BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 9, pp. 1827-1833, 1995

0032-3861/95/$10.00+0.00

Real-time cryo-deformation of polypropylene and impact-modified polypropylene in the transmission electron microscope*

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Dynamic plane-stress failure has been observed directly in the transmission electron microscope as a function of temperature using a commercially available cooling/straining holder in conjunction with a copper deformation cartridge. The low-temperature cooling stage permits studies of the ductile–brittle transition when the transition is between +23 and −170°C. A change in deformation mode was observed on the submicrometre level for polypropylene and impact-modified polypropylene. At room temperature, polypropylene and impact-modified polypropylene deform by shear yielding. Below the ductile–brittle transition the polymer chain mobility is curtailed and crazing dominates. The stage allows observation of the deformation at varying temperature, and events occurring during the deformation can be recorded in real time using a CCD camera.

(Keywords: polypropylene; TEM; cryo-deformation)

INTRODUCTION

A previously described technique[1-3] allows the real-time observation of dynamic plane-stress polymer failure in the transmission electron microscope. After bonding a thin section of polymer to an annealed copper cartridge, it is plastically deformed in tension in the TEM using a screw-driven tensile stage while a low-light CCD video camera records the deformation and fracture processes. Recently, a low-temperature cryo-tensile stage has become commercially available. The stage can be used from room temperature down to −170°C. Thus, the failure of a polymer can be studied below its ductile–brittle transition temperature. This paper demonstrates the use of this stage to study failure and toughening in polypropylene (PP) and impact-modified polypropylene.

The deformation of polypropylene has been extensively reviewed by Friedrich[4]. Jang, Uhlmann and Vander Sande have conducted tensile experiments on PP and rubber-modified PPs over a wide range of temperatures and strain rates[5]. These investigators have shown that the ductile–brittle transition is strongly affected by both temperature and strain rate. The process is complex owing to the varying crystallinity within the microstructure. For a given temperature, there is a critical strain rate above which crazing dominates and below which shear yielding is dominant[5,6]. The ductile–brittle transition was explained as being due to the alteration in deformation mode[7]. The experiments conducted herein allow visualization of the change in deformation mode with temperature.

EXPERIMENTAL

The single tilt cold strain holder and CCD camera were manufactured by Gatan (Gatan Inc., 6678 Owens Drive, Pleasanton, CA 94588-334, USA). The key to performing these experiments directly in the transmission electron microscope was the development of a specimen cartridge that could support the thin section of bulk polymer and still deform plastically under load. The cartridge manufactured by PCM Products (PCM Products, PO Box 5399, Tittusville, FL 32783-5399, USA) was designed at Dow. Several cartridge configurations now exist. Details on the design and applications of the grids are described in ref. 1. The entire deformation and fracture process is recorded in real time using a low-light charge-coupled device (CCD) video system with image intensification. The camera choice is important, because many polymers are beam-sensitive and may crosslink or undergo scission during examination. With this system we are able to work using a defocused 500 Å beam spot with beam currents less than $10^{-1}\,\mathrm{A\,m^{-2}}$. The polymers were also deformed with electron beam off and then re-examined with the beam on to ensure that beam damage did not alter the deformation process. The deformation rate was between 0.1 and $1\,\mu\mathrm{m\,s^{-1}}$. The microscope was a Philips CM12 operating at 120 keV.

Isotactic polypropylene homopolymers obtained from Himont Inc. had a melt flow (*MF*) of 12, corresponding

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* Presented at 'Aspects of Imaging in Polymer Science', 51st Annual Meeting of the Microscopy Society of America, 1–6 August 1993, Cincinnati, OH, USA

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to a molecular weight (M_w) of 163 700. EPDM (ethylene-propylene-diene) elastomers (Royalene™ 521) were acquired from Uniroyal Chemical. The polyethylene elastomer (Insite™) was prepared at Dow's Polyolefins Research Facility in Freeport, Texas, and had a density of $0.87\,g\,cm^{-3}$.

All blends were prepared using a 20 mm Welding Engineers counter-rotating twin-screw extruder running at 200 rpm. Zone temperatures profiled from 170 to 210°C from the feed zone to the die, respectively. The molten polymer blend strand was cooled in a water bath and pelletized. Compression moulding of test specimens was carried out at 200°C for 5 min on a Tetrahedron Compression Molding Machine. Elastomer melt flow rates were determined at 190°C using a Tinius-Olsen extrusion plastometer according to the specifications of ASTM D-1238. Polypropylene melt flow rates were determined in a similar manner at 230°C.

