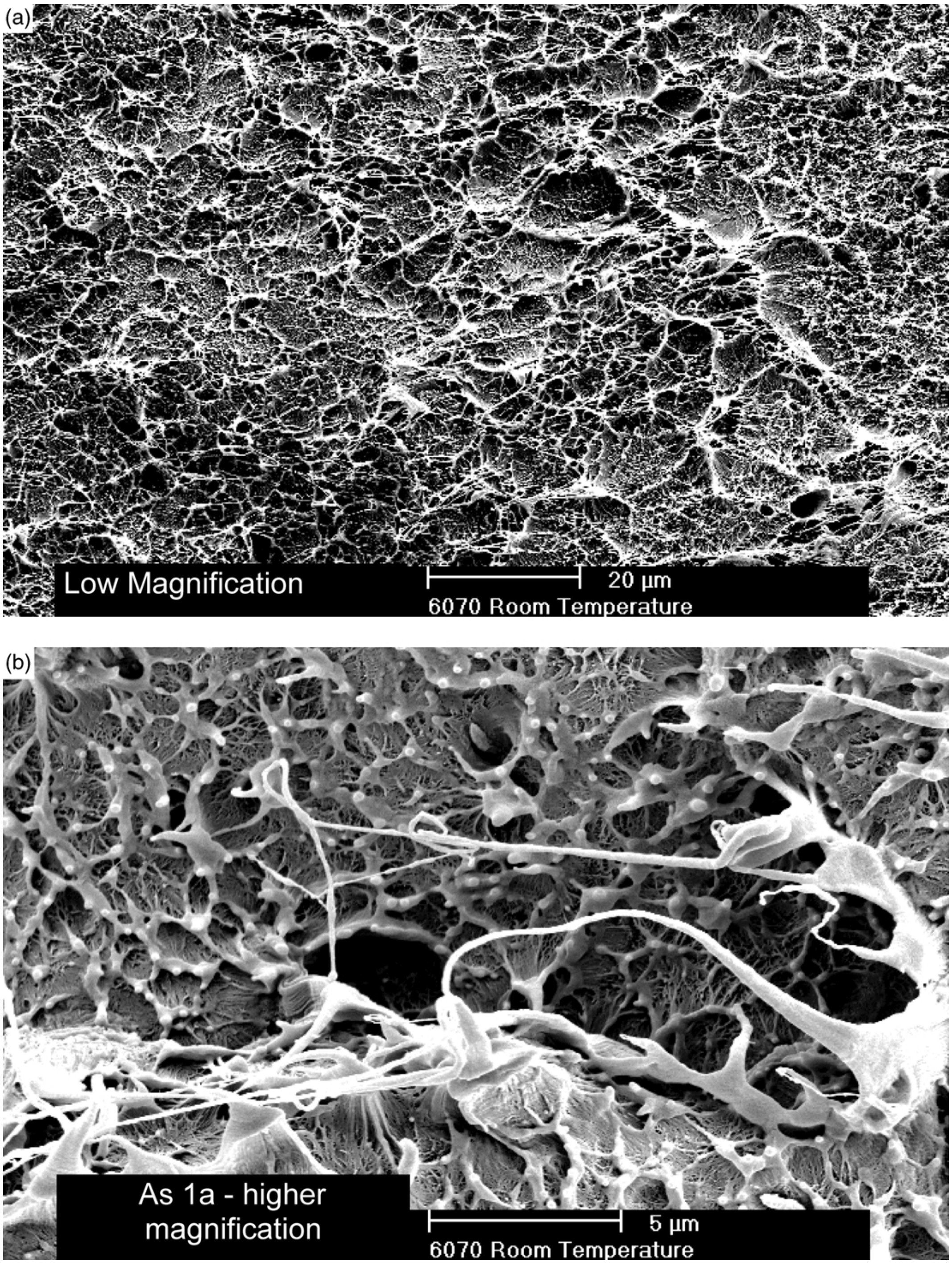

Fig. 1. (a) Low molecular weight polymer. Numerous unresolved areas surrounded by ridges of localised strain. (b) A surface discontinuity with attendant fibrils. Top left area as in 1(a) with terminal rounded nodules. (c) Microfibrils with swellings and grape like features probably formed by the relaxation of hot material.

18,800. Density 962 Kg m^{-3}, melt flow rate 0.6 g/600 s. Yield stress 30.5 MPa.

