

Effects of sorbed water on properties of low and high molecular weight PMMA: 1. Deformation and fracture behaviour

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(Received 23 March 1984)

The influence of sorbed water on deformation and fracture behaviour of both low and high molecular weight poly(methylmethacrylate) has been investigated. In the low molecular weight polymer, addition of water produces a rise in internal friction in the -100°C region but it has no apparent effect on the β -relaxation process. The tensile strength falls gradually with increasing concentration of water and more rapidly at high concentrations. Ductility initially increases with increasing water content but it reduces at high concentration. In the high molecular weight polymer, in contrast to the low molecular weight material, a yield maximum is observed for both dry and air-equilibrated samples of low moisture content and some samples show both necking and cold drawing prior to fracture. Observed deformation modes include shear bands, crazes, and diamond-shape surface cavities. However, water saturated samples fail in a brittle manner. From the observed deformation behaviour, as well as from observation of fracture surface morphology, it is suggested that sorbed water acts as a mild plasticizer for PMMA up to a concentration of about 1.1% and, at higher water concentration, water clustering occurs.

(Keywords: poly(methylmethacrylate); water content; molecular weight; tensile properties)

INTRODUCTION

The tensile deformation behaviour of poly(methylmethacrylate), (PMMA), has been examined by various investigators over wide ranges of temperature and strain rate¹⁻⁶. At temperatures between 20°C and 40°C , PMMA is generally considered to be a semi-brittle, glassy polymer. Reported tensile fracture stresses vary from less than 50 MPa to more than 80 MPa and reported fracture strains vary from about 4 to 20%, with most of the data falling in the 4 to 8% range. This wide divergence in reported values of tensile strength and elongation to fracture is partly due to differences in testing procedure but probably more so to variations in composition, microstructure and thermal history of the material.

Two material variables that may affect the mechanical response are molecular weight and water content. It is known from various studies on PMMA and/or other glassy polymers that increase of molecular weight, particularly in the low molecular weight range, leads to appreciable increases in fracture surface energy^{7,8}, in craze stability⁹⁻¹², and in resistance to fatigue fracture¹³⁻¹⁶. However, the influence of water, especially its effect on mechanical properties, has received much less attention. This is somewhat surprising since PMMA is a polar polymer that can absorb appreciable amounts of water¹⁷⁻¹⁹. Even in a hydrophobic polymer like polystyrene (PS), where only a very small amount of water is sorbed under fully saturated conditions²⁰ it has been observed that significant changes can occur in the craze initiation stress due to the presence of moisture^{21,22}.

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The purpose of the present paper is to investigate the effects of sorbed water on mechanical properties of PMMA. Properties investigated include relaxation behaviour, initiation and development of crazing, tensile fracture (or yield) stress, strain to fracture and fracture surface morphology. Also, to study the combined, and possibly synergistic, influence of molecular weight and water content tests have been made on both low molecular weight and high molecular weight material (hereinafter referred to as LMW and HMW polymer). Water content has been varied from dry to full saturation.

MATERIALS AND TEST PROCEDURE

The two grades of PMMA investigated were a LMW extrusion grade and a HMW cast grade. The weight and number average molecular weights, as determined by g.p.c. analysis, were $\bar{M}_w = 79\,300$ and $\bar{M}_n = 38\,900$ for the LMW polymer and $\bar{M}_w = 665\,000$ and $\bar{M}_n = 359\,000$ for the HMW polymer. Both types were essentially pure grades free of plasticizer or comonomer content. The respective densities of dry samples, as determined by use of a density gradient column, were 1.180 gm/cc for the cast material and 1.170 gm/cc for the extruded grade. Young's modulus was determined by placing strain gauges on tensile samples and recording their stress-strain response by use of an Instron servohydraulic testing unit. The elastic modulus, within the accuracy of our measurements, was found to be 2.93 GPa for both materials.

The materials were received in the form of rods 1.27 cm in diameter. Tensile specimens, machined from these rods, had a rectangular cross-section of 6.3 mm by 3.2 mm and a reduced gauge length of 12.7 mm. Some tests were made

on cylindrical samples of comparable gauge length and with a reduced diameter of 5.08 mm. Samples were carefully polished prior to testing. The tensile tests were performed in the Instron apparatus at a displacement rate of 0.51 mm/min. This corresponded to a strain rate of about $2 \times 10^{-4} \text{ s}^{-1}$. Strain gauges were used only for the modulus measurements; hence all recorded strains are nominal strains based on measured displacements and an estimated effective gauge length. Similarly, recorded stresses are nominal stresses based on measurements of the load and the original cross-sectional area.

To obtain dry samples, the test specimens were heated in a vacuum oven at 50°C for a period of 70 h. It was observed, for one specimen, that further annealing for two hours at 110°C caused no additional weight change. Samples in equilibrium with laboratory air were found to contain, based on dry weight and depending on existing temperature and humidity values to which they were previously exposed, 0.25 to 0.30% of water for the LMW polymer, and from 0.4 to 0.5% for the HMW polymer. Water saturated samples were obtained by storing test specimens in liquid water for 22 days at 60°C, followed by 13 days at room temperature. For both PMMA materials, the saturated water content was found to be 2.25%. Samples of high water content were observed to be somewhat hazy and less transparent than normal PMMA.