Low-temperature Dynatup impact measurements were carried out using a model 8000 Dynatup drop tower following the procedure outlined in ASTM D3763-86. The drop height was 12 inch (~30.5 cm) with a 138.5 lb (~62.8 kg) weight. The ram diameter was 0.625 inch (~15.9 mm) and the unsupported tup diameter was 1.25 inch (~31.8 mm). The ram velocity at impact is approximately 5800 inch/min ($\sim 2.45\,m\,s^{-1}$). The specimens were unclamped and tested at various temperatures. Data acquisition and calculations were done using DYN730 software.

Thin sections for cryo-deformation required cryogenic preparation with a Reichert-Jung Ultracut FC 4E to ensure that the morphology remains unaltered during sample preparation. The samples were not stained in order to avoid any alteration of polymer properties.

RESULTS

Polypropylene

The unique capability to do tensile deformation directly in the transmission electron microscope allows one to examine the details of the deformation in real time as a video camera records the deformation. The two limiting conditions, plane strain and plane stress, are often used to describe the deformation of a thermoplastic subjected to a tensile loading; for a thin microtomed polypropylene film, plane stress dominates. In this case the deformation usually continues by a semi-homogeneous yielding process. *Figure 1* shows a thin section of polypropylene deformed at 23°C to an elongation of 66%. During the deformation, shearing in the surrounding matrix material was observed on the video display. The void produced during the deformation was associated with an unidentified nucleating aid. Because the nucleating aid is not well bonded to the polypropylene matrix, a void forms with continuing deformation. The nucleating aid concentrates stress and initiates the deformation. Deformation around the void occurs at the equator, as predicted by Goodier because the stress is highest at the equator of the nucleating aid[8]. A whitened area resembling crazing is seen emanating from the equators of the void. However, this is not a craze because the white area is thinned (i.e. yielding) during deformation without the voids that are typical of crazing. This type of deformation has recently been termed fibrillated shear in crystalline polymers[9], but since it is not voided and distinct fibrils are not present perhaps this zone should be viewed as a hybrid between a craze and shear mode of deformation. The hybrid zones crossed PP spherulite boundaries and were increased in number as the amount of nucleating aid increased. Voids always formed around the nucleating aid, and at extensions exceeding 200% the void would become a crack, which upon further extension would propagate through the hybrid zones until the film failed.

Temperature effects are illustrated in *Figure 2*. As the temperature decreased, the elongation of the specimen is reduced and shear yielding gradually gives way to crazing. The first appearance of crazing in the shear zones occurred at −5°C; voiding occurred in the deformation zone and the boundaries between this zone and the matrix material became sharp. The temperature at which voiding and fibrils are observed correlates closely with the ductile-brittle transition obtained in a bulk specimen. As the temperature was further lowered, the boundaries became sharper and increased voiding resulted in fibrils in the deformed region. The shape and aspect ratio of the crazes also changed as the temperature was lowered. Low-aspect-ratio crazes formed near the ductile-brittle transition and high-aspect-ratio crazes formed below the transition. Donald[10] observed similar results in her studies on polystyrene films as a function of temperature and molecular weight. Her films[10] were deformed and strained outside of the TEM in a manner similar to that of Kramer *et al.*[11-14]. It was observed that crazing occurred almost exclusively in a temperature range between 40 and 90°C on low-molecular-weight samples,

