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Fatigue failure of poly(methyl methacrylate) in alcohol environments

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Fatigue tests of poly(methyl methacrylate) were conducted in environments of methanol, 1-butanol, and 1-octanol at room temperature under cyclic tensile loading at 10 Hz. The fatigue lifetime increased as the molar volume of the environmental alcohol increased, and indicated no correlation with the solubility parameter. The scanning electron micrographs of the fracture surfaces reveal that crazes strongly participate in the fatigue fracture, and suggest that a great increase in the fatigue lifetime in methanol brought about by pre-soaking the specimen in methanol for a period below 100 h, which has been previously reported, is caused by the combined effects both of the case II diffusion of methanol producing the softened matter and the internal compressive stress in the swollen surface layer and of a cooperative work of crazing, shear flow and/or shear cracking taking place under cyclic tensile loading.

1. Introduction

The effects of environmental liquids on fracture behaviour of polymers have been extensively studied [1, 2]. Most of the studies, however, focus their attention on the phenomena under static and/or quasi-static loadings. In view of the practical use of polymers as structural materials, information on fatigue behaviour under dynamic alternating loading is preferably required.

A definite study of environmental fatigue failure has been made by Warty *et al.* [3]. They measured the fatigue lifetime of the cylindrical specimens of polystyrene (PS) in various organic media, and found that the lifetime takes the minimum value in the media with the solubility parameters which are near to those of PS. This trend parallels that of the critical crazing strain which Kambour and co-workers [4–6] obtained for a wide variety of combinations of liquid and polymer. Our previous investigation [7], however, revealed that the critical crazing stress in poly(methyl methacrylate) (PMMA) measured in *n*-alkanes under constant tensile and torsional loadings is not correlated with the solubility parameter at all, but probably with the diffusion rate of the reagent into the polymer. In addition, the fracture load of PMMA measured in alcohol environments under diametral compression also showed a similar trend [8].

The first purpose of this study was to investigate the effects of environmental alcohols on the fatigue failure of PMMA as an extension of the above studies under static and quasi-static loadings.

The diffusion of methanol into PMMA is well known to exhibit the case II behaviour [9, 10] in which the sharp boundary separating an inner glassy core from an outer swollen layer advances at a constant velocity. As a result, the weight gain of the PMMA sample increases linearly with soaking time in methanol, contradicting Fick's law. It is noted that the surface layer is not only softened but also biaxially compressed under the constraint by the inner core. According to Thomas and Windle [11], this induced compressive stress is interpreted as an osmotic pressure, and strongly characterizes case II diffusion. The softening effect [12] and the internal compressive stress are expected to affect the strength of the polymer. A previous study [13] demonstrated that great increases in the critical torsional stress for crazing and the fatigue lifetime are brought about by pre-soaking the PMMA specimens in methanol for comparatively short periods. It was also emphasized that a specific pre-soak time exists, above which the fracture mode of the specimen discontinuously shifts from that associated with nucleation and growth of numerous crazes and cracks, to that associated with preceding shear flow and subsequent formation of a few cracks. A model has been proposed to explain these features of failure following case II diffusion.

This work secondly aimed to examine the failure mechanism associated with the absorption of methanol by making precise observations of the fracture surfaces.

For the purposes mentioned above, the fracture behaviour of the PMMA specimens was investigated in methanol, 1-butanol, and 1-octanol under cyclic tensile loading, and their fracture surfaces were observed in detail with a scanning electron microscope (SEM).

2. Experimental procedure

The material used was commercially available PMMA rod, 25 mm diameter (Mitsubishi Rayon Co.). Solid cylindrical specimens were machined from the

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rods to the dimension shown in Fig. 1. The preliminary experiments conducted by using various types of specimen indicated this shape, with a narrow part and a tapered grip, to be appropriate for the fatigue tests in alcohols. The surface of the narrow part was polished circumferentially with a fine buffing compound of 0.05 μm alumina. Then the specimens were annealed at 90 °C for 2 h and slowly cooled to room temperature in a forced-air oven.