For the LMW polymer, samples were tested in the dry state, in the air-equilibrated state, in the saturated state and at four other water contents ranging from 0.70% to 1.60%. Test specimens having 1.6% H₂O were obtained by storing dry samples in saturated water vapour at 60°C for 22 days and at room temperature for 13 days. Water content of 1.45% was realized by storing dry samples in saturated water vapour for 37 days at room temperature. Other samples containing 1.1% and 0.70% were obtained by storing dry samples in saturated water vapour at 60°C for 95 and 30 h respectively and then holding them in a closed vessel at room temperature for 19 days prior to testing. During tensile testing of the water containing samples, the liquid or vapour environment in which the samples were brought to equilibrium at that particular water concentration, was maintained around the specimen until completion of the test. All tensile tests were performed at ambient temperature ($24^\circ\text{C} \pm 2^\circ\text{C}$).

Visual and optical examination of specimen surfaces were made during the test and after fracture to obtain information relative to the effects of water, and of molecular weight, on the initiation and subsequent development of crazes. Fracture surfaces were examined by the optical microscope and by use of an Etec scanning electron microscope (SEM). Prior to SEM examination, the surfaces were coated with a thin layer of gold-palladium to prevent surface charging.

For the LMW polymer containing various water contents, measurements were made over a broad temperature range from 150 K to the glass transition temperature of the mechanical relaxation behaviour. These measurements were made in a Piezotron apparatus operating at 3 Hz. The heating rate was 2°C per minute.

TEST RESULTS AND DISCUSSION

Mechanical relaxation behaviour of LMW polymer

Loss tangent vs. temperature data are shown in Figure 1

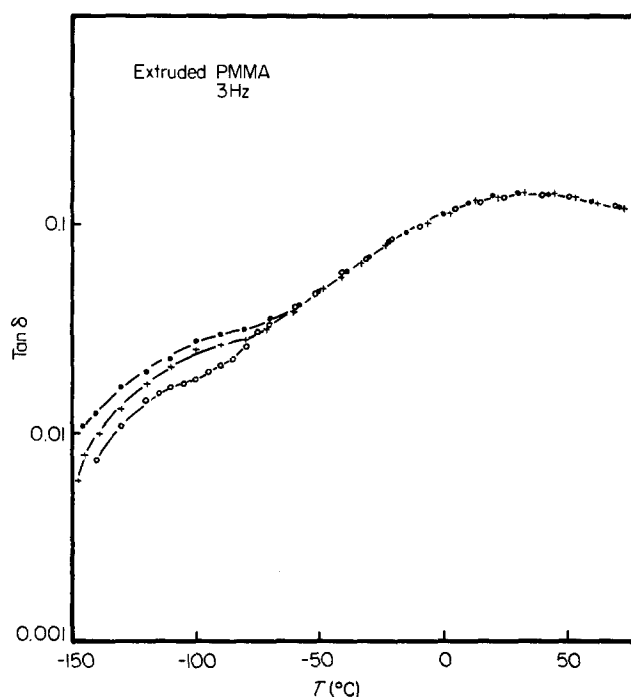


Figure 1 Tan δ vs. temperature for samples of extruded PMMA: dry (—○—); 1.1% water (---+---); 2.25% water (····●····)

for three samples of PMMA containing respectively 0%, 1.1% and 2.25% water. The principal effect of the sorbed water is to cause a rise in intensity of the internal friction in the region near -100°C . This 'water peak' or shoulder was first observed by Gall and McCrum²³ from torsion pendulum observations of PMMA samples subject to various relative humidities at room temperature prior to testing. Janacek and Kolarik¹⁷ also observed a rise in the loss modulus in the -100°C temperature range with increasing molar concentration of water in PMMA.

It is evident from Figure 1 that sorbed water has essentially no effect on the magnitude or position of the β -peak, centred near 25°C , which is attributed to the onset of reorientational motion of side groups in PMMA²⁴. However, although the low strain relaxation behaviour of PMMA in the region of room temperature appears to be unaffected by sorbed water, this is not the case, as we shall see, for the macroscopic large strain mechanical properties. Sorbed water also causes some changes in the glass transition temperature but its quantitative effect is difficult to determine because of loss of water during the heating period. It has been noted that drying of as-received samples causes a rise in T_g of several degrees; hence sorbed water appears to have a slight plasticizing action on PMMA and this becomes more evident from the results of the tensile stress-strain measurements.

Influence of water on mechanical behaviour of LMW polymer

The tensile stress-strain response is shown in Figure 2 for individual test samples having 0%, (Curve A), 1.1% (Curve B) and 2.25%, (Curve C) of sorbed water. The average stress to break σ_B , and the strain to fracture are shown as a function of water concentration in Figure 3. With increase of water content, the tensile strength falls gradually to about 1.1% and then more rapidly at higher concentrations. At water contents to 1.1% the strain to fracture increases and there is a significant reduction in

