Effects of sorbed water on properties of low and high molecular weight PMMA: 11. Fatigue performance

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The influence of sorbed water on average fatigue life and on fracture surface morphology for unnotched samples of low and high molecular weight poly(methyl methacrylate) has been investigated. For air-equilibrated samples, the effects of test frequency on fatigue performance, and on associated thermal effects, have been determined. Average fatigue lifetimes are about two decades higher for the high molecular weight polymer. Sorbed water, at concentrations from 0 to 1 %, produces a significant drop in fatigue resistance. At higher water contents, fatigue life tends to become independent of water content. It is suggested that the transition in behaviour near 1 % is associated with onset of water clustering.

(Keywords: poly(methyl methacrylate); fatigue; water content; molecular weight)

INTRODUCTION

The performance of poly(methyl methacrylate), PMMA, under alternating loading has been the subject of a number of recent investigations[1-15]. In most of these studies, fatigue tests have been carried out on notched specimens and interest has focused on the geometry of the craze ahead of the fatigue crack[1-4], and on the effects of variables such as composition, molecular weight, stress intensity factor range and test frequency[5-10]. In other investigations, tests have been made on unnotched samples and interest has focused on thermal effects[11,12], on changes in properties produced by cycling[13], on fracture surface morphology[14] and on the influence of stress and frequency on macroscopic fatigue response[15]. However, little attention has been given to the possible effects of sorbed water on mechanical behaviour of PMMA despite the fact that PMMA is a polar polymer that can sorbe appreciable quantities of water[16-18].

A principal objective of the present investigation is to determine the influence of sorbed water on deformation and fracture modes and on fatigue lifetime of PMMA specimens of both low molecular weight (LMW) and high molecular weight (HMW) subject to alternating stressing. The effects of sorbed water on tensile properties and on tensile fracture surface morphology have been considered in a subsequent paper[19] and in a recent conference paper[20].

Another aim of the present study is to enhance our understanding of the influence of molecular weight and test frequency on fatigue performance of PMMA and on associated thermal effects due to hysteretic heating. Results of this study will provide a basis for establishing suitable test conditions for the water sorption experiments and will enable comparison of data obtained on unnotched samples, with reported data obtained from study of fatigue crack propagation (FCP) by fracture mechanics methods[3,21,22]. Conclusions drawn from these two different approaches may differ for several reasons. Firstly, in tests on polished, unnotched samples, both a crack initiation phase and a crack propagation phase are involved. Secondly, in tension–compression fatigue tests on unnotched samples, the associated temperature changes may have an appreciable effect on bulk properties and deformation modes[11,23]. In notched samples, the specimen temperature rise due to viscoelastic effects is localized to the region of high stress near the crack tip. Hence it has little effect on bulk properties, although it may have an appreciable effect on fatigue performance[21,22] and on fracture toughness[24] by producing crack tip blunting.

MATERIALS AND TEST PROCEDURES

The molecular weights for the two grades of material used in this study, as determined by g.p.c., are: for the *LMW* extruded polymer, $\bar{M}_w = 79\,300$ and $\bar{M}_n = 38\,900$ and, for the *HMW* cast polymer, $\bar{M}_w = 665\,000$ and $\bar{M}_n = 359\,000$. Both grades were free of plasticizer and comonomer content. The material was received in the form of rods, 1.27 cm in diameter. Cylindrical test specimens, threaded at the ends to engage the grips of the testing machine, were machined from the rods and carefully polished. The test samples had a reduced diameter of 5.08 mm and a reduced gauge length of 12.7 mm.

Samples of varying water content, ranging from dry to saturated samples containing 2.25 wt% based on dry weight, were obtained by different treatments involving exposure to either water or water vapour[19]. The liquid or vapour environment in which the samples were brought to equilibrium was maintained during the fatigue testing. All tests were conducted at an ambient temperature of 24° ± 2°C. For samples equilibrated in laboratory air, the equilibrium moisture content varied, depending on exist-

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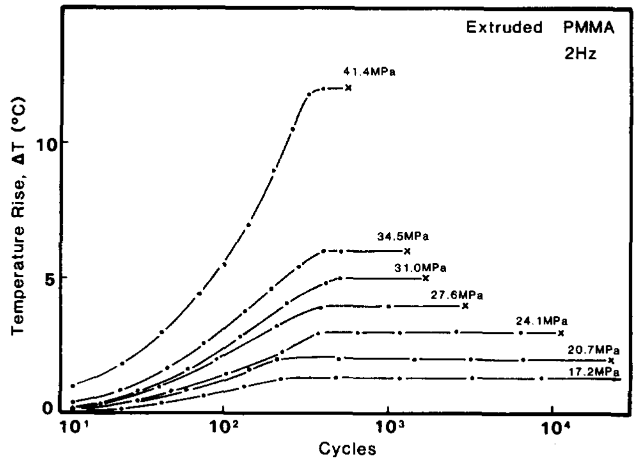

Figure 1 Temperature rise vs. cycles at various stress amplitudes in *LMW*, extruded PMMA tested at 2 Hz

ing temperature and humidity conditions, from 0.26 to 0.30% for the *LMW* material and from 0.4 to 0.5% for the *HMW* polymer.

The fatigue tests were carried out under load control in a tension–compression mode using an Instron servohydraulic testing machine and the number of cycles to fracture, N_f, was recorded. The load was varied sinusoidally. Tests were generally made on 4 to 5 separate samples for each water content or for each new condition or stress and frequency. Average lifetime values given herein are based on averaging log N_f values. To ascertain the influence of sorbed water on fatigue performance, test were made at a frequency of 2 Hz at a specified stress amplitude that would not involve severe thermal effects. For air-equilibrated samples of both low and high molecular weight, the specimen temperature rise due to hysteresis and the average fatigue lifetime were determined over a wide stress amplitude range and over a broad range of test frequency. To monitor thermal effects during cycling, a Barnes infra-red microscope was focused on the specimen gauge length and the associated specimen temperature rise was recorded as a function of N, the number of applied cycles.

The fracture surfaces of many samples were examined by an optical microscope and by an Etec scanning electron microscope (SEM). Prior to SEM examination, the fracture surfaces were coated with a thin layer of gold–palladium.