2.3. Ultra high molecular weight polyethylene (UHMW)

Sheet material supplied by Simona. AG. Teichweg 16, D 55606, Kirn, Germany. Molecular weight $4.4-7.3 \times 10^6$ [12]. Density 940 Kg m^{-3}. Yield stress 21–24 MPa [17,18].

3. The fast fracture procedure

The intention was to break the sample fast enough so that the process was adiabatic. A charpy test piece with a span of 13 cm was very lightly cut at the notch base with a razor blade to secure reproducible crack initiation. It was then broken in an impact tester with a hammer weight of 4.2 kg and an impact velocity of 3.45 ms^{-1}. Assuming no deceleration we estimated the fracture time at about 20 ms and with a fracture strain of 5 this would give a strain rate of 2.5×10^2 s^{-1}. We can then assume that there is a minimum rate of 10^2 s^{-1}, which, because of the chaotic nature of the separation process may be locally increased by orders of magnitude.

All specimens were tested at ambient temperature. However, in order to examine the effects of low temperatures, a further group of samples were immersed, with contact, in liquid nitrogen for a minimum of 30 min. They were then individually removed and subjected to the impact test within 15 s of removal.

4. Sample preparation scanning electron micrography

The samples were carbon coated at a vacuum of about 10^{-5} mbar to give an electrically conducting surface layer. During the treatment the sample was rotated to give a uniform carbon layer and avoid directional deposition effects. This is necessary with samples showing a lot of surface topography. Examination was carried out with a Philips XL30 Field Emission Gun scanning Electron Microscope using the lowest practicable voltage of 5 kV to avoid excessive beam penetration or sample charging. The combination of a small aperture, together with a short working distance was employed to obtain the best achievable resolution.

5. Experimental results

5.1. General

In a Charpy or Izod test fracture takes place as a result of a bending process so that conditions at the head of the crack change as the crack travels through the test piece. Some differences in the fracture surface were observed at the point where the crack was initiated and at the final stage where a hinge effect is to be expected. The pictures shown were all taken at points away from the ends where similar features were visible over a significant area (Figs. 1(a), 2(a) and 3(a)).

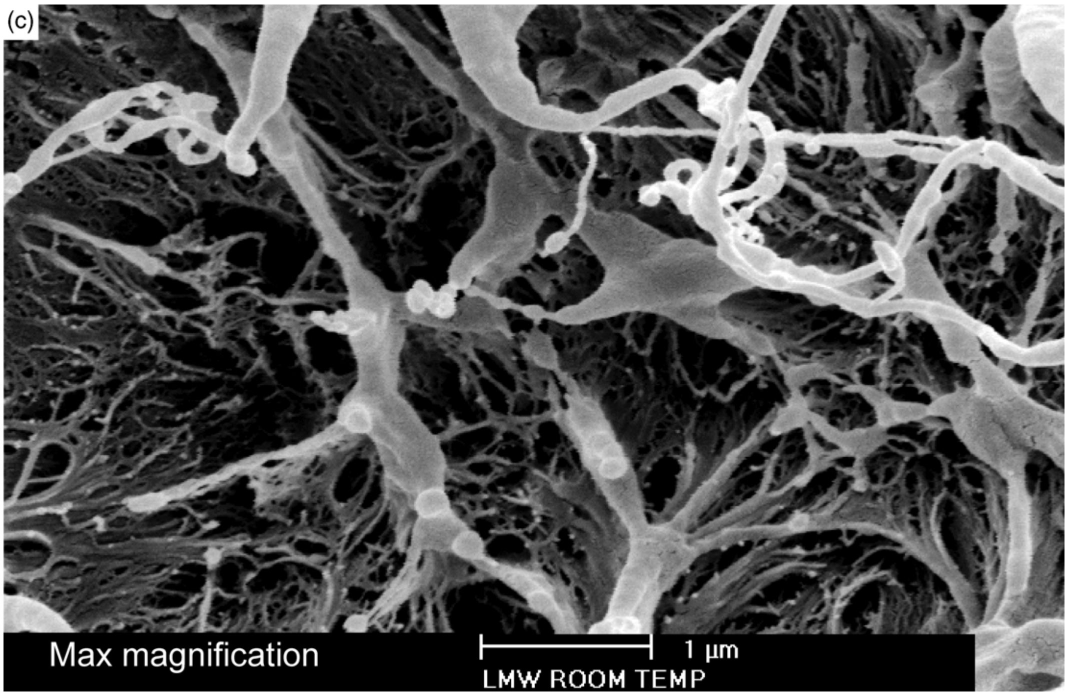

Fig. 1 (*continued*)