The fatigue tests were performed by means of the hydraulic servo-controlled testing machine (Dynamic Servo FT-5, Saginomiya Co.) in environments of methanol, 1-butanol, and 1-octanol. The lower part of the specimen marked by a broken line in the figure, was immersed in a vessel filled with each reagent just before the tests. However, in the experiments to investigate the effect of methanol absorption, as already reported [13], the specimens were previously soaked in methanol at room temperature (21 ± 2 °C) for different periods, and then subjected to the tests. The fatigue lifetime, i.e. the number of cycles to failure, N_f, was measured under sinusoidal tensile stress alternating at 10 Hz between nominal values of zero and 14.7 MPa. The temperature of each alcohol was at room temperature (20 ± 1 °C) during the tests, but was varied between 19 and 25 °C during the test in methanol using specimens pre-soaked in methanol, probably due to the hysteresis in the material.

The basic properties of the three alcohols used are given in Table I [14]. They are considered to wet perfectly the surface of the PMMA specimen because of their lower values of surface tension than the critical surface tension of PMMA, 39 mN m^{-1}.

The fracture surfaces of the specimens were observed by scanning electron microscopy (SEM) with a field emission gun (Hitachi, S-4000). Before observation in the SEM, the fracture surfaces were sputter-coated with a thin layer of gold.

3. Results and discussion

The data of fatigue lifetime, N_f, are plotted against the molar volume of alcohol, V_1, in Fig. 2. It is clear that the values of N_f increase with increasing V_1. Similar trends to V_1 of the environmental reagent were previously obtained in PMMA on the critical crazing stresses under static tension and static torsion in n-alkanes [7], and on the fracture load under diametral compression in alcohol environments [8]. The behaviour of environmental fatigue failure has already been investigated by Warty *et al.* [3] on PS in various organic liquids. They revealed that the minimum value of N_f is measured for liquids in which the solubility parameter takes the value near to that of PS. Their results is consistent with the trend of critical crazing strain obtained mainly by Kambour and coworkers [4–6] under fixed bending strain in a wide variety of combinations of polymer and reagent. The previous experiment in n-alkanes mentioned above [7], however, indicated that the crazing stresses were correlated with neither the solubility parameter nor the equilibrium solubility predicted from the solution theory. The present data for N_f are plotted against the solubility parameter of the alcohol, δ_1, in Fig. 3, where the extent of the solubility parameter of PMMA is represented by the hatched lines. It is evident that the trend of N_f, as in the crazing stresses, is opposed to that given by Warty *et al.* Andrews *et al.* [15] investigated the properties of diffusion and solution of several alcohols in PMMA and their effects on the yielding behaviour. According to them, the diffusion of reagent with smaller V_1 is faster than that with a larger one. The higher equilibrium solubility is achieved in alcohols with a solubility parameter near that of PMMA, but the effect is only slight. In alcohol environments, the influence of the hydrogen bonding may also be considered. The hydrogen-bonding parameters quoted from the literature [16] of three test alcohols show

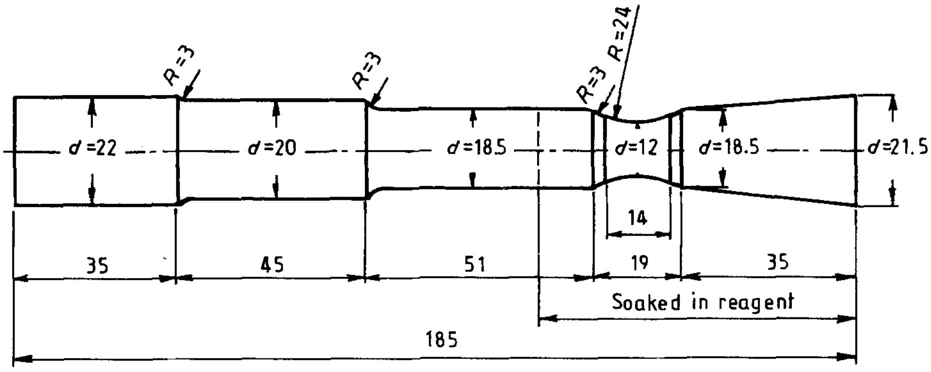


Figure 1 Sample geometry. d = diameter, R = radius.