RESULTS AND DISCUSSION

Effects of molecular weight and frequency for air-equilibrated samples

Figure 1 shows the specimen temperature rise, ΔT, for fatigue tests run at 2 Hz, as a function of the number of fatigue cycles for samples of the *LMW*, extruded PMMA containing about 0.30% of H_2O. The imposed stress amplitudes are well below the tensile fracture stress of 64.2 MPa[19]. ΔT rises with increasing number of cycles until the heat developed as a result of hysteresis becomes equal to the amount of heat given up by radiation, convection and conduction to the surroundings. Thereafter the temperature stabilizes at a constant value whose magnitude increases approximately as the square of the stress amplitude. This result appears to be in accord with the expected stress dependence of the rate of energy dissipation due to internal friction, which is given by Ferry[25] as

$$\dot{E} = \pi f D'' \sigma^2 \qquad (1)$$

where f is the frequency, D'' the loss compliance and σ the stress amplitude.

It is evident from *Figure 1* that fatigue lifetime increases with decrease in the stress amplitude. For this *LMW* polymer, the resulting S–N curve, based on average lifetime values to fracture for each stress amplitude, gives no indication of approaching an endurance limit over the stress range investigated. The extrapolated endurance strength at 10^6 cycles is about 12 MPa and the ratio of endurance strength to tensile strength is 0.19, a relatively low value for polymers.

If the test frequency is increased, the ΔT vs. N response changes appreciably. *Figure 2* shows this response for samples of the air-equilibrated *LMW* polymer tested at a frequency of 21 Hz. At this frequency, and for stress amplitudes of 24.1 MPa or higher, the specimen temperature rises continuously until fracture results. Temperature stabilization is found only for samples tested at 20.7 MPa or lower whereas, for samples of the same polymer tested at 2 Hz, thermal stabilization occurred even at a stress amplitude of 41.4 MPa. In view of these results, it was decided to sacrifice speed of testing and carry out the fatigue tests, designed to study the influence of sorbed water on performance, at the lower test frequency of 2 Hz. A small difference in stress amplitude values between stabilization and thermal runaway has also been noted in the fatigue testing of other polymers[22].

To study the specific influence of test frequency on fatigue life and on associated thermal effects, some additional fatigue tests were carried out on the *LMW* polymer containing 0.3% of sorbed water at a specific stress amplitude of 27.6 MPa and over a wide range of test frequencies ranging from 0.02 Hz to 21 Hz. No measurable temperature rises were observed at frequencies of 0.2 Hz or below. At 2 Hz the maximum temperature rise was 4°C and at 21 Hz it was about 42°C. Over this frequency range, the maximum ΔT rise was found to be approximately proportional to test frequency as might be expected in view of equation (1). The average fatigue life is shown as a function of test frequency in *Figure 3*. There is an increase in fatigue life of about 1/3 of a decade per

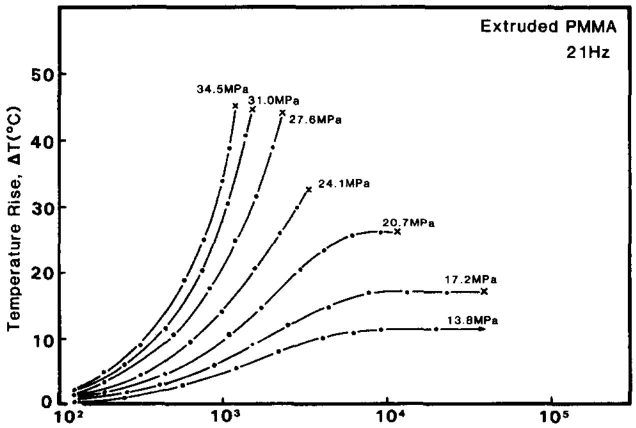

Figure 2 Temperature rise vs. cycles at various stress amplitudes in *LMW*, extruded PMMA tested at 21 Hz

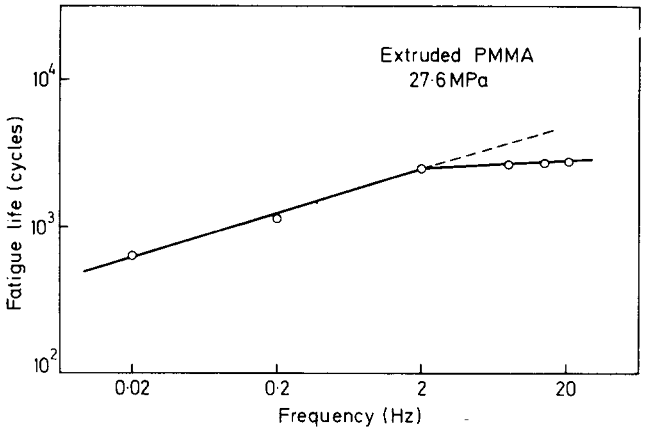

Figure 3 Average fatigue life vs. frequency for *LMW*, extruded PMMA tested at 27.6 MPa

Table 1 Effects of stress amplitude on fatigue behaviour of air-equilibrated samples of PMMA tested at 2 Hz

Type PMMA	Stress amplitude (MPa)	Number of samples	Average lifetime (cycles)	Temperature rise (°C)
HMW	34.5	2	> 233,000	10
	41.4	5	52,940	18
	44.8	6	2,376	62
	48.3	4	890	74
	51.7	4	405	83
	55.2	4	284	50
LMW	34.5	4	1,341	6.5
	41.4	4	577	12

decade increase of frequency over the range from 0.02 to 2.0 Hz. This increase is less than that noted in other unnotched glassy polymers such as polystyrene (PS) or rubber modified PS[26]. The reduction in slope above 2 Hz is a result of the higher associated thermal effects.

The relatively mild dependence of fatigue resistance on frequency observed in this study contrasts with reported results based on measurements of fatigue crack propagation in pre-cracked samples of PMMA. In these studies, PMMA was found to be the most frequency sensitive of the various polymers tested[21,27]. Evidently, as noted earlier, results obtained by fracture mechanics methods may not carry over to the results of tests on unnotched specimens. Slight differences in composition or microstructure, due to differences in molecular weight, water content, or past history may also play a part. In fact, some recent studies of FCP in notched samples of PMMA have indicated there is little dependence of test frequency on craze dimensions at the crack tip or on the fatigue crack propagation rate[1,4].