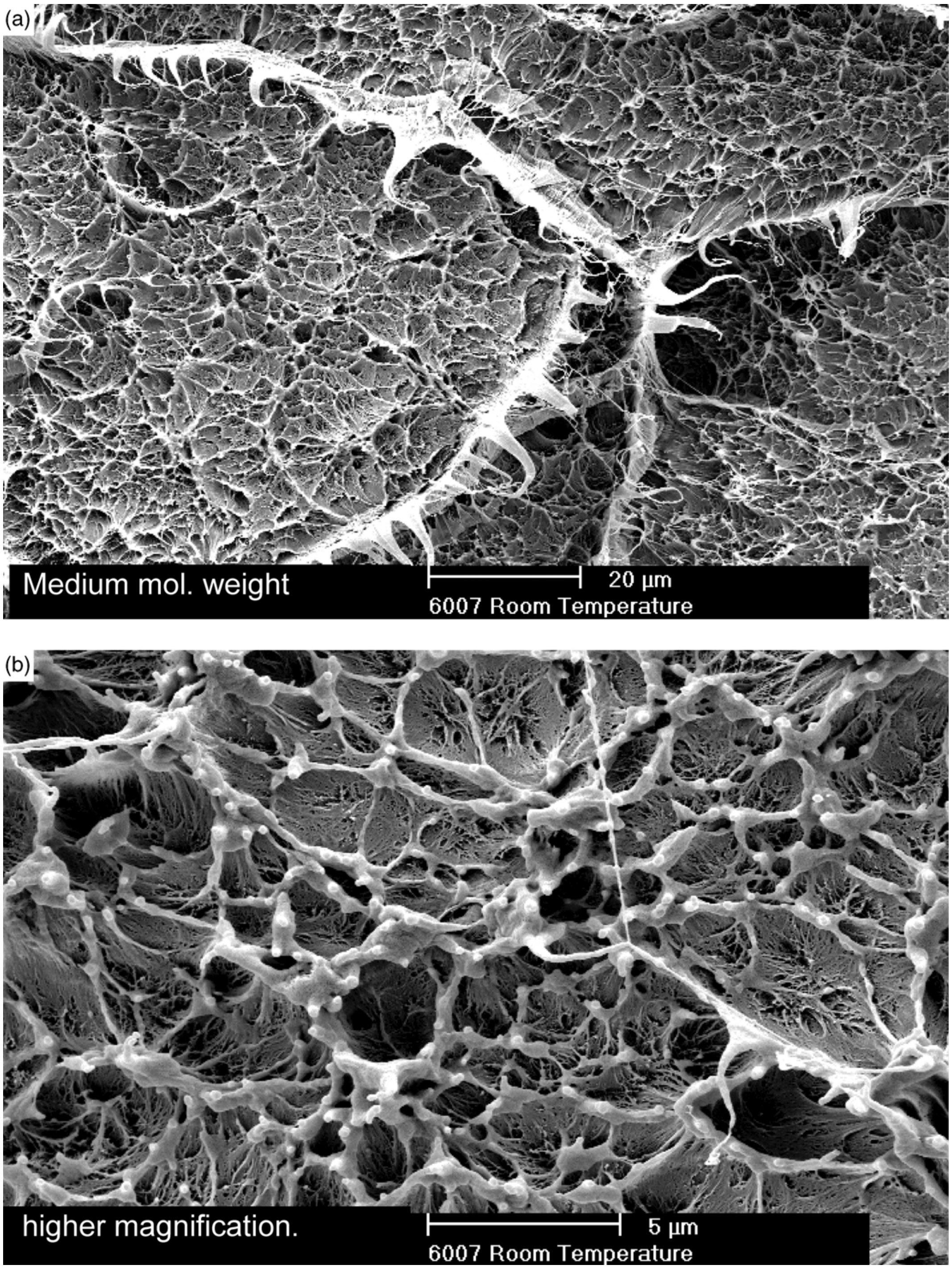

Fig. 2. (a) Showing edge discontinuity with areas on left similar to 1(a) but with a larger scale. (b) Many rounded nodules where final separation seems to have occurred.

