Crazing and fatigue of poly(methyl methacrylate) due to case II diffusion of methanol

M. Kawagoe
Department of Mechanical Systems Engineering, Faculty of Engineering, Toyama Prefectural University, 5180 Kurokawa, Kosugi, Toyama 939-03, Japan

and S. Nunomoto
Department of Industrial Chemistry, Toyama National College of Technology, 13 Hongo, Toyama 939, Japan
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Static torsion and dynamic fatigue tests were performed on poly(methyl methacrylate) in methanol at room temperature using solid cylindrical specimens which had previously been soaked in methanol for various periods. Presoaking for times in the range 8–96 h brought about dramatic increases in both the critical torsional moment for crazing and the fatigue lifetime. The latter, for instance, attained a value 10^4 times that of the specimen without presoaking. Presoaking for longer times, however, allowed shear flow to occur prior to crazing, and contributed less to the increase in fatigue life. These results are explained in terms of both the softening of matter and the generation of internal compressive stress in the swollen surface layer following the case II diffusion of methanol.

(Keywords: craze; fatigue; diffusion; poly(methyl methacrylate; methanol)

INTRODUCTION

The diffusion of methanol into poly(methyl methacrylate) (PMMA) is well known as a typical example of case II diffusion, which exhibits different behaviour from the usual Fickian diffusion. The differences are: (i) the formation of a sharp boundary which separates an inner glassy core from an outer swollen layer advancing at a constant velocity; and (ii) the swollen polymer is almost in equilibrium behind the advancing front of penetrant[1].

The diffusion of penetrant generally affects the mechanical properties in such a manner as to reduce the elastic modulus and the shear yield stress (softening or plasticization effect). Campbell *et al.*[2] have investigated the effect of methanol absorption on the crazing behaviour in PMMA under static tension, and revealed that the crazing stress increases monotonously with the progress of methanol absorption. They interpreted this result as being due only to the softening effect as the soft surface layer neutralizes the stress concentration at the tips of surface flaws. For case II diffusion it should be noted that the internal compressive stress is induced near the boundary in the surface swollen layer under constraint by the inner glassy core. The tensile stress, on the contrary, is generated near the boundary in the core, which frequently becomes large enough to cause fracture or shear flow of the core polymer[3,4]. The build-up of these internal stresses seems to characterize case II diffusion more strongly than softening or plasticization effects. Both the changes in the mechanical properties and the generation of the internal (residual) stresses are expected to exert considerable effects on the strength of the polymer. Warty *et al.*[5] have already pointed out these factors in interpreting their experimental results: they observed a large increase in fatigue life in a polystyrene (PS) specimen, the surface of which was coated with low molecular weight (M_w 600) PS oligomer.

Although the mechanical properties and the fracture behaviour of PMMA in methanol have been extensively investigated from various points of view[6–8], few results have been obtained to verify the above expectation. The purpose of this study is to show the effects exerted on the strength of PMMA by case II diffusion of methanol with special reference to both crazing under static torsion and fatigue failure under cyclic tensile loading.

EXPERIMENTAL

Two types of cylindrical specimen, type (a) and type (b) with the geometries shown in *Figure 1*, were prepared by machining from commercially available PMMA rods (purchased from Mitsubishi Rayon Co.). Their gauge surfaces were polished circumferentially with a fine buffing compound of 0.05 μm alumina. The specimens were then annealed at 90°C for 2 h in a forced-air oven.

These specimens were soaked in methanol at room temperature (21 ± 2°C) for different periods before being subjected to the tests. The static torsion and the dynamic fatigue tests were performed in methanol by means of a testing machine of our own making[9] and the hydraulic servo-controlled testing machine (Dynamic Servo FT 5, Saginomiya Co.), respectively.