TABLE I Physical constants for the alcohols used

	Molar volume (cm^3 mol^{-1})	Viscosity (mPa s, 20 °C)	Surface tension (mN m^{-1}, 20 °C)	Solubility parameter ((MJ m^{-3})$^{1/2}$)	Hydrogen bonding parameter
Methanol	40.7	0.59	22.6	29.7	19.8
1-butanol	91.5	2.95	24.6	23.3	18.0
1-octanol	157.7	8.93	26.1	21.1	18.7

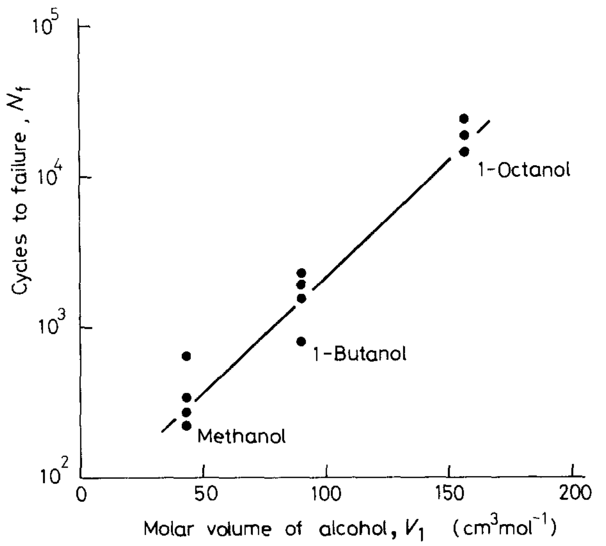


Figure 2 Fatigue lifetime versus molar volume of alcohol.

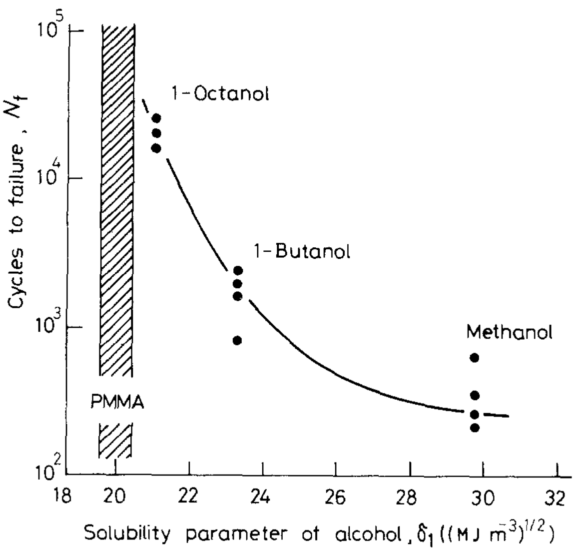


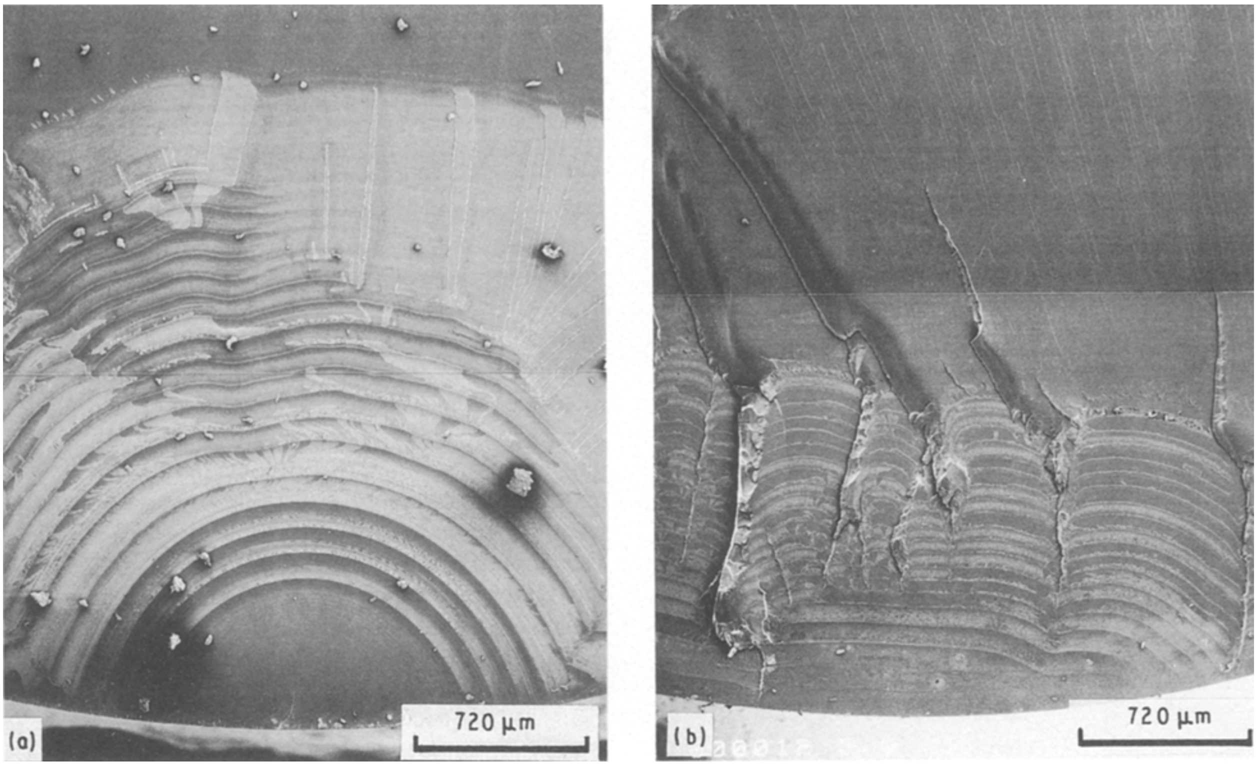
Figure 3 Relation of fatigue lifetime to solubility parameter of alcohol.