5.1.1. Low and medium molecular weight polyethylenes LMW and MMW. Micrographs at room temperature

In Fig. 1(a)–(c) SEMs are shown at three levels of magnification for the low molecular weight material broken at room temperature. Number 1(a) shows an overall view of the central fracture surface at low magnification. There is clearly a large amount of small deformation all over the area with a number of longer fibrils, some of them starting from points of apparent discontinuity in the progress of the crack. There are also numerous tiny features, roughly spherical, which are largely unresolved. In Fig. 1(b) we see at the bottom fibrils coming from an edge where there has been an apparent change in level and in the top left hand area, against a back ground of deformed material, there are a large number of knobs or nodules with a smooth rounded surface. Finally, at the highest magnification (1(c)) we see a large

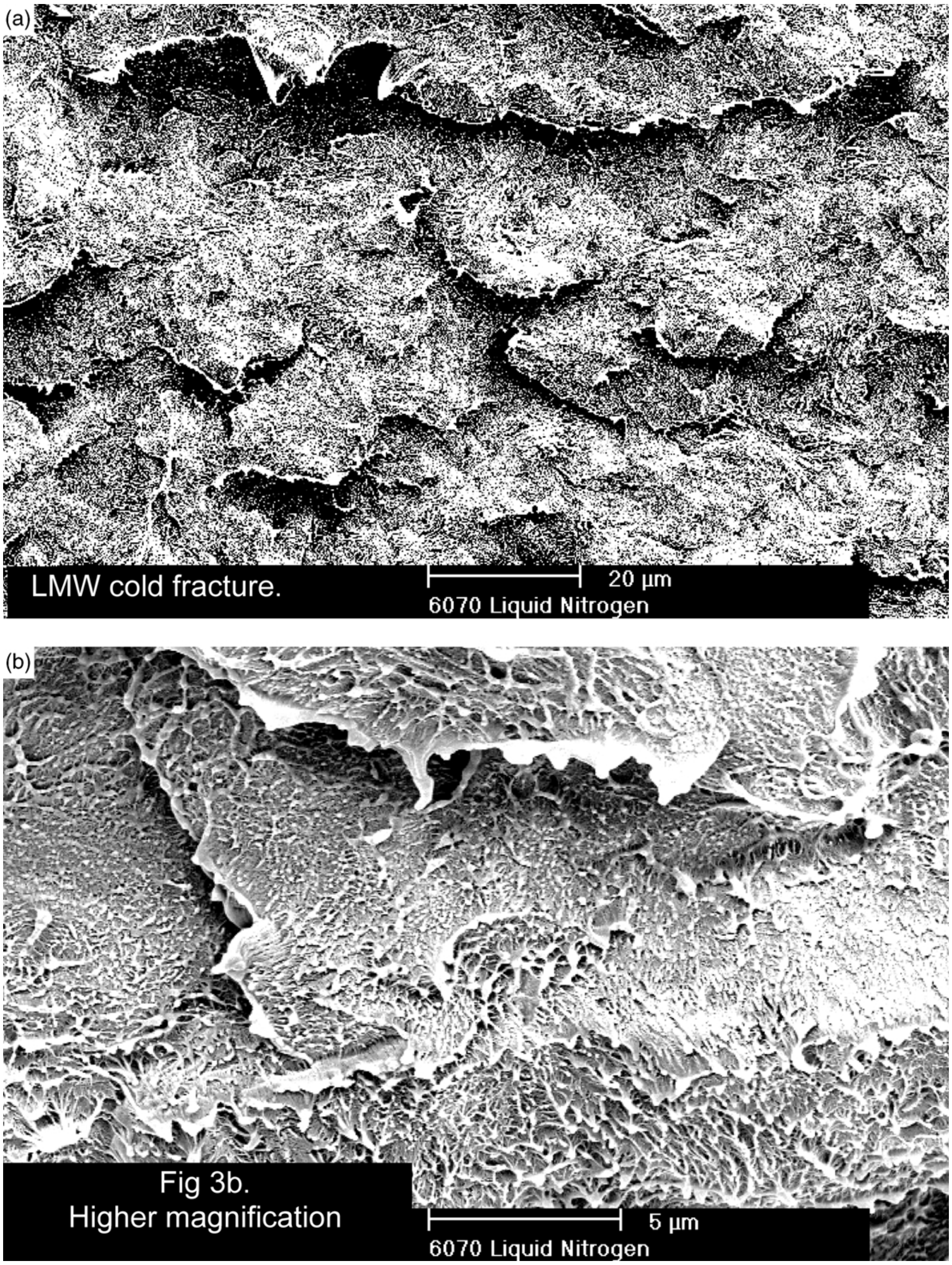

Fig. 3. (a) A block like structure with discontinuities. With fine surface structure not well resolved. (b) Widespread termination with rounded nodules analogous to 1(b) and 2(b). (c) Showing edge with rounded nodules. (d) Several spikes of pulled out material with rounded nodules.

amount of chaotically drawn polymer much of it in contorted coils, which could result from the contraction and cooling of hot fibrils. There are also some small grapelike swellings in the smaller fibrils, one of them at the point of fracture. The general appearance suggests widespread softening of the material during the fracture process.

Micrographs with the medium molecular weight polymer 6007 are shown in Fig. 2(a) and (b). At low magnification Fig. 2(a) shows large areas covered with small-scale deformation similar to Fig. 1(a), but in this case several edge discontinuities are included with attendant fibrils. In Fig. 2(b) an area with the small-scale deformations is shown at higher magnification. As with 1(b) there are numerous rounded nodules of polymer where actual separation seems to have occurred. Many of these are arranged along curved lips surrounding a cavity. As with 1(b) they have a smooth