The effects of stress amplitude on average fatigue life and on the maximum specimen temperature rise for samples of the *HMW*, cast PMMA containing 0.5% water are presented in *Table 1*, for tests performed at 2 Hz. For the four higher stress amplitudes, the associated temperature effects are very large and temperature stabilization was not achieved, even though all stresses were below the tensile yield stress of 68.9 MPa[19]. Thermal runaway at stresses above 41.4 MPa has also been noted in cast PMMA samples of unspecified molecular weight tested at 2.5 Hz in flexure[15]. Fatigue-induced temperature rises can lead to the development of unusual deformation modes, such as onset of necking and the development of large surface, diamond-shaped cavities[11,23], similar in general geometry to those observed in uniaxial tensile tests of PMMA made at elevated tempertures[28].

When the imposed stress amplitude was reduced to the value of 41.4 MPa thermal stabilization was achieved with a temperature rise of 18°C above ambient. At the still lower stress of 34.5 MPa, where the maximum temperature rise was 10°C, the samples did not fracture or show any signs of fatigue-induced cracks even though the test was extended for over 230000 cycles. The S–N response for the high molecular weight PMMA samples containing 0.5% of water, obtained from the test data of *Table 1*, is shown in *Figure 4*. This curve is similar in shape, but has a higher number of cycles to fracture for any given stress amplitude, to that reported for samples of a cast PMMA material tested at 0.5 Hz[29]. The fatigue data of *Figure 4* show a tendency to approach an endurance limit, but the high associated temperature rises, especially for the samples tested at 44.8 MPa and above, undoubtedly distorts the true S–N response. If we arbitrarily select the rather low figure of 34.5 MPa as a conservative estimate of the endurance strength below which no failure occurs at least up to 10^6 cycles then the ratio of the endurance strength to the tensile yield stress for the *HMW*, cast PMMA would be 0.50. This is a very high value for any polymer, even for reinforced plastics[22], and it indicates the great increase in fatigue fracture resistance that is possible by use of high molecular weight material.

The relative fatigue performance of the air-equilibrated samples of the *HMW* and *LMW* polymer can be determined by comparing test results obtained for the two polymers at the specific stress amplitudes of 34.5 and 41.4 MPa. From the tabulated test data of *Table 1* it is evident that, at both of these stress amplitudes, the average fatigue life of the high molecular weight material is about two decades higher than values obtained for the low molecular weight material. This superior fatigue performance is developed despite a higher temperature rise and a higher water content, 0.5% vs. 0.3%, in the *HMW* polymer; and both of these factors would be expected to lower fatigue resistance.

The enhanced fatigue resistance of the *HMW* polymer is attributed to a greater craze and craze fibril stability, as a result of an increased number of topological entanglements between adjacent molecular coils and a reduced

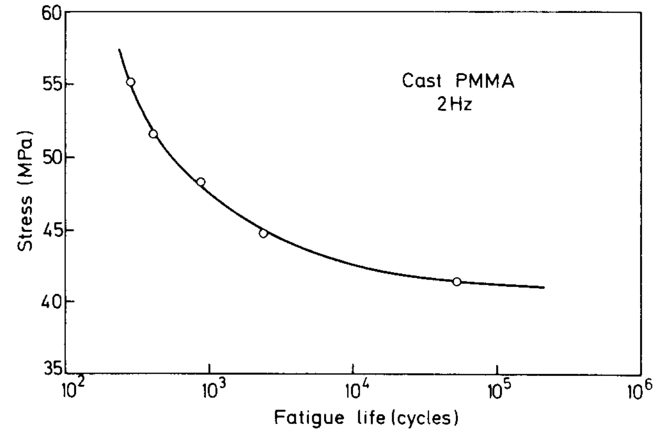

Figure 4 S–N curve for *HMW*, cast PMMA tested at 2 Hz

Table 2 Effects of test frequency on fatigue behaviour of air-equilibrated samples of *HMW*, cast PMMA tested at 41.4 MPa

Test frequency (Hz)	Number of samples	Arerage lifetime (cycles)	Temperatore rise (°C)
0.5	2	209 000	5
2	5	70 600	18
6	5	901	110

number of chain end defects[22,30,31]. An increased degree of chain entanglement would also be expected to lower fatigue crack propagation rates and this has been observed in the testing of pre-cracked samples of PMMA[32]. Similarly, in polystyrene, increasing molecular weight has been found to increase craze stability of notched specimens tested in tension[33] as well as of unnotched specimens tested under alternating tension–compression loading[30].

The influence of test frequency on the fatigue behaviour of the *HMW* polymer containing 0.5% of water has been studied, at a stress amplitude of 41.4 MPa, over a limited range of frequencies. The test results are presented in *Table 2*. Upon increasing the test frequency from 0.5 Hz to 2 Hz, the fatigue life decreased from over 200 000 cycles to about 70 000 cycles. Normally one would expect, in the absence of serious thermal effects, that a rising frequency would increase fatigue life as a result of an increasing strain rate effect. It appears, however, that in the current experiments the higher specimen temperature rise for the samples tested at 2 Hz reduces the value of the bulk properties, such as the modulus and yield strength, more than they are raised by an increasing strain rate. Upon further increase of the test frequency to only 6 Hz, the specimen temperature rose over 100°C and fatigue failure occurred quickly in less than 1000 cycles. Thus the beneficial effects of a greatly increased craze stability on fatigue resistance of high molecular weight polymer, as indicated by the comparative test data of *Table 1*, may be seriously impaired if the stress and frequency conditions that are present lead to severe specimen heating.