In the torsion tests a type (a) specimen was completely

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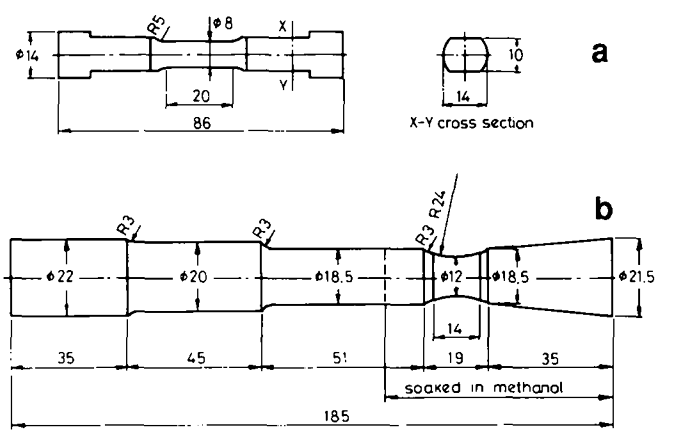

Figure 1 Specimens for (a) static torsion tests and (b) dynamic fatigue tests. Dimensions are in millimetres

immersed in methanol in a vessel and a constant torsional moment was applied for 20 min, by means of a pulley and dead-weight loading system. The specimen was observed by optical microscope at a magnification of × 100 after unloading and removal from the apparatus. The critical torsional moment required for crazing, T_c, was determined as the middle point between the moment levels of crazing and no crazing. The static tension tests, which were also undertaken at the outset of the investigation, were regrettably abandoned because most of the specimens fractured just after loading when they were tested in methanol without any presoaking treatment. In the fatigue life measurements the lower part of the type (b) specimen, marked by a broken line in *Figure 1b* was immersed in methanol in a liquid vessel. The fatigue lifetime, i.e. the number of cycles to failure, N_f, was measured under sinusoidal tensile stress alternating at 10 Hz with a maximum of 14.7 MPa and a minimum of 0.0 MPa. The methanol was at room temperature (21 ± 1°C) during the torsion tests, but varied between 19 and 25°C during the fatigue tests, probably due to the hysteresis in the material.

RESULTS AND DISCUSSION

In *Figure 2* the critical torsional moment for crazing or cracking, T_c, in methanol is plotted against the presoak time in methanol. It is emphasized that presoaking even for short times brings about great increases in T_c, and also that although T_c initially increases with the presoak time, it soon attains the maximum and after that slightly decreases. For the specimen without presoaking treatment the critical torsional stress for crazing, τ_c, is proportional to T_c, and thus easily calculated to be 12.5 MPa. But the real value of τ_c is not expected to vary in the same way as T_c with the presoak time, because the specimen surface is swollen and softened to indicate lower elastic modulus and shear yield stress in association with methanol absorption. More detailed discussion on this point will be made in a future publication. Only a few crazes or cracks were observed to be initiated and grow in the direction perpendicular to the maximum principal stress on the specimen surface. Crazes formed in the specimens presoaked for short times (below 96 h) tended to change immediately into cracks leading to general fracture. On the other hand, in the specimens presoaked for longer times visible shear flow was allowed to take precedence and cracks, rather than crazes, were subsequently formed and grew slowly.

Figure 3 shows the relationship between the number of cycles to failure, N_f, and the presoak time in methanol. The dramatic increase in fatigue life is observed for presoaking periods as short as 8 h. It is of interest that presoak times up to about 100 h have almost the same effect on increasing the fatigue life, whereas presoaking for longer times, above 120 h, has less effect on increasing the fatigue life.

The fracture surface of the fatigue specimen which had not been previously immersed in methanol is shown in *Figure 4*. In this case the specimen behaved in an exceedingly brittle manner in methanol. The fracture

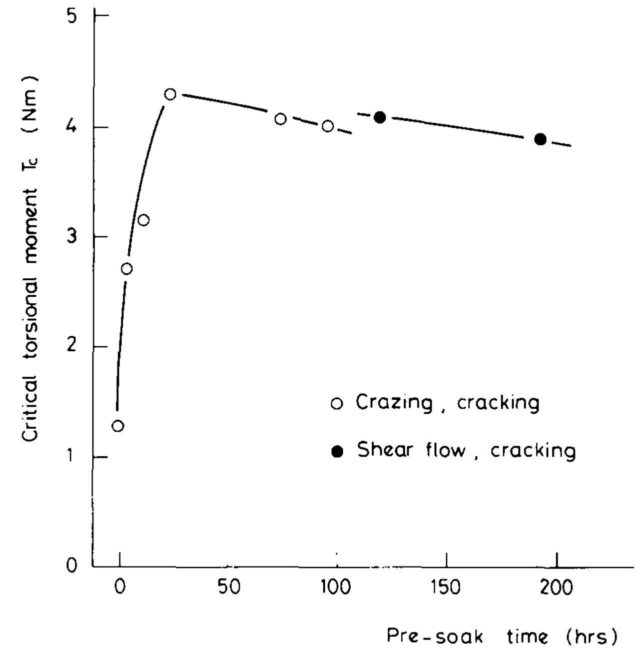

Figure 2 Effect of presoaking in methanol on the critical torsional moment for crazing in methanol at room temperature