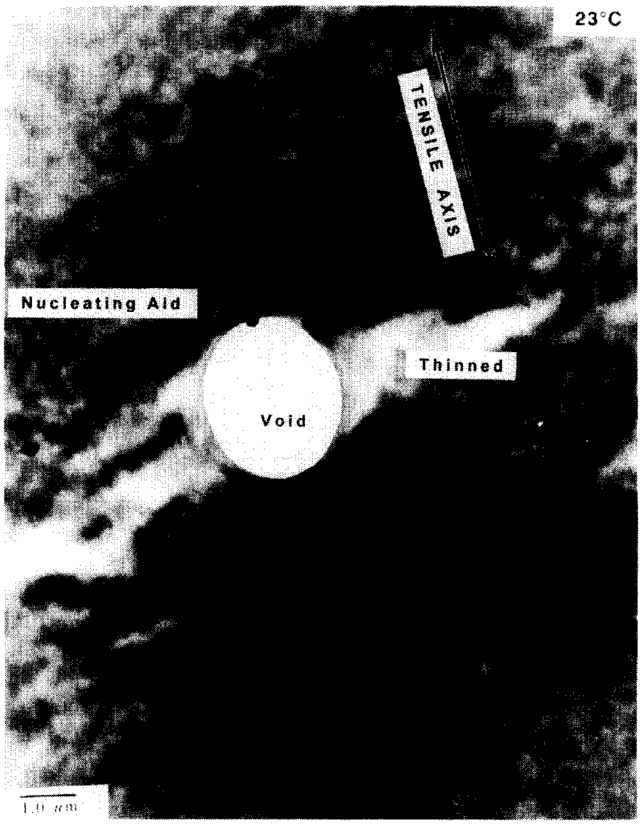

Figure 1 Polypropylene deformed at room temperature (23°C). Arrows indicate nucleating aid and tensile direction

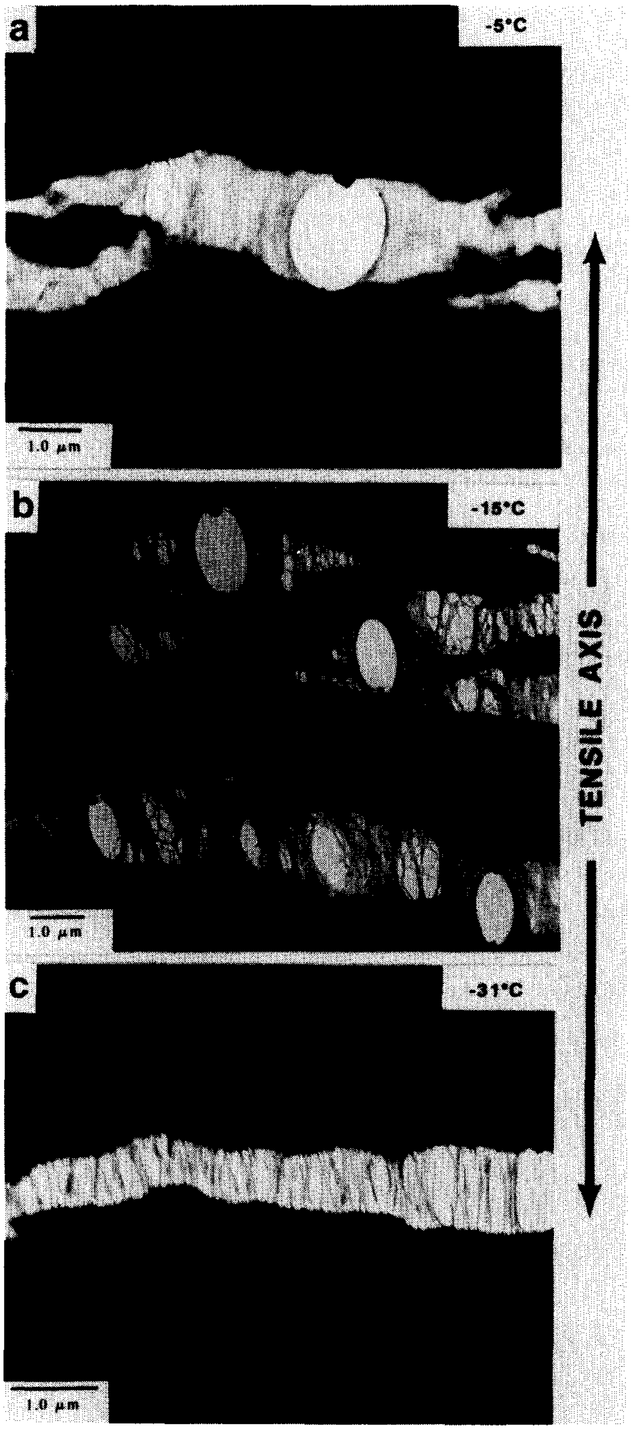

Figure 2 Polypropylene deformed at (a) −5°C, (b) −15°C and (c) −31°C showing a transition from fibrillated shear to crazing

whereas the shear process became important for higher-molecular-weight materials with the formation of shear zones occurring as the glass transition temperature T_g was approached. These observations were consistent with the idea that disentanglement processes become increasingly important at the higher temperatures. At lower temperatures, molecular chain movement is restricted and scission is the dominant mechanism for the alteration of the entanglement network required in crazing.