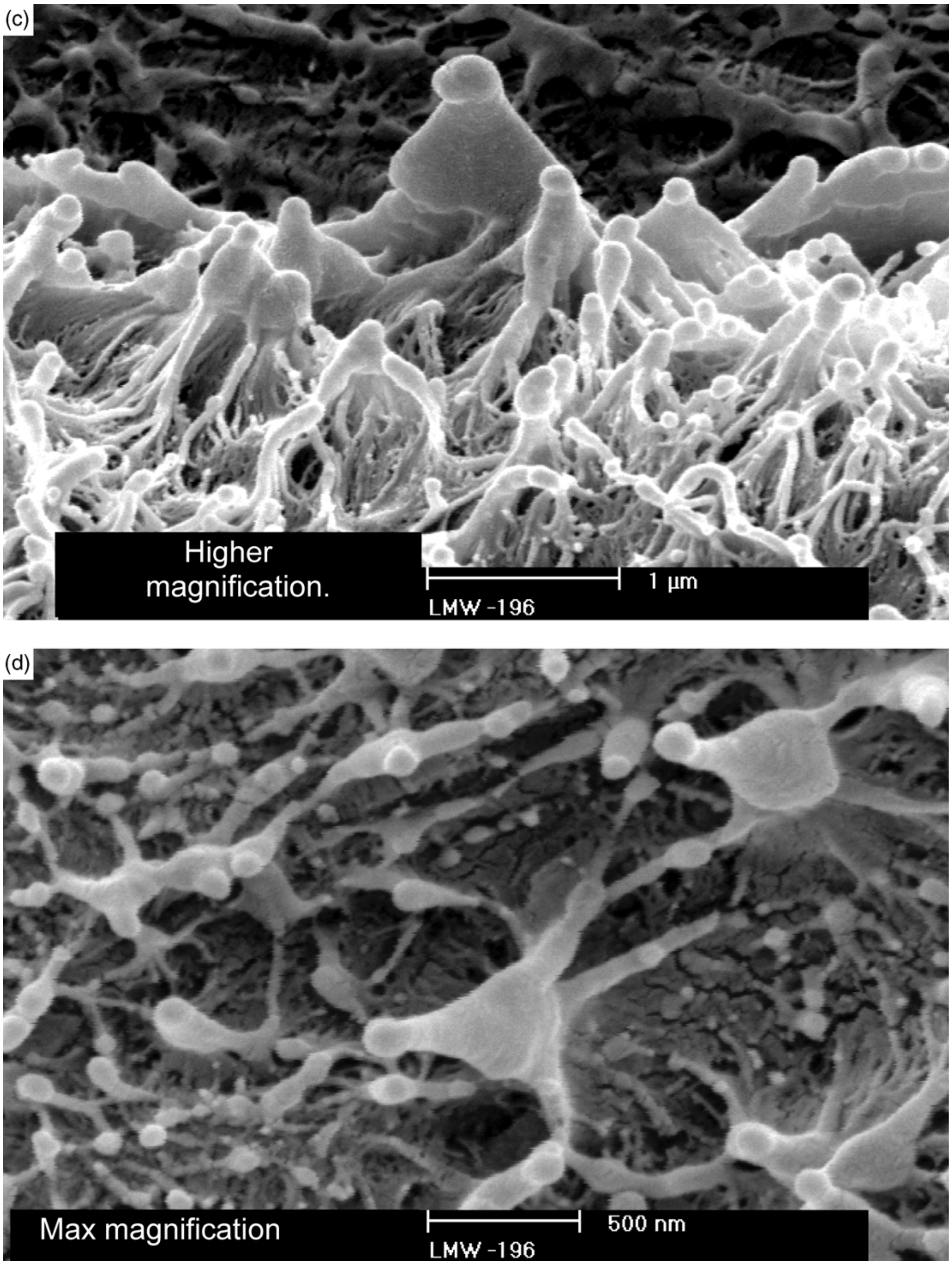

Fig. 3 (*continued*)

appearance, which could be associated with fast cooling of a relatively low viscosity material.

6. Samples cooled in liquid nitrogen

Figs. 3(a)–(d) were obtained with the LMW polymer. Fig. 3(a), at low magnification includes a number of discontinuities or jumps in the fracture process leading to a blocky structure. However, all the surfaces are covered with a very fine mesh of deformed polymer, similar to that observed at room temperature, which is hardly resolved at the magnification employed. When the magnification is increased to the next stage, as in Fig. 3(b), the general form of the structure can be seen. As with the room temperature micrographs, the discrete extensions of deformed material, pulled out from the matrix are terminated by a nodule, which in this picture seems smaller than those seen in 1(b) and 2(b). There is also a sense that their orientation has been influenced by the direction of the crack propagation but the significance of this feature is not known and would require further work. Because the structure of the deformed material seemed to be smaller than in the room temperature fractures, the highest magnification used was increased as shown in Fig. 3(c) and (d). Both these micrographs show material pulled out from the matrix and terminated by a smooth nodule as in Fig. 1(c). In Fig. 3(c) a small discontinuity is present which enables the knobs to be seen more clearly at an angle. As with the room temperature micrographs, the smooth surfaces of the terminal nodules carries the implication that, even with