no significant difference, as presented in Table I. Therefore, the order of N_f, (in other words, the relative value of N_f) does not appear to be affected by the hydrogen bonding of these alcohols, although the value of N_f may be strongly influenced in itself. From the above discussion, it is supposed that the fatigue fracture of PMMA will also be dominated by the diffusion process of the environmental alcohol, which plasticizes a local region such as the bottom of a surface scratch, and subsequently produces microscopic deformation of crazing.

A precise observation of the fracture surface may demonstrate that crazes participate in the environmental fatigue to a greater extent. The scanning electron micrographs in Fig. 4 show the regions near the source in the fracture surfaces obtained in three test alcohols. In methanol, concentric circular bands spreading from the source are clearly observed, whereas in the other two alcohols, slender bands extend circumferentially and thus the crack nucleation sites cannot be easily identified. Although not presented in these micrographs, both hyperbolic and coarse rib marks surrounding the band area are commonly seen for all the specimens, which are identical to those observed in the fracture surface obtained in air [17]. Therefore, only the band area seems to be affected by the environmental reagent. As shown in Fig. 5, the coarse bands clearly consist of numerous patch marks which are different from the morphology of the retarded crack growth (RCG) band observed for the specimens fatigued in air [17]. This implies that in alcohols the early stage of the fatigue crack growth results entirely from the fracture of the crazed matter by detachment from the surrounding polymer matrix. Somewhat detailed observation reveals that on moving away from the fracture source, the structure of the patch becomes more porous. Fig. 6 shows magnified views of the patch marks in the first and the third bands, respectively, obtained in methanol. Dense small cavities are evident in the latter. This may be interpreted that as the crack-advance velocity increases, the strain rate in the crazed matter deformed at the crack tip also increases, and as a result no time can be afforded for the development of cavities to grow sufficiently to interconnect. In other words, at a high strain rate, a large number of small cavities are needed to digest a large deformation applied per unit time.

Next, the effects of the absorption of methanol on the fatigue fracture were examined. Fig. 7 shows the relationship of the fatigue lifetime, N_f, in methanol to the pre-soak time in the same environment. Because the trend of N_f presented in the figure has been already discussed in detail [13], only the outlines are mentioned here. It is noted that N_f dramatically increases on pre-soaking in the time range 8–96 h at room temperature. This great variation may be explained in terms of both the softening effect and the induced compressive stress in the swollen surface layer following case II diffusion of methanol. That is, the former causes the shear flow at the preceding craze tip, and the latter reduces the level of tensile stress at the surface scratch. These effects result in the relaxation of stress concentration at the flaw tip, and consequently, suppress the crack initiation and growth. The longer pre-soak, however, produces a large-scale deformation at the bottom of a surface scratch, and keeps it away from the generation site of the compressive stress near the boundary between the outer swollen layer and the inner glassy core. As a result, only a lower increase in N_f is achieved.