Rubber-modified polypropylene

The addition of a low-modulus elastomer to polypropylene greatly increases the low-temperature impact toughness[15–18], reduces the yield stress and shifts the ductile–brittle transition to lower temperatures. Ethylene–propylene–diene elastomer (EPDM) is used to modify isotactic polypropylene for use in automotive applications. The *in situ* cryogenic deformation of polypropylene was compared for two modifiers, EPDM and a new class of ethylene–octene copolymers. The new polyolefin elastomers are prepared using Dow's constrained-geometry catalyst technology (CGCT) and have recently become commercially available under the INSITE trademark. The main advantage of the INSITE technology elastomers, other than their relatively low cost, is their ability to impart ductile failure in PP blends with high melt flow ($MF \geqslant 20$) at low temperature (−20°F (−28.9°C)). The PP/INSITE blends have higher net melt flows than their EPDM analogues, resulting in easier processing. The ductile–brittle transition measured by Dynatup impact for polypropylene/INSITE blends as a function of temperature for various INSITE technology elastomer concentrations is shown in *Figure 3*. Polypropylene without elastomer was not included in *Figure 3*, since it exhibited brittle failure under the test conditions. The blends show poor low-temperature impact until a critical level of impact modifier is reached. This, in part, defines the relative impact efficiency of the elastomer.

Figure 4 is a plot of the blend impact energy vs. percentage elastomer loading in a 12 melt flow rate polypropylene homopolymer. Typical applications require ductile failure at −20°F (−28.9°C). The materials were deformed in the transmission electron microscope down to a temperature of −31°C. The effects of room-temperature deformation for the INSITE technology elastomer-modified materials are shown in *Figure 5*. Similar results were observed for the PP/EPDM blends. The rubber functions as a stress concentrator and nucleates shearing (rubber-assisted shear deformation). During deformation the rubber particles yield as the film is stretched; this in turn causes the PP matrix between particles to yield and thin at an angle characteristic to

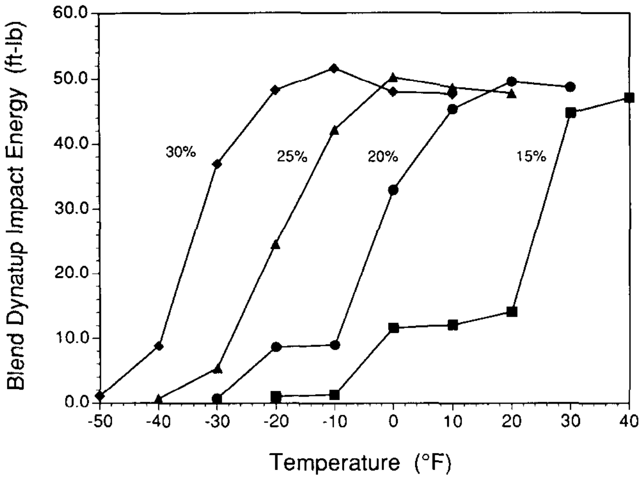

Figure 3 Ductile–brittle transition temperatures of polypropylene/Insite blends for 15, 20, 25 and 30 wt% Insite technology olefin elastomer loading (1 ft lb = 1.3558 J, so vertical scale extends to 81.35 J; temperature scale extends from −45.6 to 4.4°C)

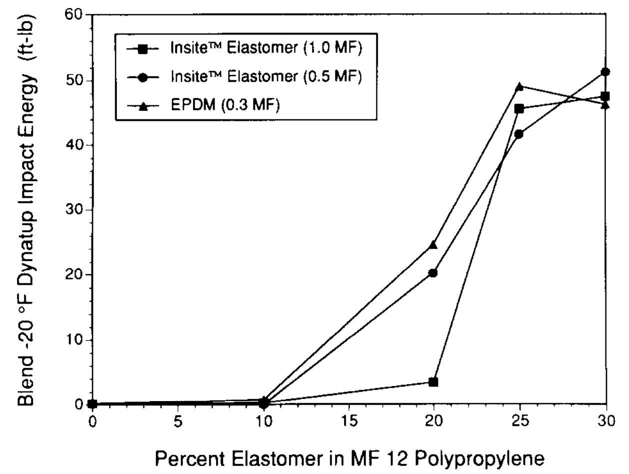

Figure 4 Polypropylene–elastomer impact energy vs. percentage elastomer loading in 12 melt flow polypropylene homopolymer