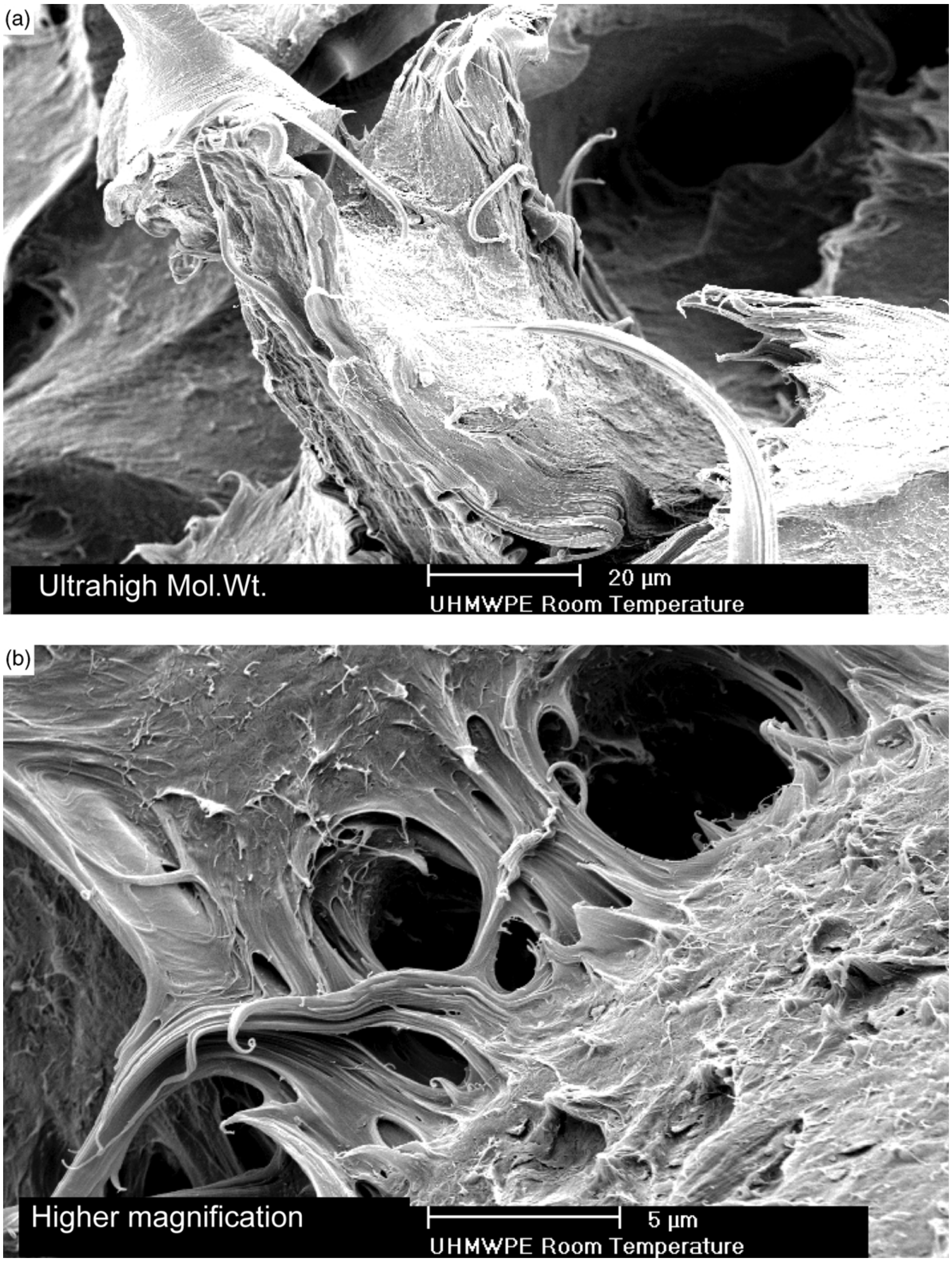

Fig. 4. (a) Relatively massive deformation with curved fibrillated termination of thick drawn material. (b) Shows massive deformation and cavitation. (c) Cold fracture with large cavities. Not significantly different from 4(a).

the cold polymer, high temperatures are generated in the fracture process. This proposition will be considered later.

Micrographs with the MMW polymer cooled in liquid nitrogen were generally similar to those described above.

6.1. Ultrahigh molecular weight polyethylene (UHMW)

Micrographs from room temperature fractures are shown in Figs. 4(a) and (b) and from liquid nitrogen cooled material in Fig. 4(c). Both conditions yield fracture surfaces entirely different from the two polymers with molecular weights within the normal commercial range. Although some pictures give an indication of scattered small scale deformations, the general impression is that of material being drawn apart during a large scale, relatively homogeneous, deformation process. Although there is a good deal of highly extended material some of its curved as though it had been cooled from a raised temperature, but there is no pattern of smooth knobs of the type believed to be formed by very hot material retracted after fracture.

7. Discussion

7.1. Thermal effects

It is clear that scanning electron microscopy has the capability of providing valuable information about the fracture process of high density polyethylenes. It therefore seems appropriate, in spite of the limitations of the work, to make some comments on the experimental results. In particular, the widespread observation of nodules or swelling at the point where separation has taken place deserves attention. These features may be compared with the results of Hearle et al. [13] who observed mushroom shaped formations at the point of fracture when thermoplastic fibres were broken by a pendulum in a fast fracture process. This was ascribed to localised thermomechanical heating of the material; after separation the softened material left by the separation process expanded to give the mushroom shaped feature. A similar mechanism could equally apply to the large numbers of smooth knobs visible in Figs. 1–4. It could also account for the terminal grape-like formation visible in Fig. 1(c) and for the other swellings in continuous sections of the smallest fibres present. All this generally supports the earlier conclusions of Preuss [6] that significant heating and melting occurs during fracture. More particularly it also agrees with the work of Haward and Brough [4] who obtained replica micogaphs with polystyrene showing rounded nodules very similar to 1(b) and 2(b) described here and also proposed that they could have been formed by the retraction of a hot filament. Further some of the present high magnification micrographs as, for example 3(d), show a likeness to those reported by Schinker, Konszol and Doll [14] in a study of the stepwise fatigue fracture of PVC, who also concluded that surface melting had occurred. More recently it has been argued by Hillmansen and Haward [9], as earlier by Vincent [12], that where substantial heating takes place, it becomes impossible to transmit stress from one matrix surface to