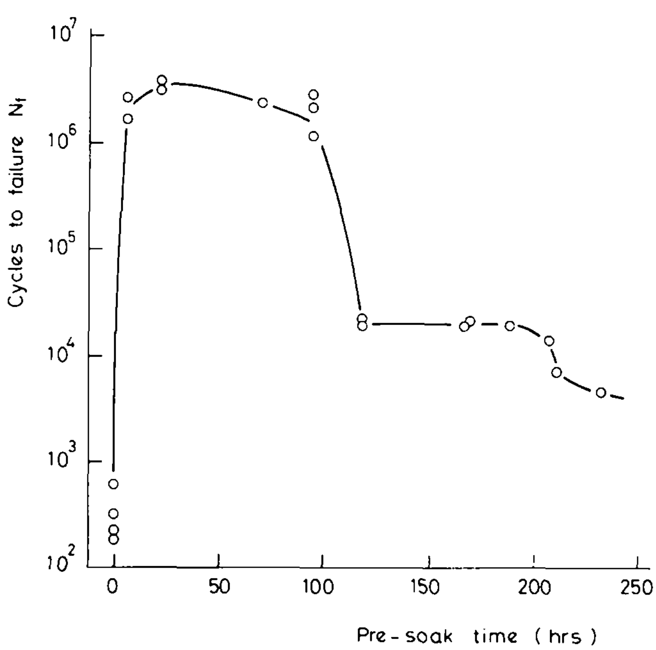

Figure 3 Effect of presoaking in methanol on fatigue lifetime in methanol at room temperature