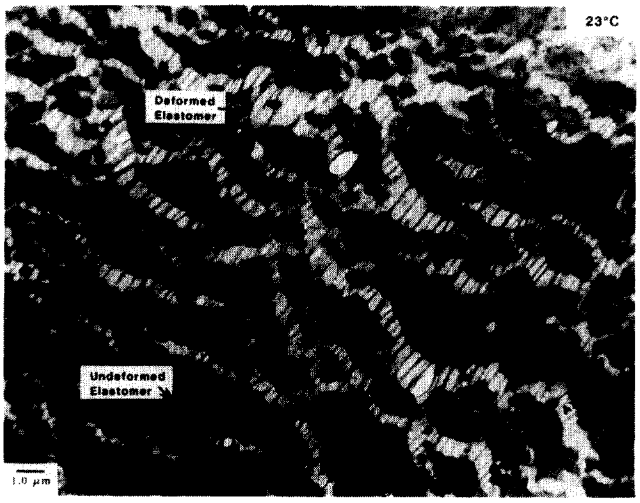

Figure 5 Room temperature (23°C) deformation for 30% INSITE technology olefin elastomer loading in polypropylene

the deformation process. The stress concentration is strongly affected by the number of elastomer particles. At the high loadings used in commercial applications, local yielding is caused by overlap of particle stress fields. Wu[18] has suggested that there is a critical interparticle distance that reduces the critical stress for matrix yielding to about half of that required without rubber. The particle size of the INSITE technology elastomer is smaller than the EPDM, resulting in a smaller interparticle distance for the same loading and thus providing a higher extent of yielding. The addition of the INSITE technology elastomer reduced the average spherulite size of the PP from 4.6 to 3 μm, which has been shown previously to increase the fracture resistance[2,3]. While there is poor adhesion between ethylene–propylene rubber (EPR)[19] and PP, good adhesion was found between both EPDM and INSITE technology elastomers with the matrix. Earlier work has demonstrated that when a polymer has low miscibility and/or poor compatibilization between phases in a blend, delamination will occur immediately with the onset of deformation[1]. During deformation the rubber can be observed to expand by several hundred per cent before the elastomer eventually cavitates. Cavitation relieves stress[6,20,21] and the rubber fibrils bonded to the PP stabilize the cracks that form during cavitation.

As the temperature was decreased, shear yielding gave way to crazing (*Figure 6*). The angle of the deformation between rubber particles was less and voids and fibrils formed in the matrix. The change in the mode of deformation occurred at approximately −5°C, the same temperature at which crazing started in the unmodified PP and not at the transition temperature shown in the Dynatup impact studies. The differences between the Dynatup impact data results arise because of the stress states and strain-rate differences in a bulk specimen. The impact tests were conducted at a rate of approximately $2.4 \times 10^6 \mu\mathrm{m\,s}^{-1}$ whereas the material was deformed in the TEM between 0.1 and 1 $\mu\mathrm{m\,s}^{-1}$. Jang *et al.* conducted extensive tensile testing over a wide range of temperatures and strain rates[5]. When they plotted the normalized yield stress (defined as the maximum engineering stress in the stress–strain curve divided by the test temperature) vs. the log strain rate, they noted a transition zone in which crazes and shear bands coexist. For a given test temperature, there is a strain rate that is dominated by crazing, and for a given test rate, there exists a