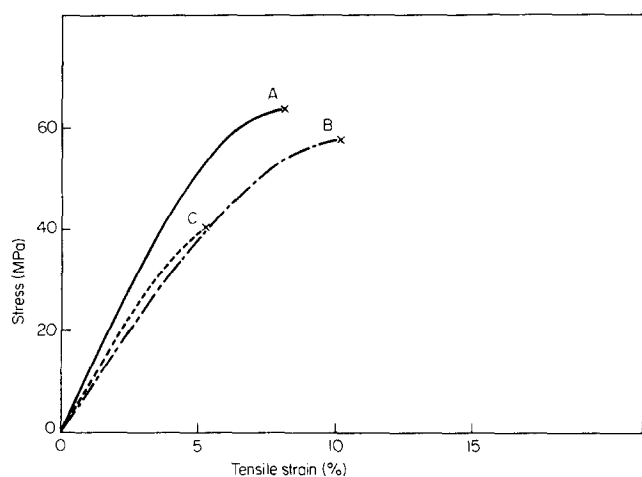


Figure 2 Tensile stress-strain curves for LMW extruded PMMA: A, dry (—); B, 1.1% water (---); C, 2.25% water (-.-)

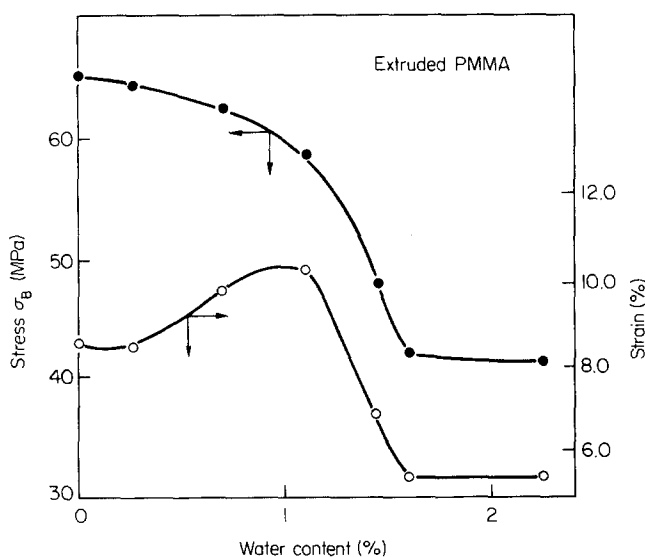


Figure 3 Tensile strength (●●●) and tensile strain (○○○) to fracture vs. water content for LMW extruded PMMA

the modulus. This behaviour is indicative of water acting as a mild plasticizer for PMMA, a conclusion similar to that drawn from rheo-optical studies¹⁹ and from studies of yield stress in plane strain compression²⁵. At water concentrations above 1.1% the behaviour changes and a marked decrease in strain to fracture with little further change in the modulus, is found. The mechanism by which water is accommodated in the PMMA microstructure appears to be changing with increase in water concentration. Initially the sorbed water, probably by hydrogen bonding to the carbonyl groups in the PMMA side chains, lowers interchain interaction and thereby reduces T_g . However, as water concentrations reach one per cent or so, it is suggested that some water molecules begin to cluster and act more as filler particles than as a plasticizer. This leads to stress concentration effects, accentuates craze development and causes earlier fracture. These findings are in general accord with the results of Turner's study of sorption kinetics in PMMA, viz. that approximately 50% of the sorbed water is taken up by swelling and the remaining 50% is accommodated in microvoids¹⁸. It is evident from the relatively low value of

the measured density, 1.170 gm/cc for the LMW polymer, that microcavities are present even in the dry polymer.

An approximate estimate of the stress for craze nucleation was obtained from visual observation of the specimens during the tensile test. While this method is not as sensitive as the light reflection method for detecting craze initiation²⁶, it does give an indication of how craze initiation depends on water concentration. The greatest resistance to craze initiation was found for the dry samples with an estimated craze nucleation stress of about 52 MPa. As samples sorb water the craze nucleation stress drops, falling to a value of about 35 MPa at 0.26% water. With increasing water content, the craze nucleation stress continues to fall but at a lower rate. The observed value for the fully saturated samples is about 27 MPa. A significant drop in craze initiation stress between dry and water saturated samples has also been observed in a crosslinked PMMA²⁷.

In dry samples the crazes were quite small, with an average length of about 17 μm . As the water content rises, the average craze length increases and this increase becomes greater at high water concentrations. The craze length was estimated to be about 34 μm for the samples containing 1.1% water and 246 μm for the samples containing 2.25% water. Since the variation in time to fracture for the water containing samples, as compared to dry samples, is never large and actually decreases at high water content, as Figure 2 shows, the preceding results indicate that the presence of sorbed water favours craze growth as well as craze nucleation. The more rapid increase in craze growth rate at high water contents probably results from local stress concentration effects as water clusters form. Long environmental crazes and brittle behaviour have been noted in PMMA samples of unknown molecular weight tested in a water environment⁵.

The fracture surface morphology of the LMW polymer did not vary appreciably with the water content of the sample. The reason for this is that, despite significant differences in craze initiation stress and in average craze size with sorbed water, all of the low molecular weight samples fractured without shear yielding by craze breakdown and subsequent rapid crack propagation. Figure 4a shows a portion of the fracture surface near to the fracture origin for a dry, rectangular sample and Figure 4b is a similar scan for an air-equilibrated, cylindrical sample. In both cases fracture has occurred from growth, and then breakdown, of a surface craze and the smooth region surrounding the source is indicative of the extent of craze growth prior to rapid crack propagation. Several broad, ribbed bands surround the smooth, slow-growth portion of the fracture surface and the fast growth region beyond the banded area is rough. The smooth pre-cracked source area, the ribbed bands, and the remaining rough fracture surface are characteristic features of tensile fracture in the LMW polymer. The ribbed bands are indicative of an instability in the crack propagation process. Their presence has been discussed by Doyle²⁸ and attributed by him to a periodic slowing of the crack front movement due to energy expenditure in the development of craze bundles ahead of the fast moving crack front.