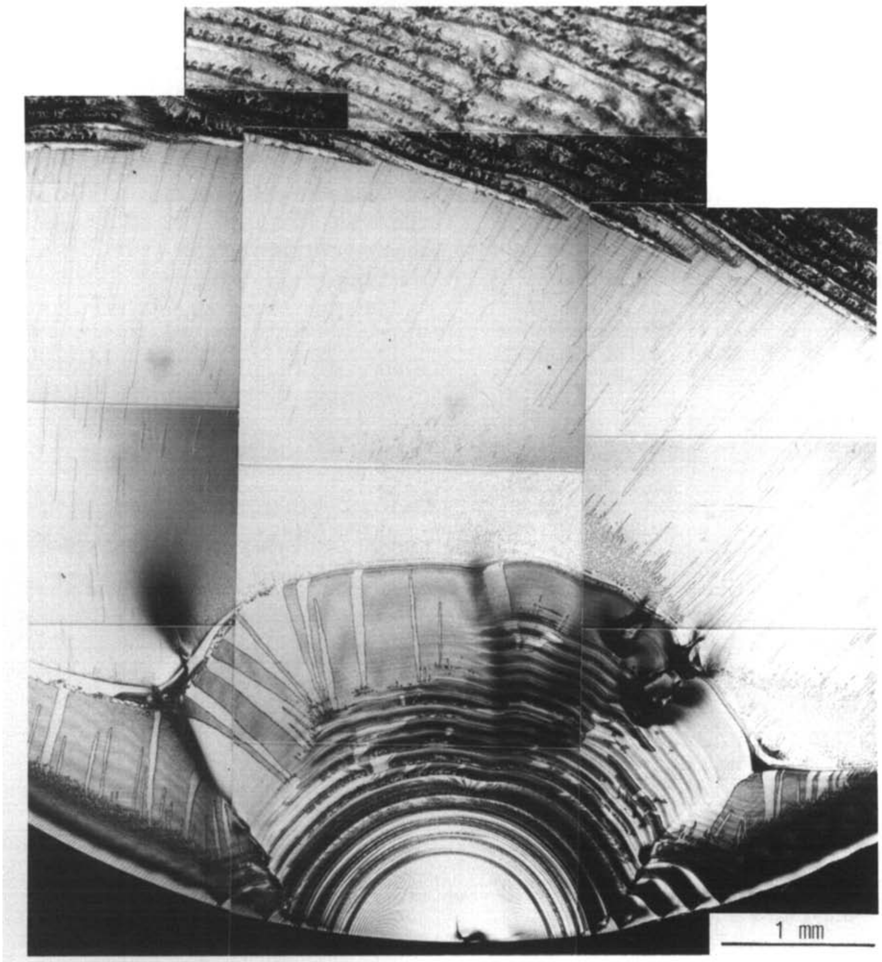

Figure 4 Fracture surface of the fatigue specimen without presoaking treatment. $N_f = 590$

surface consists mainly of three types of mark: concentric circular, hyperbolic, and coarse rib marks. In the first region with circular marks very fine striations, peculiar to fatigue fracture, can also be observed. The thick circular band is made up of many granular marks, representing where a craze was first formed at the advancing crack front, and then fractured. As the velocity of the crack advance increases, hyperbolic and subsequently rib marks are produced. Particularly in the third region with rib marks, the crack is thought to propagate with very high velocity so as to be no longer caught up with methanol, since the same type of marks have been observed in the fracture surface obtained in air[10].

Figure 5 shows the fatigue fractured specimen presoaked in methanol for 24 h. It is noted that a number of crazes are formed in the swollen surface layer. Observation through an optical microscope reveals that most of the crazes are transformed to cracks which are opened out to resemble the diamond cavities observed in air at high temperatures (below T_g)[11]. The fracture surface is composed of an outer ring damaged by numerous crazes and an inner core region with features fundamentally identical to those in *Figure 4* for the specimen without presoaking treatment. More precise observations indicate that two layers exist in the outer ring, which are interpreted as the layer formed by the presoaking and that developed during fatigue tests in methanol. From the above observations the formation and growth of numerous crazes in the swollen surface layer are also thought to contribute to the dramatic increase in the fatigue lifetime of this specimen.

Figure 6 shows the specimen tested after presoaking for a longer period of 120 h. In contrast to *Figure 5* only a few crazes or cracks are found on the surface. The fracture surface comprises an outer layer with a very smooth surface and a core region showing the characteristic features common to all the specimens fatigued in methanol. In view of their appearances and the smooth fracture surface of the outer layer these surface defects are regarded as complete cracks.

The variations of N_f and the fracture mode with time of presoaking correspond to those in T_c and the deformation mode under static torsion, respectively, in *Figure 2*.

Campbell *et al.*[2] have reported an increase in the crazing stress of PMMA under static tension by presoaking in methanol; they interpreted this as being due to a soft surface layer formed by methanol absorption which has the effect of neutralizing the stress concentration of surface flaws. Our preliminary experiments also demonstrated the swollen surface layer to be softened to a great extent. *Figures 7–9* show the results of experiments conducted in methanol at room temperature using sheet specimens of PMMA of 1 mm thickness. Variations in the dynamic viscoelastic properties following methanol