The scanning electron micrographs of the fracture surface of the specimen tested in methanol after pre-soaking in methanol for 24 h are shown in Fig. 8. An outer ring layer can be seen, indicating a complicated morphology and an inner core region with the band structure, which is regarded as the same as that in Fig. 4a for the case without pre-soaking treatment, providing only lower values of N_f. Thus it is supposed that the great increase in N_f of this specimen may be entirely attributed to the formation of the outer damaged layer. This layer, in addition, is broadly composed of two layers with smooth and rough surfaces. The smoothness of the fracture surface indicates this



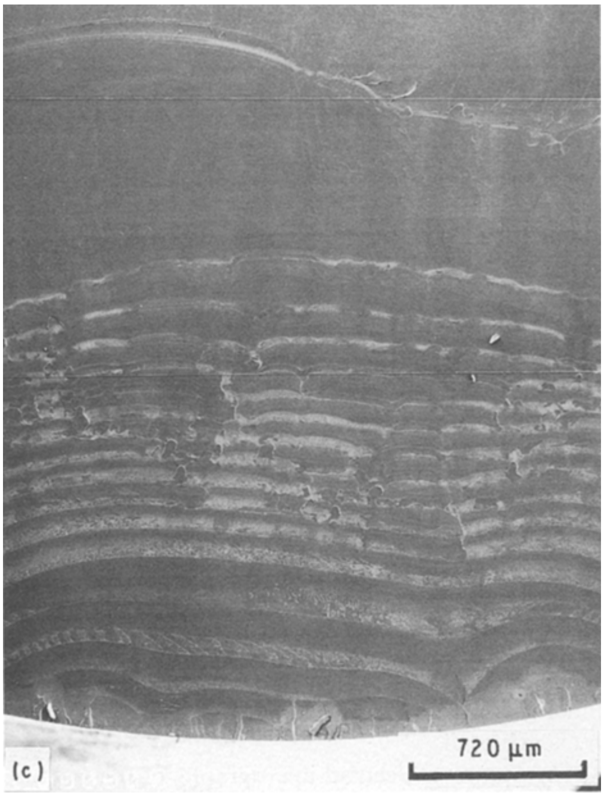


Figure 4 Scanning electron micrographs of a region near the source in the fracture surface: (a) in methanol, (b) in 1-butanol, and (c) in 1-octanol.

layer to be highly swollen and softened, showing the high energy loss by the pre-soak treatment in methanol. In Fig. 8b the subsequent inner rough region of the outer layer is magnified. It is of interest that many inclined striations and cracks are seen on the fracture surface. According to Ma *et al.* [18], the shear yielding of the thin sheet specimen of polycarbonate, which is a typical ductile polymer, is governed by the mechanism of intersecting shear. In our experiments, the swollen

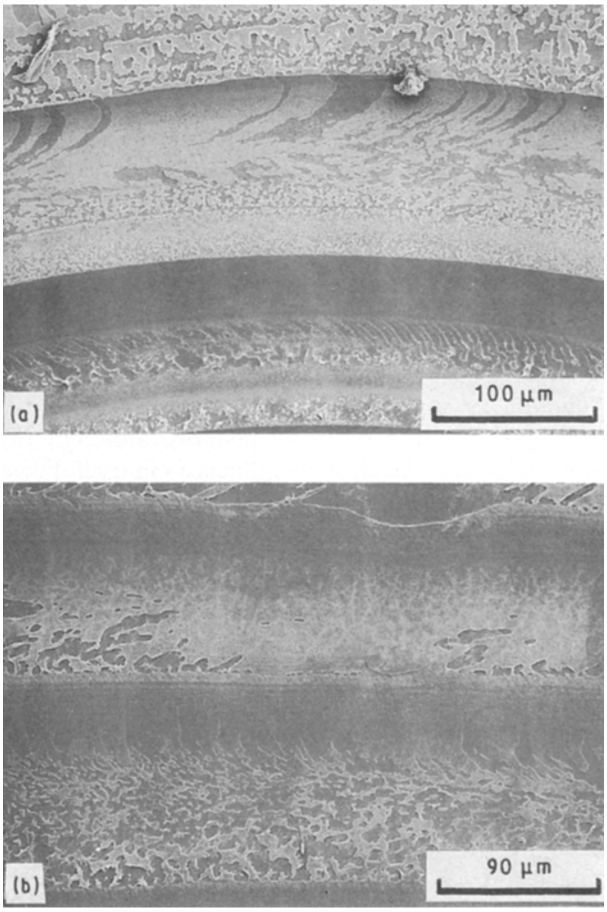


Figure 5 Scanning electron micrographs of coarse bands in the fracture surface: (a) in methanol, and (b) in 1-octanol.