The fracture surface of a fully saturated sample is somewhat different. The low magnification view of Figure 5a shows that, for this specimen, the fracture source is an internal one. The comparatively smooth region surround-

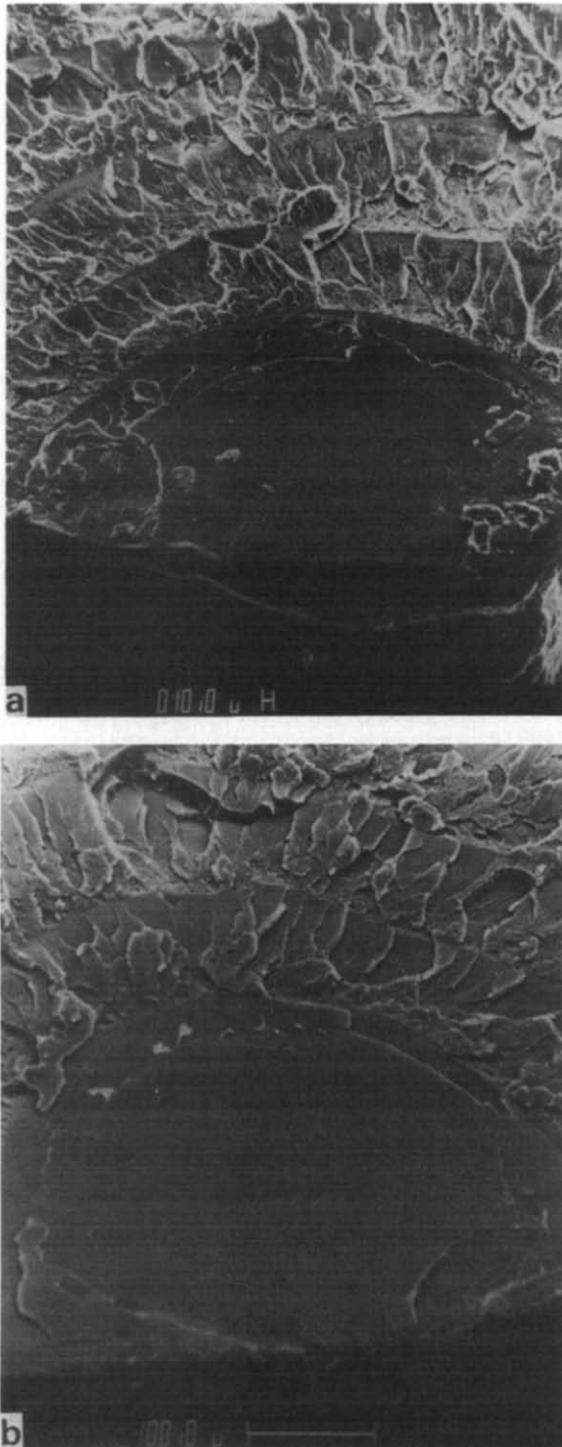


Figure 4 SEM scans of the tensile fracture surface of a LMW sample: (a) 0% water; (b) 0.26% water

ing the fracture source, which represents the extent of craze growth prior to rapid crack propagation, is larger than the corresponding portion of the fracture surface of dry samples or of samples of low water content. This finding is in accord with the already noted larger surface craze size for samples containing high concentrations of sorbed water. The banded region separating the mirror zone from the rougher fracture surface beyond, is also more extensive than for samples of low water content. At higher magnification, 10 or more successive bands are evident. Another significant difference, shown by the high magnification scan of *Figure 5b* of a portion of the smooth

region near to the fracture source, is the presence of numerous small voids or cavities ranging in size from about $0.1\ \mu\text{m}$ to about $1\ \mu\text{m}$. Since these features were not seen in dry samples or samples of low water they reflect a change in craze microstructure caused by the presence of sorbed water. One possibility is that they arise from the presence in the water saturated PMMA of clustered water droplets. Somewhat similar features have been observed in the tensile fracture surfaces of saturated PS samples²¹. The water clusters are also responsible for the development of the observed haziness in the PMMA samples of high water content.