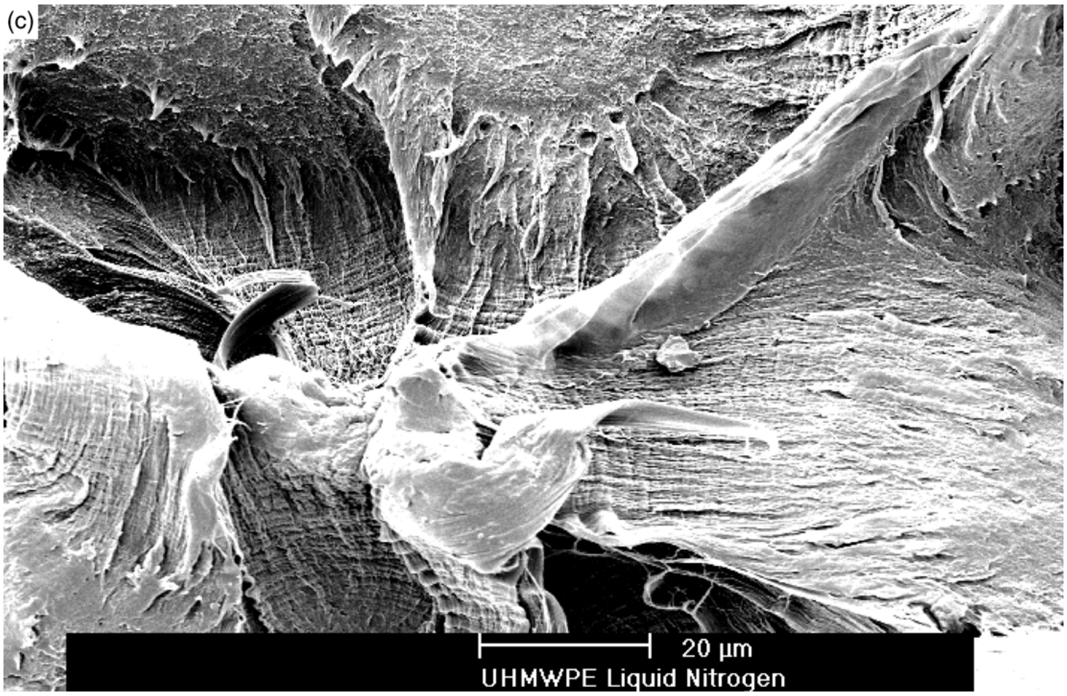

Fig. 4 (*continued*)

another across a craze or deformation zone. Separation should then take place through the plane of most highly softened material.

In Figs. 3 and 4(c) the sample was cooled in liquid nitrogen before fracture. In such cases a much larger temperature rise is obviously required to reach the softening or melting point of the polymer. However this may not be as unlikely as it seems at first, as the scaling factor which determines the rate of heating of the polymer can be formulated as $\sigma_n/\rho C_p$, where σ_n is the nominal stress, in this case taken as the yield stress, ρ the density and C_p the specific heat. This scaling parameter rises as the temperature falls, so that its value between room temperature and −140 °C increases by a factor of 7 [9]. This means that the temperature increases much more quickly with strain when the cold material is deformed so that high temperatures during fracture are also possible.

7.2. UHMW polymer

According to the model proposed in Ref. [9] the competition between the strain rate in the deformed material and the rate in which new material is dragged into the deformation zone in fast fracture depends on the relation between strain hardening and thermal softening. However it has been known for a long time that strain hardening is strongly affected by molecular weight [11,12,15,16]. It has also been shown that with the UHMW type of material the strain hardening is high enough to suppress necking in tensile tests at moderate strain rates [17,18] It is not therefore surprising to find that also in these studies of fracture surfaces this material seems to deform more in a bulk fashion than with the two lower molecular weight polymers. It would be expected that the ability to bring more material into the deformation zone would increase the energy required for crack propagation.

8. Conclusions

Large deformations occur during the fast fracture of polyethylene. With medium and low molecular weight materials electron micrographs of fracture surfaces exhibit numerous rounded nodules suggestive of a melting process. With UHMW material deformation takes place on a larger scale, probably due to the high level of strain hardening.

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