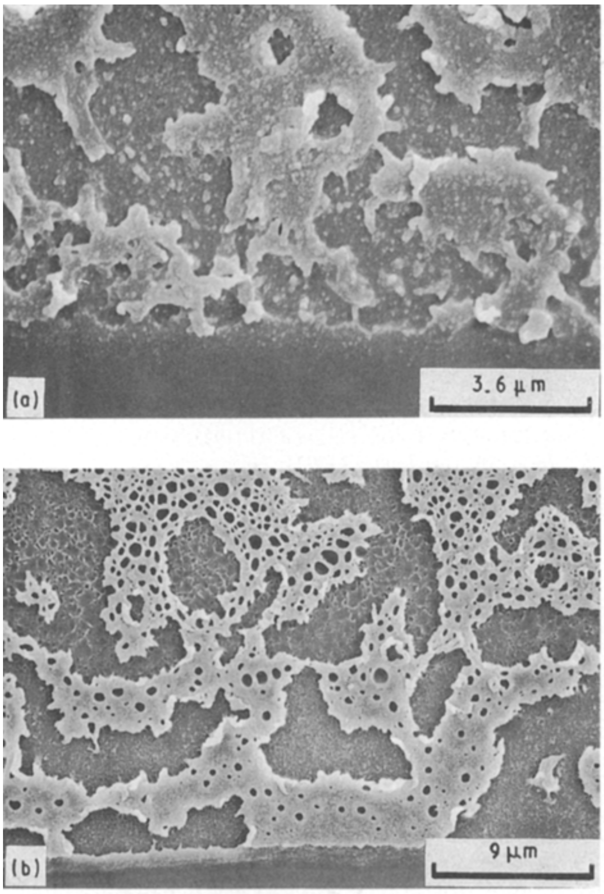


Figure 6 Scanning electron micrographs of patch marks in fracture surface in methanol, (a) in the first band, and (b) in the third band.

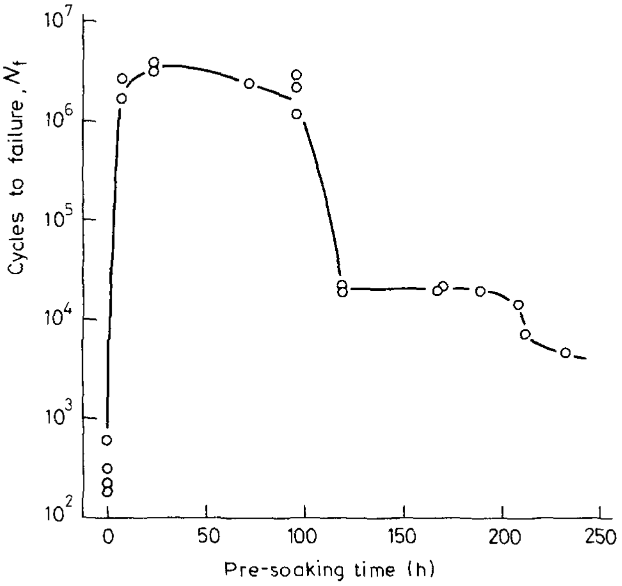


Figure 7 Fatigue lifetime in methanol versus pre-soak time in methanol.