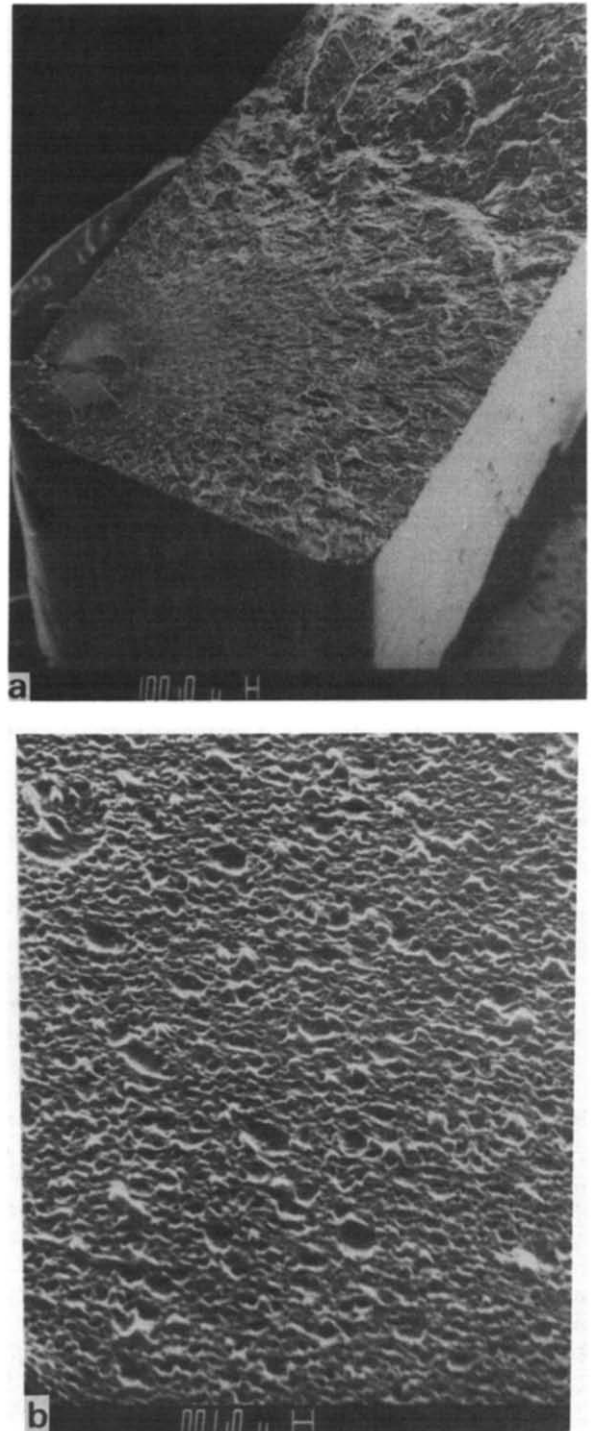


Figure 5 SEM scans of the tensile fracture surface of an LMW sample containing 2.25% water: (a) Low magnification view; (b) Higher magnification view of a portion of the fracture surface within the pre-crazed area

Influence of sorbed water on mechanical behaviour of HMW polymer

The influence of sorbed water on tensile strength and fracture strain for the HMW polymer is shown in *Table 1*. All test samples of this series were initially annealed for two hours at 110°C. Data are also included in *Table 1* for the LMW polymer so that comparisons can be made. All values cited are average values obtained from tests on two specimens unless otherwise noted. Dry samples have the highest average tensile strength and also the highest craze initiation stress, viz. 59 MPa. With increase of water content the tensile strength falls gradually at first and then more rapidly at high water concentrations. The drop in tensile strength at full saturation is about 30% for the HMW polymer and about 36% for the LMW polymer. These values may be compared with a reported drop of 20 to 40% in the plane strain compressive yield stress of PMMA upon saturation with water²⁵. The craze nucleation stress falls more rapidly with water content than does the tensile strength. Estimated values are ~30 MPa for samples of 0.5% water and ~20 MPa for saturated samples of 2.25% water. Thus upon full saturation the craze stress falls by over 60%. A comparable reduction has also been observed to occur in a crosslinked PMMA²⁷.

The elongation to fracture for the HMW polymer initially increases with water content and then decreases again at high water contents. A similar trend, as shown in *Figure 3*, was observed also in the LMW polymer. It was noted that all dry and air-equilibrated samples of the HMW polymer developed a yield maximum in their stress-strain response, but there was a considerable variation in strain to fracture from sample to sample. For the two dry samples, where the average strain to fracture of 15% was almost double that of the LMW polymer, one sample fractured after necking and drawing at 20% strain while the second sample fractured at 10% strain. For the air-equilibrated samples, four specimens of both rectangular and circular cross-section were tested. Two samples necked appreciably before fracture and one of these was drawn over 45%; the other two samples failed shortly after reaching their maximum stress. The average strain to fracture for these air-equilibrated HMW samples was about 2.5 times that of the LMW samples.

In the LMW material the only mode of deformation appears to be crazing and, since craze stability is low as a result of a low entanglement density, a crack soon forms with rising applied stress in one of the surface crazes and fracture then develops from rapid crack propagation prior to any shear yielding. In the HMW polymer, where chain entanglement density is high, the crazes that form are more resistant to breakdown. The average craze size for these samples was observed to be quite small, ~5 µm for dry samples and ~7 µm for the air-equilibrated samples. Instead of continued craze growth, shear deformation modes develop and these produce necking and more extensive plastic deformation. Evidently, at the

temperature and low strain rate used in this study, a transition region between brittle to ductile response is being encountered with increase of molecular weight and entanglement density.