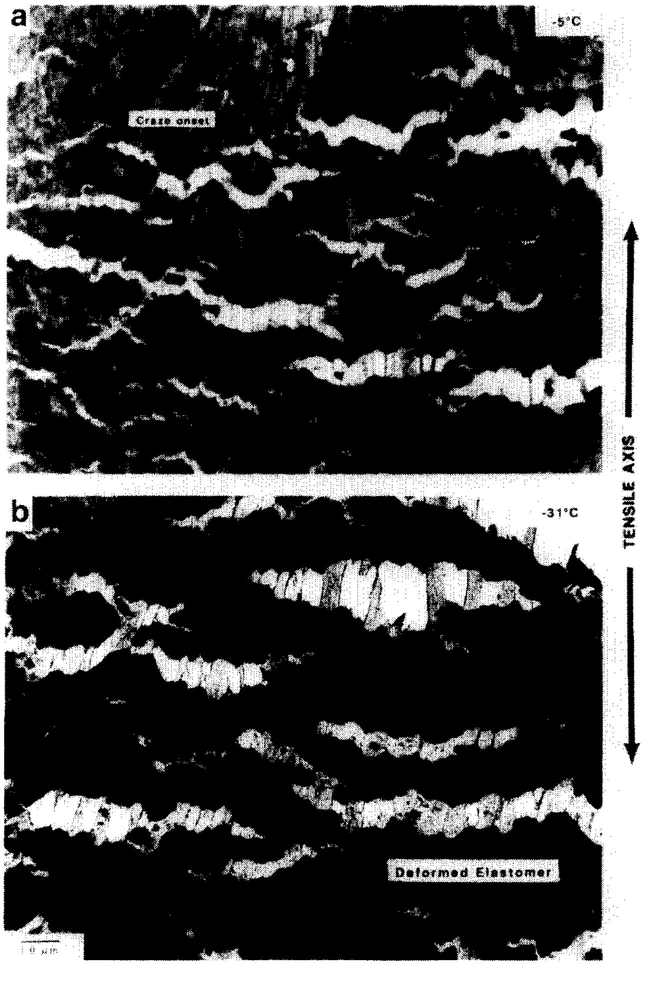

Figure 6 (a) Crazing formation initiated at −5°C and (b) well developed crazes at −31°C. Note rubber bridging across broken craze fibrils

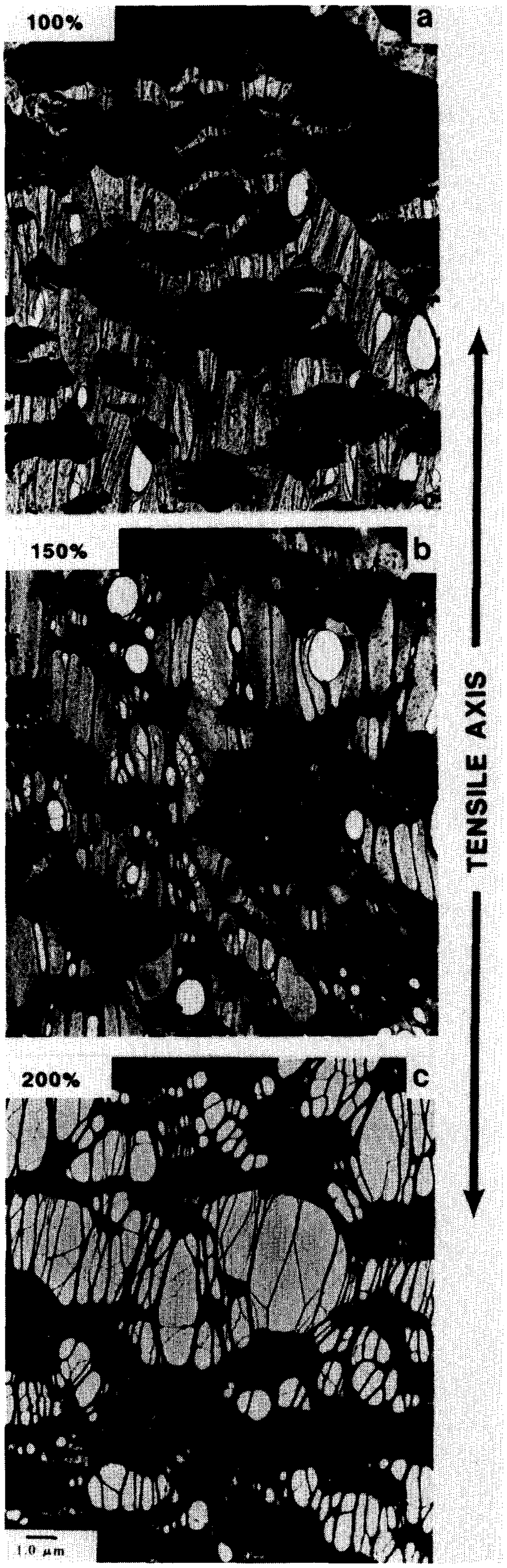

Figure 7 EPDM rubber-modified polypropylene as a function of grid elongation showing the breakdown of rubber particles

temperature that restricts crazing from shear yielding. In this investigation, deformation mechanisms were studied as a function of temperature only because of the limited strain-rate range capability with the present stage. Within this range (0.1–1 $\mu m\, s^{-1}$), the onset of crazing was the same for PP and rubber-modified PP. The deformation volume is considerably higher in the presence of rubber.