Effects of sorbed water on fatigue life and fracture surface morphology

For the *LMW* extruded polymer, seven different water contents ranging from zero to 2.25% were investigated. It was decided, based on the results of the preceding tests on the air-equilibrated samples, to run the experiments on samples of varying water content at a stress level of 27.6 MPa and a frequency of 2 Hz as, under these test conditions, temperature stabilization at a value only a few degrees above ambient is achieved. The average fatigue life, as a function of the amount of water present in the samples, is shown in *Figure 5*. With increasing water content, the fatigue life drops sharply from a value near 10^4 cycles for the dry specimens to a value about one-fourth of this for samples containing 0.3% of water and to about 10^3 cycles for samples containing about one per cent of water. Thereafter, there is little further change in average lifetime with continued increase in water content. The marked improvement in fatigue resistance that is developed upon drying is attributed to a greater resistance to craze initiation and to craze breakdown in the unplasticized polymer.

A transition in behaviour near 1% water concentration has also been noted in results obtained from tension tests. These tests have shown that tensile ductility increases with increase of water content over the range from zero to about 1%; but, at higher water contents, the ductility decreases[19]. It is suggested, based on the results of both the tension and the fatigue tests, that water acts predominantly as a plasticizer at concentrations, below one per cent or so; at higher water concentrations, the water molecules tend to cluster and aggregate. As a result, there is little further weakening of the fatigue-induced crazes or of the craze fibril network by continued plasticization and fatigue life becomes essentially independent of water content.

All test samples of the low molecular weight PMMA, regardless of water content, fractured in a brittle manner from inception, and subsequent breakdown, of a fatigue-induced surface craze. A typical fatigue fracture surface for a sample containing 0.3% water and tested at 27.6 MPa is shown in *Figure 6a*. The smooth region represents the slow growth portion of the fracture surface where the fatigue crack moves discontinuously through craze planes. At higher magnification this region shows discontinuous crack growth (DCG) bands. When the stress amplitude is increased to 41.4 MPa, the smooth slow growth region is found to reduce in size[23]. A reduction in size of the mirror area with increase of stress amplitude has also been noted in a commercial PMMA tested in rotating bending[34]. The slow-growth mirror region is followed by a much rougher region as the crack reaches a critical size and catastrophic fracture occurs.

The fracture surface morphology of the dry samples of the *LMW* polymer, tested at 27.6 MPa, is rather similar to that of *Figure 6a*, except that the DCG bands on the fracture surface are more sharply delineated. *Figure 6b* is a high magnification view of the source region of a dry sample. Many concentric crack growth bands, each representing a position of crack arrest, surround the surface source. The band spacing represents the craze extension, or the size of the Dugdale plastic zone ahead of the crack tip, prior to crack jumping through the craze[21]. There is a linear increase in band spacing with crack depth. This is in accord with the dependence of the plastic

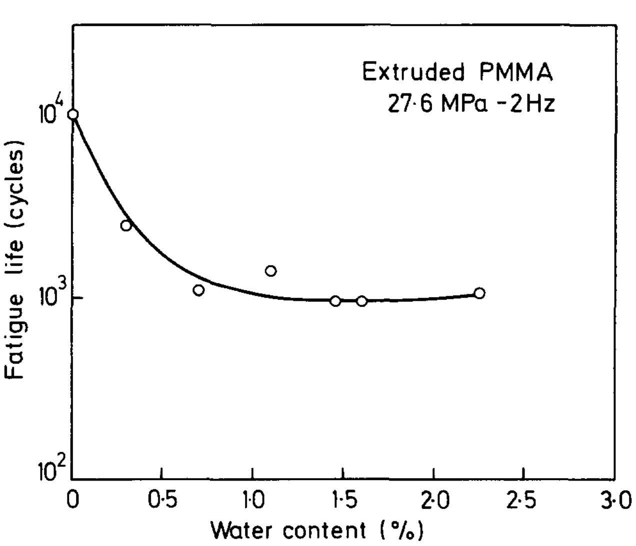

Figure 5 Average fatigue life vs. water content in *LMW*, extruded PMMA tested at 27.6 MPa and 2 Hz

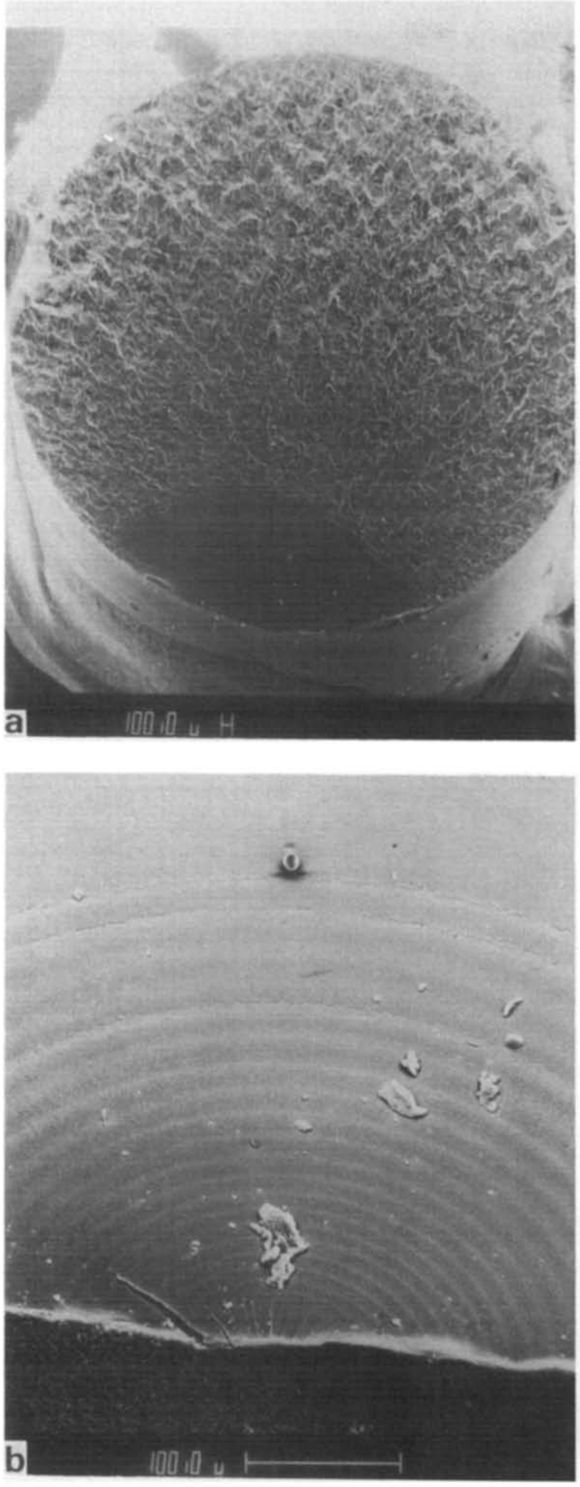

Figure 6 Fatigue fracture surfaces of a *LMW*, extruded PMMA sample tested at 27.6 MPa and 2 Hz. (a) Low magnification view of sample containing 0.3% of water; (b) high magnification view near source for dry sample