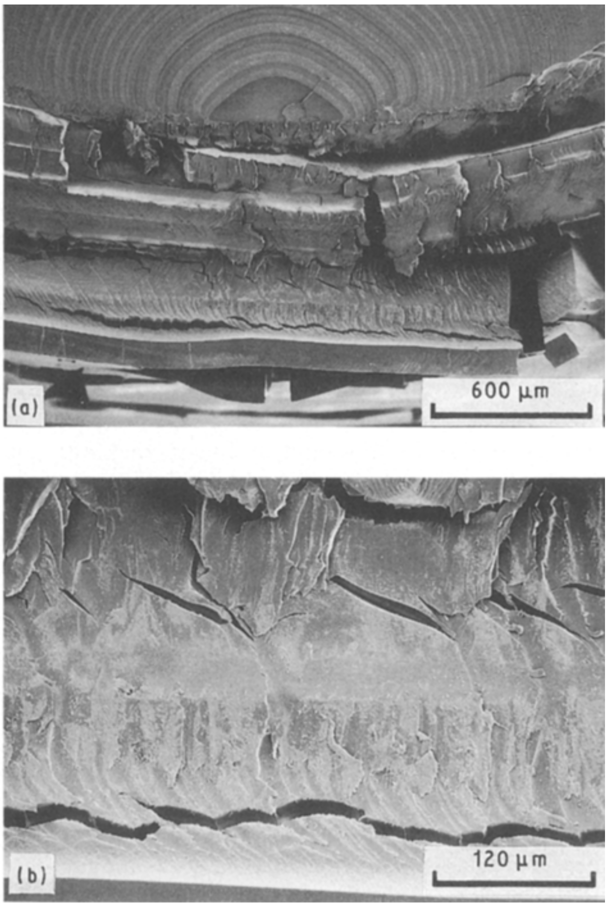


Figure 8 Scanning electron micrographs of the fracture surface of a specimen pre-soaked in methanol for 24 h before fatigue testing in methanol. $N_f = 3750480$. (a) Region near the fracture source, and (b) a rough region of the outer ring layer.

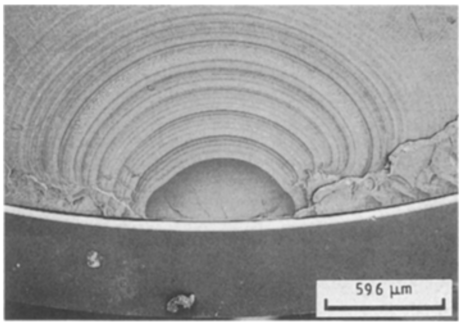


Figure 9 Scanning electron micrograph of the fracture surface of a specimen pre-soaked in methanol for 120 h before fatigue testing in methanol. $N_f = 22430$.

polymer, which is highly ductile, near the boundary between the outer layer and the inner core is not only biaxially compressed due to case II diffusion, but is also subjected to applied cyclic tension. Although the precise mechanism remains to be elucidated, it is speculated that both the softening and the combination of the induced biaxial compressive and the applied cyclic tensile stresses produce a number of localized shear-yielded regions and/or shear cracks in the thin softened layer, probably at the tips of preceding crazes or normal cracks. If the applied tensile stress is considered to be relatively enhanced against the shear flow stress of the thin softened layer with an increase in the pre-soak time, this may indicate that the result for N_f presented in Fig. 7 show a phenomenon similar to the transition from craze-dominated fracture to shear-dominated fracture which Takemori [19] has demonstrated on several ductile polymers in air.

Fig. 9 shows the scanning electron micrograph of the fracture surface of the specimen tested after pre-soaking for a longer time of 120 h. In this case, a thick outer layer with a very smooth surface and a core region with the band morphology common to all the specimens fatigued in alcohols, are seen, but the heavily damaged layer showing the characteristic feature is never observed. It is implied that in the thick swollen layer, relatively slow crack growth takes place in association with a large shear flow at its tip, and consequently causes a slight increase in the fatigue lifetime.

As is evident from the above, the surface softening has a restricted effect on the improvement of brittleness of a polymer due to the stress concentration at the flaw tip. The combined effects of different mechanisms, namely, softening and generation of compressive stress following case II diffusion, and the joint work of crazing and shear flow and/or shear cracking, may cause a great increase in the fatigue lifetime in methanol.

4. Conclusions

The environmental fatigue behaviour of PMMA was investigated in methanol, 1-butanol, and 1-octanol. Observations of the fracture surfaces in the SEM and the experimental results show that the fatigue lifetime increases with increasing molar volume of alcohol. Thus we may conclude that craze formation and breakdown promoted under diffusion of environmental alcohol strongly participate in the fatigue fracture, as well as in the fracture under static and quasi-static loadings. A great increase in the fatigue lifetime in methanol brought about by the pre-soak treatment in methanol is supposed to be resulted from the softening of the polymer and the generation of compressive stress, due to case II diffusion of methanol, and in addition from the combined fracture mechanisms of crazing and shear flow and/or shear cracking in the swollen surface layer.

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