At −31°C, rubber particles nucleated crazing in the polypropylene matrix. As the material deforms, the rubber bridges the crazes, maintaining the craze integrity. EPDM rubber will expand by a factor of 2 before cavitation occurs. *Figure 7* shows the average elongation, as measured from the amount of grid deformation that the EPDM was subjected to during the deformation. Some particles undergo greater elongation depending on the amount of shear and critical stress around the particles. During this elongation the EPDM is thinning and at 200% the EPDM particles have broken down into rubber fibrils. The cavitation and the stretching into rubber fibrils relieves the stresses, while the rubber fibrils, still well bonded to the PP matrix, will span and maintain the stability of the cracks generated through matrix crazing. Further elongation results in breaking the rubber fibrils and cracks propagate to failure. INSITE technology elastomers were found to expand by as much as 400% before cavitation and fibrillation. The greater elongation of INSITE technology elastomers is due to higher elasticity at these temperatures. This may be due to differences in entanglement density.

The impact strengths of INSITE technology elastomer/PP blends have exhibited a molecular-weight dependence. The notched Izod impact strength at room temperature and the −20°F (−28.9°C) Dynatup impact strength for various melt flow (*MF*) INSITE technology elastomers blended into a 12 *MF* PP are shown in *Figure 8*. In an attempt to explain the sudden drop in impact properties at $MF \geqslant 3$, the blends were examined using the low-temperature tensile stage in the TEM. At −20°F (−28.9°C), crazing is the primary mode of failure. The degree of craze formation was notably less in the blend containing 18 *MF* INSITE elastomer than in the system containing 0.5 *MF* INSITE elastomer (*Figure 9*). This can be attributed to restricted chain disentanglement and less energy absorption in the higher *MF* elastomer phase. In

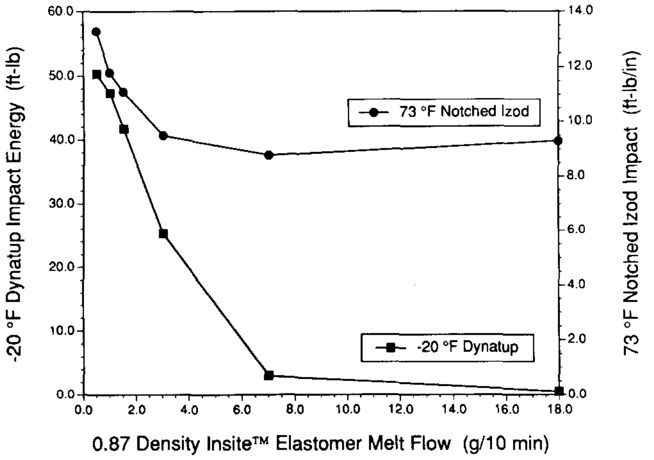

Figure 8 The 73°F (22.8°C) notched Izod and −20°F (−28.9°C) Dynatup impact data vs. Insite technology olefin elastomer melt flow indicating the impact dependence on molecular weight

the melt flow range between 1 and 5, a small change in *MF* represents a large change in molecular weight. Further work is in progress in order to understand the INSITE elastomer molecular-weight dependence. Scanning electron microscopy (SEM) of the −20°F (−28.9°C) fracture surfaces (*Figure 10*) revealed little elastomer deformation in fracturing when *MF* 3 and 18 are used, while the *MF* 1 INSITE elastomer blend shows significantly more elongation. In the higher *MF* materials, cavitation may be occurring earlier on in the deformation process, undergoing little extension, and less stress relief.

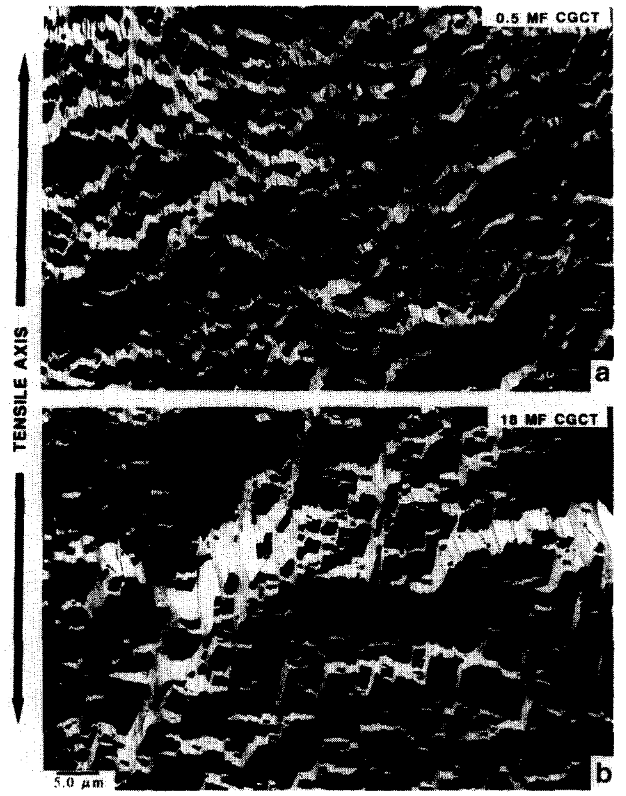

Figure 9 Craze deformation at −31°C for (a) 0.5 and (b) 18 melt flow INSITE/polypropylene blends