zone size on the square of the stress intensity factor[21]. Recent observations of fatigue-induced craze and crack geometry in PMMA suggest that the crack may not periodically jump through the entire craze but only through about two-thirds of it[2].

The better defined DCG band structure and the higher fatigue life for the dry samples is considered to arise from an increased craze stability due to elimination of the diluent, water. For fully saturated samples, the growth bands tend to be ill-defined. This is shown by *Figure 7a*. In addition, as shown by the higher magnification view of a small portion of the banded region, *Figure 7b*, there are some irregularly placed striae present between the broader bands. Fine striae have also been noted between coarser DCG bands in fatigue of polycarbonate[35].

For the high molecular weight PMMA, five different water contents ranging from zero to 2.25% were investigated. These tests could not be run at the same stress

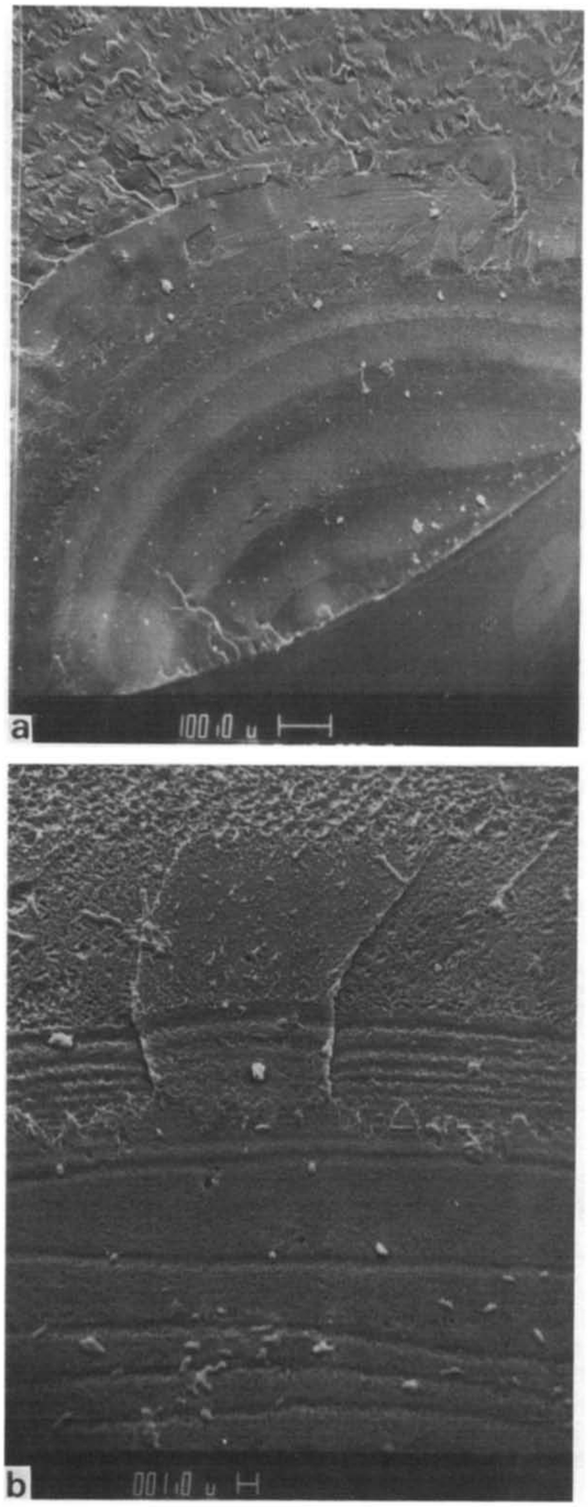

Figure 7 Fatigue fracture surfaces of a water-saturated sample of *LMW*, extruded PMMA tested at 27.6 MPa and 2 Hz. (a) View near fracture origin; (b) high magnification view near centre of slow-growth region

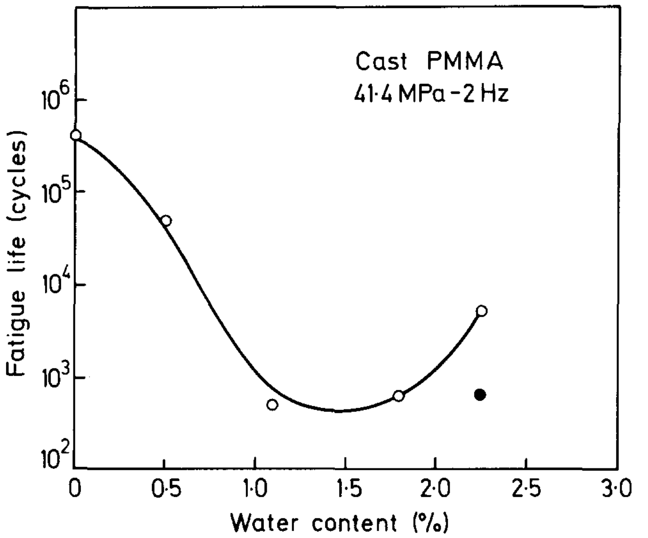

Figure 8 Average fatigue life vs. water content in *HMW*, cast PMMA tested at 41.4 MPa and 2 Hz. The dark circle represents results obtained on samples tested in air rather than in a surrounding water enviroment