Water-saturated HMW samples are more prone to crazing and the average craze size is large (>100 µm). These samples fracture without yielding and the average strain to fracture, 7.2%, is low. The initial rise in fracture strain upon passing from dry samples to air-equilibrated ones indicates that water is acting as a plasticizer for the high molecular weight PMMA. However, the subsequent drop in fracture strain for the water-saturated samples implies that some of the sorbed water is now being accommodated in a different fashion. It is suggested, as already noted for the LMW polymer, that water clustering occurs. This clustering induces earlier craze development, faster craze growth, and more rapid craze breakdown. Additional evidence for the presence of water clusters in water-saturated samples of cast PMMA comes from density measurements²⁹. These show that saturated samples have a density almost 1% higher than dry samples. Hence the sorbed water is filling microcavities rather than merely swelling the polymer. There is thus a tendency, as the water content increases from low to high values, for the deformation to change from a ductile, or semi-ductile, response to a brittle mode.

Sorbed water also has an effect on the fracture surface morphology. For the dry sample that failed soon after reaching its yield maximum, the fracture plane was transverse to the load axis and relatively smooth, although covered over most of its surface with numerous secondary fracture features. *Figure 6a* is a high magnification scan of a portion of the fracture surface of this sample near to the source of the fracture. This region is very smooth indicating that crack propagation has taken place through crazes. There is no evidence here of concentric ribbed bands, arising from instability in the crack propagation phase, as was observed for dry samples of the LMW polymer. Instead, as the primary crack advances, one sees many parabolic features arising from interaction between the primary crack and secondary cracks nucleated ahead of the primary crack at sites of impurities or other heterogeneities. *Figure 6b* is a view of some of these secondary fractures. The source of each fracture, and the radial flow lines emanating therefrom, are clearly visible. Similar features have been noted in PMMA, and other materials, by various investigators^{9,30,31}.

For the second dry sample that necked appreciably before fracture, new deformation modes have developed and the fracture surface morphology changes. *Figure 7a* shows a high magnification scan of the lateral free surface of the fractured sample. Both crazes and shear bands are present. The surface crazes are relatively small, averaging about 5 µm in length, and their growth is impeded by shear bands, and hence the presence of oriented polymer,

Table 1 Effects of sorbed water on mechanical properties of PMMA

Specimen condition	Maximum tensile stress (MPa)		Strain to failure (%)	
	HMW	LMW	HMW	LMW
Dry	69.4	65.0	15	8.4
Air-equilibrated	68.9*	64.2	21*	8.3
Water saturated	48.8	41.3	7.2	5.2

* Average value of four samples of both rectangular and round cross-section

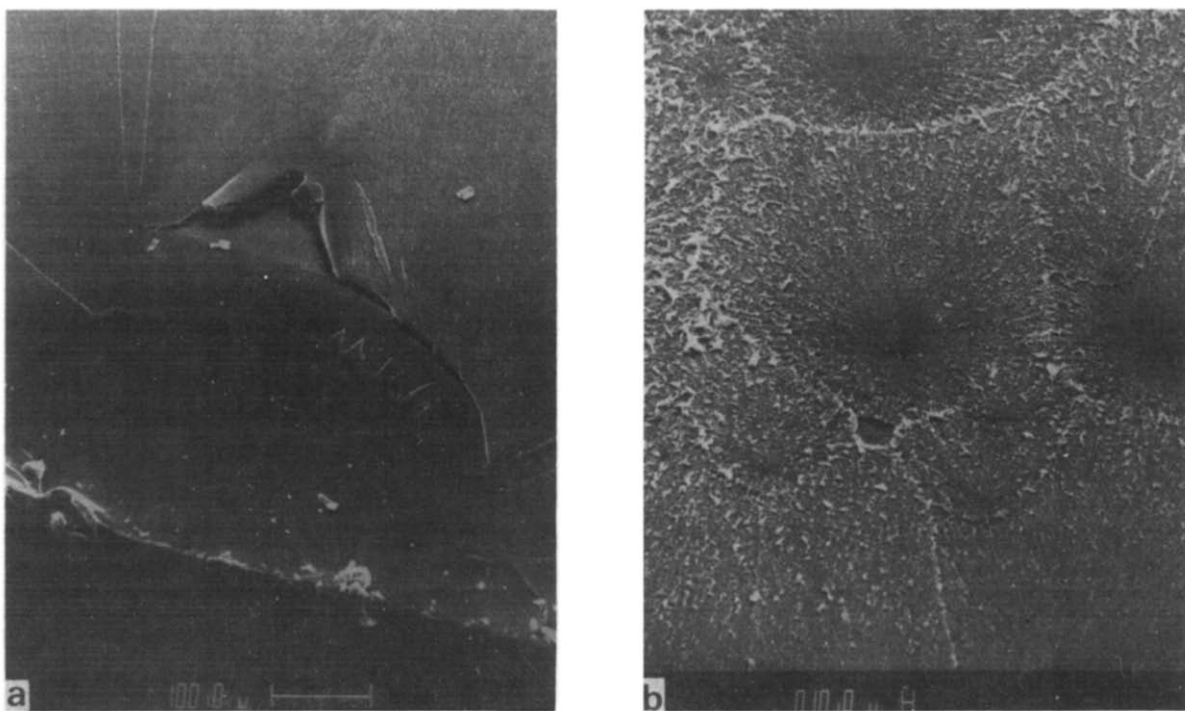


Figure 6 SEM scans of the tensile fracture surface of a dry HMW sample that fractured soon after reaching a yield maximum: (a) View near fracture source; (b) View of secondary fracture sites