CONCLUSIONS

Dynamic plane-stress failure has been observed directly in the transmission electron microscope using a commercially available cooling/straining holder in conjunction with a copper deformation cartridge. The low-temperature cooling stage permits studies of a polymer's ductile–brittle transition if the transition is accessible within the stage temperature range (23 to −170°C). A change in deformation mode was observed on the submicrometre level for polypropylene and impact-modified polypropylene. The present results are in accord with others[6,7,10,16] in that the ductile–brittle transition of a polymer is associated with a change in the mode of deformation. At room temperature, PP and impact-modified PP deform by shear yielding. Below the ductile–brittle transition the polymer chains become less mobile and crazing will dominate. The change in mode is temperature- and strain-rate-dependent[5]. The stage allows observation of the deformation at varying temperature and events occurring during the deformation can be recorded in real time with the CCD camera. It was not possible to demonstrate the shift in the ductile–brittle transition with rubber loading because of the low strain rates employed. At low temperatures, the rubber elastomers were found to bridge cracks generated through matrix crazing, thereby increasing the stability of the crack. The INSITE technology elastomer performed better than EPDM because it could elongate more before failure.

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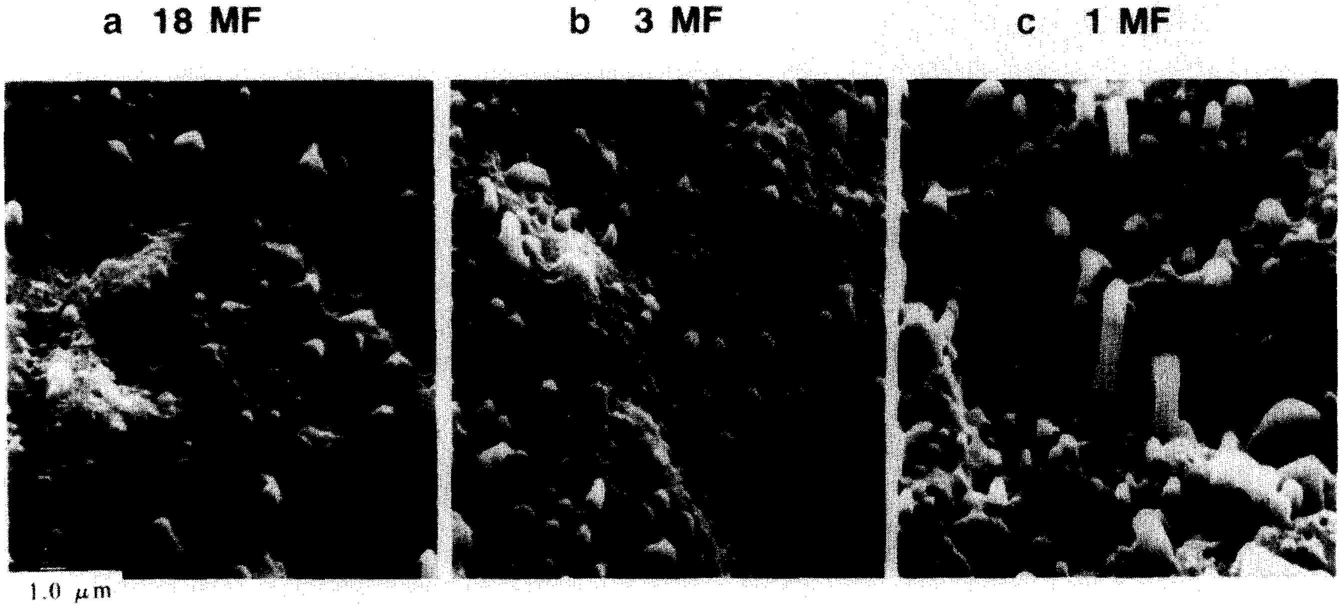

Figure 10 Scanning electron micrographs (SEM) of Dynatup impact fracture surfaces at −20°F (−28.9°C) containing INSITE technology olefin elastomers with (a) 18, (b) 3 and (c) 1 melt flow rate

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