level as for the low molecular weight material because no fatigue fracture was obtained in the *HMW* polymer even when tests were made at the higher stress level of 34.5 MPa. It was decided therefore to run all tests on the *HMW* polymer at 41.4 MPa while retaining the same test frequency of 2 Hz. The results of these tests are presented in *Figure 8*. Dry samples proved to have the highest fatigue life. Hence here too, as also in the low molecular weight polymer, sorbed water is acting as a plasticizer. With an increase in water content to about 1%, average fatigue life continues to fall, but again there is a transition in behaviour occurring at about this water content. The test data show an apparent increase in average fatigue life at higher water contents but this is probably a result of the cooling effect of the surrounding water. If the water-saturated samples are tested in air rather than in water the lifetime falls by almost one decade. The marked decline in fatigue resistance with concentration in the range from zero to 1% is attributed to a decreased resistance of the *HMW* polymer to both craze initiation and craze breakdown as the amount of sorbed water increases. The transition in behaviour near 1% and the relative independence of fatigue life on concentration that is noted at higher water contents is considered to result from the onset of significant water clustering. Evidence for the presence of water clusters also comes from visual observation. Samples of high water content show a loss of transparency and an increasing degree of haziness.

For any given water content, the *HMW* polymer shows a greater resistance to fatigue fracture than does the *LMW* polymer. This is evident from comparison of the data of *Figure 8* with that of *Figure 5*. For example, for dry samples or for air-equilibrated samples, the average fatigue life for the high molecular weight polymer is more than a decade greater than that of the low molecular weight polymer even though the *HMW* samples have been tested at a stress amplitude some 50% higher than that for the *LMW* material. This superior performance is a direct result of the greater craze stability associated with the heavily entangled molecular chains of the *HMW* polymer.

The fatigue fracture surface morphology of the *HMW* polymer differs appreciably from that of the *LMW* samples. *Figure 9a* is a typical fatigue fracture surface for a dry sample that ran for over 550 000 cycles at 41.4 MPa before it failed. Air-equilibrated samples show a rather similar fracture surface, though their time to failure is appreciably less. On comparing *Figure 9a* with *Figure 6a*, we see that a striking feature in the case of the *HMW* samples is the presence of numerous parabolic features in the region outside of the slow-growth portion of the

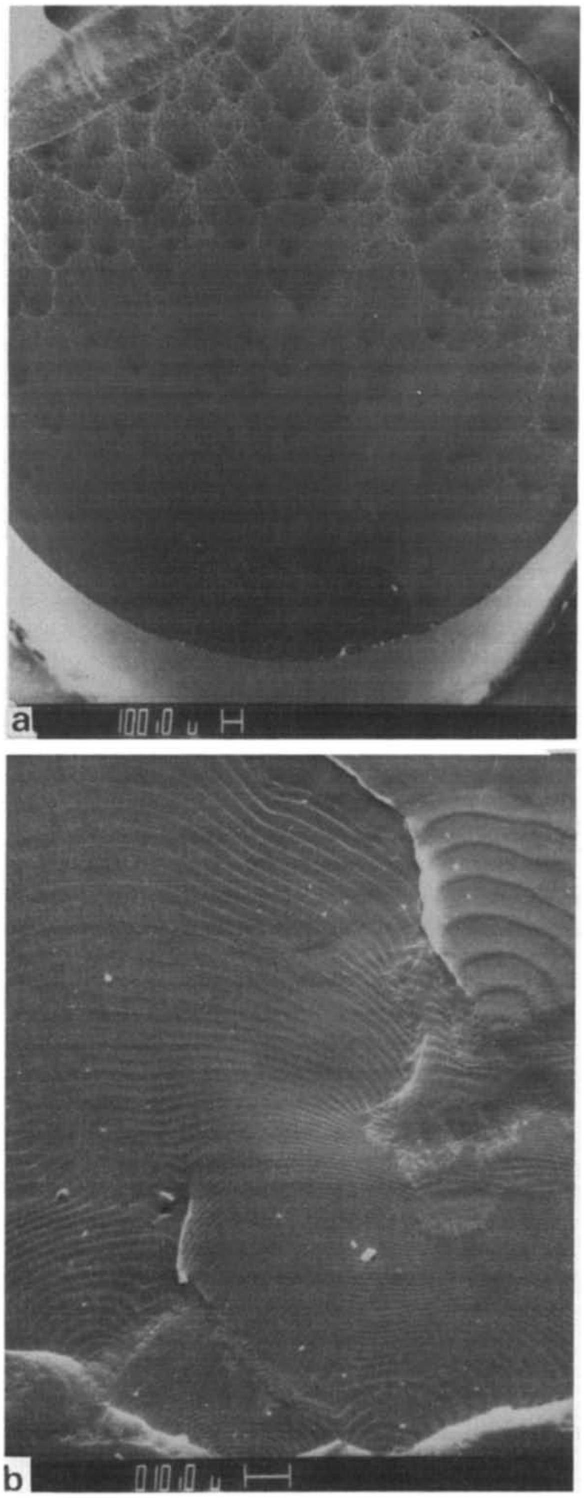

Figure 9 Fatigue fracture surfaces of a dry sample of *HMW*, cast PMMA tested at 41.4 MPa and 2 Hz. (a) Low magnification view; (b) high magnification view within slow growth region

fracture surface. These concical features, which are not seen in the *LMW* polymer, arise from interaction of the primary crack moving on one plane with secondary cracks moving on slightly displaced planes. The secondary fractures initiate in the high stress field near the tip of the primary crack, usually at some heterogeneity. Flow lines emanating from each secondary fracture site are clearly visible at higher magnification. Somewhat similar features have been observed in tensile fracture of cast PMMA[36], and their absence in tensile fracture of low molecular weight PMMA has also been noted[37].