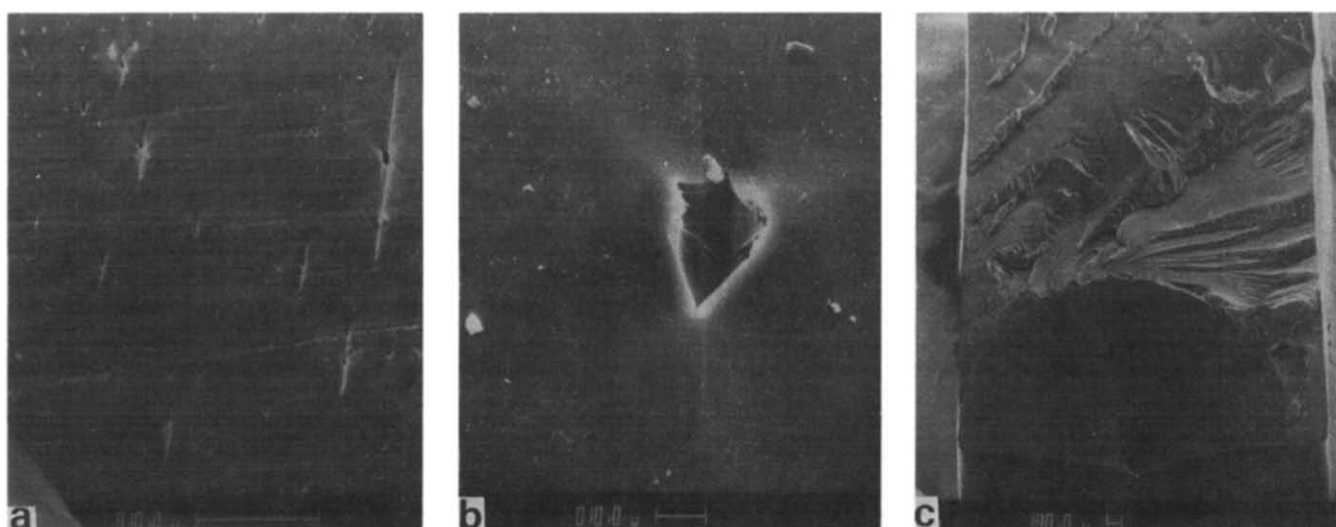


Figure 7 SEM scans of free surfaces and the fracture surface of a dry HMW sample that necked appreciably before fracture: (a) Lateral surface with many crazes; (b) Lateral surface with diamond shaped cavity; (c) Fracture surface

at the tips of the crazes. The possible impediment to craze growth by the presence of shear flow in cast PMMA of normal water content has been noted^{5,32}. In many of the surface crazes, the SEM scan shows that a central cavity has started to form. With continued deformation, some of these small cavities open up into relatively large diamond shaped, or truncated diamond shaped, cavities. Such cavities were first noted in tensile tests of poly(vinylchloride) (PVC) by Cornes and Haward³³. An interesting feature of *Figure 7a* is that, while many of the small cavities have formed at the centre of surface crazes, others have apparently formed in regions where there is no visible evidence of crazes. These may have initiated from local stress concentration sites arising from the presence

of contaminants. Similar cavities are reported to occur in cellulose acetate, which does not craze³⁴.

Figure 7b depicts a large diamond cavity that has formed in a dry sample of the HMW polymer from the continued growth of one of the small cavities. Intersecting shear bands, visible in both *Figures 7a* and *7b*, are probably responsible for the growth of these large cavities. Diamond cavities, similar to those shown in *Figure 7b*, have been previously observed in a PMMA of unspecified molecular weight but only when the tensile tests were carried out at an elevated temperature of 60°C to 70°C³⁴. Evidently, with a PMMA of high molecular weight such as that used in the present study there is sufficient craze stability, as a result of a greater chain entanglement

density, to avoid premature fracture by craze breakdown. Shear modes of deformation may then arise and lead to ductile behaviour even in tests carried out at ambient temperature. Ductile fracture of PMMA by growth of characteristic diamond cavities has also recently been observed in specimens tested at ambient temperature under alternating tension-compression loading by Shen *et al.*¹⁶. In this study, however, these features were observed only when the imposed stress amplitude was sufficiently high so that appreciable specimen heating occurred due to hysteresis effects.

A low magnification scan of the entire fracture surface of this dry HMW sample is shown in *Figure 7c*. Fracture has developed from lateral extension and tearing of a small surface diamond cavity and features of equivalent geometry are present on the opposite fracture surface. The semi-circular, fan-shaped region showing radial tear lines indicates the extent of the relatively slow crack growth prior to rapid crack extension. Somewhat similar features have been observed in the tensile fracture of rigid PVC³³.