Another striking difference in the fatigue fracture surface morphology between the cast and the extruded PMMA occurs within the slow-growth region. This region in the extruded polymer, as shown by *Figure 6b*, is very smooth even at high magnification and it contains a series of regular, concentric DCG bands. In the *HMW* cast PMMA, the slow-growth region is much less smooth; a portion of this region for a dry sample is shown at high magnification in *Figure 9b*. Instead of regular growth bands surrounding the single surface source, we see a whole series of more irregular localized bands or packets. These originate from different sites on the crack front and the spacing of the bands varies, sometimes increasing with distance from each origin and sometimes decreasing. Features rather like these have been observed in cast PMMA samples subject to reversed, triangular strain–time waveforms[38]. Clearly, in the highly entangled chain network of the *HMW* polymer, the fatigue-induced crack does not move forward as a unit; it may advance locally at one point but be retarded at another. This may be a result of molecular inhomogeneity due to a spatial distribution of entanglement density.

The fatigue fracture surface of the water-saturated samples differs in several respects from those of dry samples or samples with low water content. In the slow growth region of some samples, various microcracks appear to have originated in surface crazes which are slightly displaced from one another. These microcracks then tend to coalesce as they progress inward. This leads to the presence on the fracture surface of many sets of rather irregular, narrowly separated striations, each representing crack arrest positions prior to more rapid crack propagation over the rest of the specimen. Because of the plasticizing action of much of the sorbed water, craze stability is reduced and fewer cycles are required to reach the transition zone from relatively slow to fast fracture. Sufficient craze stability is still present, however, so that secondary cracks have time to develop ahead of the main crack. Hence conical fracture features are present in the region of the fracture surface away from the source region.

Some other samples of this same group have fractured in a rather different manner. In these, fracture developed not at the surface but near the centre of the specimen, possibly as a result of high stress concentration due to the presence of water clusters. In some portions of the fracture surface one can see, in addition to striation markings as discussed above, various small cavities. These vary in size up to about one micron. An unusual feature observed in one specimen was the visible presence of some crazes aligned essentially parallel to the loading axis in addition to some of the more usual transverse crazes. The high magnification scan of *Figure 10*, showing a portion of the fracture surface for a sample containing 2.25% water, illustrates the effect on the fracture surface of the presence of these axial crazes. Several crack-like elements are present and, in some SEM scans one can see fibrils extending transversely across these elements. This indicates that they are indeed crazes.

The mechanism of formation of these axial crazes is not well understood. Several possible reasons are suggested. They may arise as a result of the presence of high triaxial stresses in the polymer matrix near to the water clusters. This mechanism has been invoked to describe the axial crazes that have been observed upon fatigue testing of notched samples of rubber-modified PS[39]. Here too the axially aligned crazes have developed internally in the polymer matrix material near to the dispersed particles. Another possibility is that the axial crazes may arise from a combination of circumferential strain due to the compression stress portion of the loading cycle and internal strain arising from the presence of the water clusters. In this connection, it may be noted that even under purely compressive fatigue cycling axial crazes and cracks have been observed to occur in PS[40].

In fatigue tests carried out on unnotched samples of PS and of rubber modified PS, it has been observed that plastic deformation under alternating loading tends to be highly localized[26]. In the current tests on PMMA, carried out at a relatively high stress amplitude compared to the tensile strength of the material, surface crazes have been observed to occur at various sites along the gauge length. For example, in the tests on samples of the cast PMMA containing 0.5% of water, it was noted that after some critical number of cycles at 41.4 MPa and 2 Hz the specimens would whiten in the gauge length region on each tension portion of the cycle and become transparent once again during the compression half cycle. Also, in dry samples, tested at 41.4 MPa and 2 Hz a number of surface

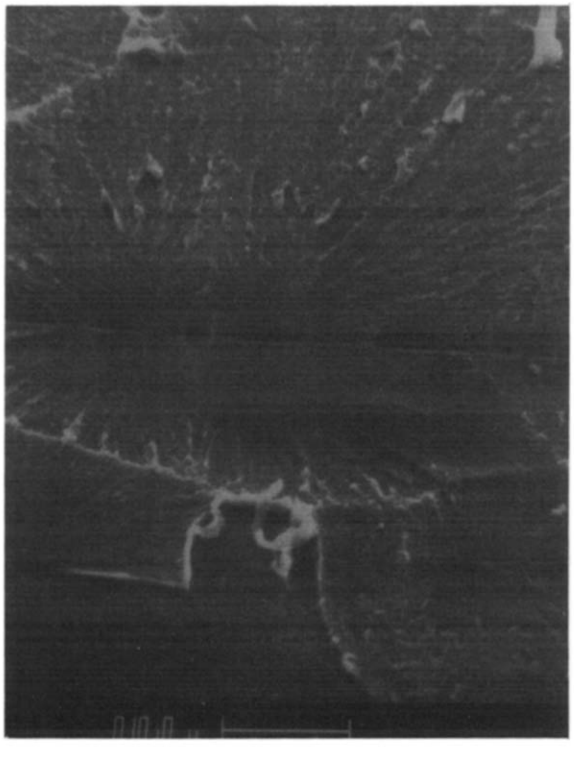

Figure 10 A portion of the fatigue fracture surface of a water-saturated sample of *HMW*, cast PMMA tested at 41.4 MPa and 2 Hz

crazes were visible in the gauge length region when the samples were examined at the end of the test. Thus, in high molecular weight glassy polymers where the heavily entangled molecular chains lead to enhanced craze stability, it appears that, even under alternating tension–compression loading, plastic deformation in the form of additional surface crazes may develop before the initial craze breaks down to form a crack.

No attempt was made in the current study to determine quantitatively what proportion of the total fatigue lifetime was spent in craze or damage initiation vs. that spent in damage or crack propagation. However, some qualitative observations may be of interest. In a sample of the *HMW* polymer containing 0.5% of water that survived over 200 000 cycles at 41.4 MPa before fracture a surface craze was observed at about 40 000 cycles. Thus about one-fifth of the total lifetime of this sample, tested at a stress amplitude of about 60% of the tensile strength was spent in damage initiation. It is interesting to compare this result with recently reported observations of craze initiation in fatigue of unnotched samples of PS[26]. In this latter investigation, at a stress amplitude of 50% of the tensile strength, the initiation phase was found to occupy about 22% of the total fatigue life. However, when the stress amplitude was reduced to about one-third of the tensile strength, the initiation phase took up about two-thirds of the total life. We have no corresponding data on PMMA to compare with this as no fatigue failures were observed in cast PMMA even when tested at a stress amplitude of about 40% of the tensile strength. The current data are, however, consistent with the conclusion that, for low ratios of stress amplitude to tensile strength, craze initiation occurs late, if at all, during the fatigue cycling; while at high ratios of the stress amplitude to the tensile strength damage initiation occurs early in the fatigue life and most of the lifetime is then spent in the damage or crack propagation process.

CONCLUSIONS

(1) In PMMA, the associated thermal effects due to fatigue cycling can be severe enough even at 2 Hz to produce a significant temperature rise in the material and to deleteriously affect fatigue performance.

(2) If the stress and frequency conditions are chosen so that thermal effects are not dominant, the high molecular weight, cast PMMA develops fatigue lifetimes that are about two decades or more higher than obtained with the low molecular weight, extruded PMMA.

(3) The presence of sorbed water over the range from zero to about 1% tends to materially reduce the fatigue resistance of both cast and extruded PMMA; but it has relatively little further effect on fatigue performance at higher water contents.

(4) It is suggested that the primary effect of water up to concentrations of about 1% is plasticization; and, at higher water contents, the water molecules tend to aggregate and form clusters.

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REFERENCES

1 Doll, W., Konczol, L. and Schinker, M. G. *Polymer* 1983, **24**, 1213
2 Konczol, L., Schinker, M. G. and Doll, W. 'Fatigue in Polymers', The Plastics and Rubber Inst. 1983, 4.1
3 Lang, R. W., Manson, J. A., Hertzberg, R. W. and Schirrer, R. Fourth Cleveland Symp. on Macromolecules, June 1983
4 Broderick, J. S., Duckett, R. A. and Ward, I. M. 'Fatigue in Polymers', The Plastics and Rubber Inst. 1983, 5.1
5 Lebedeva, M. F., Aleshin, V. I., Aero, E. L. and Kuvshinskii, E. V. *Int. J. Fract.* 1981, **17**, 327
6 Kim, S. L., Janiszewski, J., Skibo, M. D., Manson, J. A. and Hertzberg, R. W. *Polym. Eng. Sci.* 1979, **19**, 145
7 Hertzberg, R. W., Skibo, M. D. and Manson, J. A. ASTM STP 675, 1979, 471
8 Hertzberg, R. W., Skibo, M. D. and Manson, J. A. *J. Mater. Sci.* 1978, **13**, 1038
9 Kim, S. L., Skibo, M. D., Manson, J. A. and Hertzberg, R. W. *Polym. Eng. Sci.* 1977, **17**, 3
10 Radon, J. C. and Culver, L. E. *Polymer* 1975, **16**, 539
11 Shen, J., Chen, C. C. and Sauer, J. A. *Polymer* 1983, **24** (*Commun.*), 167
12 Crawford, R. J. and Benham, C. P. *Polymer* 1975, **16**, 908
13 Bouda, V. and Staverman, A. J. *J. Polym. Sci. Polym. Phys. Edn.* 1976, **14**, 2313
14 Johnson, T. A. ASTM STP 519, 1973, 79
15 Bucknall, C. B., Gotham, H. V. and Vincent, P. I. in 'Polymer Science' (Ed. A. D. Jenkins), N. Holland Publ. Co., 1972, Ch. 10, p. 621
16 Turner, D. T. *Polymer* 1982, **23**, 197
17 Moore, R. S. and Flick, J. A. in 'Water in Polymers', ACS Polym. Symp. Ser. No. 127, 1980, p. 556
18 Smith, L. S. A., PhD Dissertation, Leeds University, 1976
19 Shen, J., Chen, C. C. and Sauer, J. A. submitted to *Polymer*
20 Shen, J., Chen, C. C. and Sauer, J. A. Abstracts IUPAC MACRO '83, Sect. IV, Bucharest, 1983, p. 279
21 Hertzberg, R. W. and Manson, J. A. 'Fatigue of Engineering Plastics', Academic Press, New York, 1980
22 Sauer, J. A. and Richardson, G. C. *Int. J. Fract.* 1980, **16**, 499
23 Shen, J., Chen, C. C. and Sauer, J. A. 'Fatigue in Polymers', The Plastics and Rubber Inst. 1983, 6.1
24 Williams, J. G. and Hodgkinson, J. M. *Proc. Roy. Soc.* 1981, **A-375**, 231
25 Ferry, J. D. 'Viscoelastic Properties of Polymers', 2nd Edn., J. Wiley and Sons, New York, 1970
26 Sauer, J. A. and Chen, C. C. *Adv. Polym. Sci.* 1983, **52/53**, 170
27 Manson, J. A., Hertzberg, R. W., Kim, S. L. and Skibo, M. D. *Polymer* 1975, **16**, 850
28 Cornes, R. L., Smith, K. and Haward, R. N. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 955
29 Gotham, K. V. *Plastics and Polymers* 1973, **41**, 273
30 Sauer, J. A., Foden, E. and Morrow, D. R. *Polym. Eng. Sci.* 1977, **17**, 246
31 Kausch, H. H. 'Polymer Fracture', Springer-Verlag, Berlin, 1978
32 Kim, S. L., Skibo, M. D., Manson, J. A. and Hertzberg, R. W. *Polym. Eng. Sci.* 1977, **17**, 194
33 Kramer, E. J. and Bubeck, R. A. *J. Polym. Sci. Polym. Phys. Edn.* 1978, **16**, 1195
34 Feltner, C. E. *J. Appl. Phys.* 1967, **38**, 9
35 Mackay, M. E., Teng, T. G. and Schultz, J. M. *J. Mater. Sci.* 1979, **14**, 221
36 Doll, W. *J. Mater. Sci.* 1975, **10**, 935
37 Kusy, R. P. and Turner, D. T. *Polymer* 1977, **18**, 391
38 Johnson, T. A. *J. Appl. Phys.* 1972, **43**, 1311
39 Manson, J. A. and Hertzberg, R. W. *J. Polym. Sci. Polym. Phys. Edn.* 1973, **11**, 2483
40 Weaver, J. L. and Beatty, C. L. *Polym. Eng. Sci.* 1978, **18**, 1117