Characteristics such as those discussed above, viz. the presence of small crazes and diamond shaped cavities on the external surfaces, and a fracture that develops by further extension and growth of one of the diamond cavities, are also noted in several of the air-equilibrated HMW samples containing about 0.5% water. However, such features are never seen in any of the low molecular weight polymer samples. *Figure 8a* shows a large truncated diamond cavity that has formed within the drawn region of a cylindrical HMW sample. Near the lower tip of the diamond cavity, an unbroken ligament connecting the two sides of the cavity, is visible. Another interesting feature is the distortion, by shear deformation, of the machine marks near to the cavity. A portion of the fracture surface of this same sample is shown in *Figure 8b*. Fracture has apparently developed from slow growth of two nearby surface diamond cavities, with one of these then developing into the smooth, but radially-lined, fan-shaped region.

Shear modes of deformation are no longer evident in the water-saturated HMW polymer. Thus additional water, rather than toughening the polymer as would a normal plasticizer, appears instead to embrittle it. This is another indication that the role of water in PMMA, particularly at high concentrations, is not that of a typical plasticizer. Both bound and clustered water are evidently present in these samples and their presence leads to easier disentanglement of existing molecular chain networks and a reduction in craze stability. Thus the benefits derived from use of high molecular weight materials, such as increased toughness and ductility, as well as increased fatigue resistance³⁵, may be appreciably diminished if the material contains high concentrations of sorbed water.

CONCLUSIONS

(1) Sorbed water produces an increase in internal friction or damping in the temperature region near -100°C but it has essentially no effect on the β -relaxation process.

(2) In both low and high molecular weight PMMA, the strain to fracture rises to a maximum value with increase of water content and then drops to low values at high water concentration.

(3) Craze dominated fracture occurs in the low molecular weight PMMA at all water contents and also in

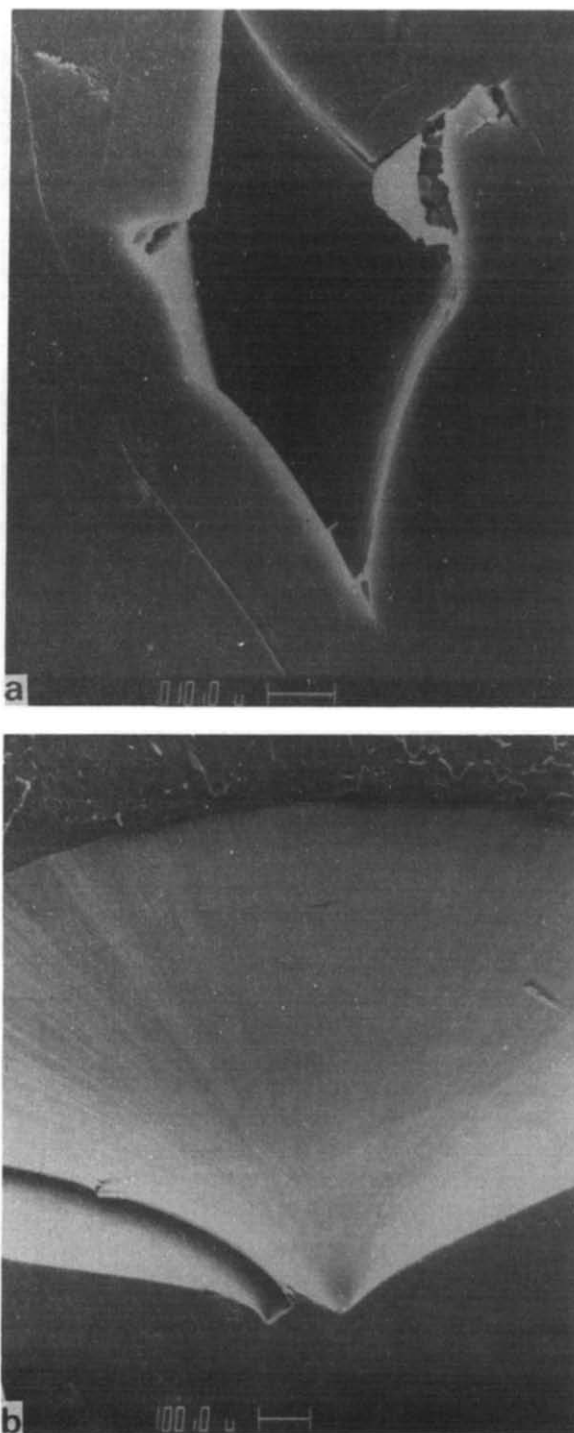


Figure 8 SEM scans of free and fracture surfaces within the drawn region of an air-equilibrated sample of HMW polymer: (a) Lateral surface with large diamond cavity; (b) Portion of fracture surface adjacent to two diamond cavity sources

water-saturated samples of high molecular weight PMMA.

(4) In dry samples of the high molecular weight PMMA, or in samples that have been air-equilibrated, there is a tendency to deform plastically before fracture and crazes, shear bands, and diamond shaped surface cavities have been observed.

(5) It is suggested that water acts predominantly as a mild plasticizer for PMMA at water contents to about 1% and at higher water contents clustering occurs, haziness arises and significant changes occur in the deformational response.

ACKNOWLEDGEMENTS

We wish to express our appreciation to the National Science Foundation for their support of this research under Grant No. DMR 78-27558. Our thanks are extended to L. S. A. Smith for helpful discussions and to T. T. Wang and the Bell Laboratories for the molecular weight measurements. We acknowledge our debt to N. G. McCrum and the Department of Engineering Science at Oxford University for their hospitality and helpful assistance in the completion of this study.

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