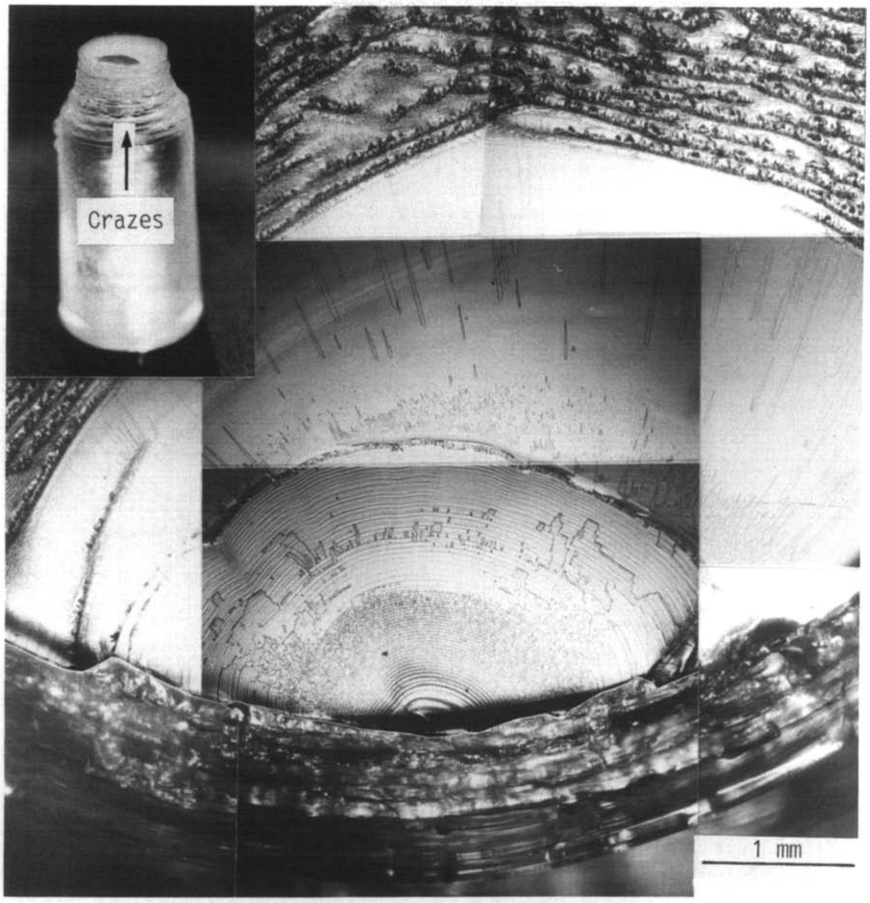

Figure 5 Appearance and fracture surface of the fatigue specimen presoaked in methanol for 24 h. $N_f = 3750480$

absorption are shown in *Figure 7*. These results[12] were obtained using a viscoelastic testing machine (Rheovibron DDV-III-EP, Orientec Co.) at a frequency of 11 Hz. The storage modulus, E', stays constant for about 5 h, then gradually decreases and finally stabilizes at about 30% or less of the initial value after 60–70 h. The energy loss, $\tan\delta$, conversely increases with methanol absorption. The minimum and the peak values of E' and $\tan\delta$ are nearly equal to those in air at T_g (about 115°C). Considering the weight gain measurements shown in *Figure 8*, in which the result for water is also presented for comparison, one supposes the penetrant fronts to have met after about 70 h immersion. *Figure 9* represents the influence of methanol absorption on the stress–strain relation of PMMA. These deformation curves were obtained from quasi-static tension tests carried out on an Instron type testing machine (Tensiron UTM-2.5TW, Orientec Co.) at a nominal strain rate of 12.5% min^{-1}. The specimens were tested after presoaking in methanol for various periods. As the swollen layer becomes thicker by presoaking for longer periods, the deformation mode changes completely from brittle to ductile. The shear yield stress in the swollen surface layer is estimated to be lowered to only 8% of that in air. It is clear from *Figures 7–9* that the surface layer involving a large quantity of methanol is greatly softened to give lower resistance to deformation. Fukahori and Andrews[13] investigated the relationship between the fracture surface roughness and the mechanical hysteresis (energy loss) of highly deformable polymers such as crosslinked elastomers and plasticized poly(vinyl chloride). They revealed that the high hysteresis offers a lower degree of roughness to fracture surface. The smooth fracture surface observed in the outer layer of our fatigue specimen presoaked for a long time seems to agree with their observation.

According to the interpretation of Campbell *et al.*[2] the crazing stress inevitably increases with increasing presoak time so as to activate the potential crazing sites, opposing the softening effect mentioned above. Our experimental results also appear to be consistent with their interpretation. It is difficult, however, to satisfactorily explain the overall features of our results by their mechanism alone, considering the great reduction of fatigue life for presoak times above 120 h. In addition, the observations of Campbell *et al.*[2] were restricted to within 6 h. The generation of the internal stresses characterizing case II diffusion should also be considered. The compressive stress induced in the swollen surface layer is expected to decrease the concentration of the tensile stress at the flaw tip, and in addition to suppress opening out of the flaw, as Warty *et al.* suggested[5].

Considering both Campbell's interpretation and the induced compressive stress in the surface layer may provide the following explanation represented schematically in *Figure 10*. The specimens which were not presoaked are severely crazed and cracked in methanol at very low stress or cycles of loading, although the exact mechanism remains to be elucidated (*Figure 10a*). Presoaking for comparatively short times reduces the tensile stress level near the flaw tip both by softening and

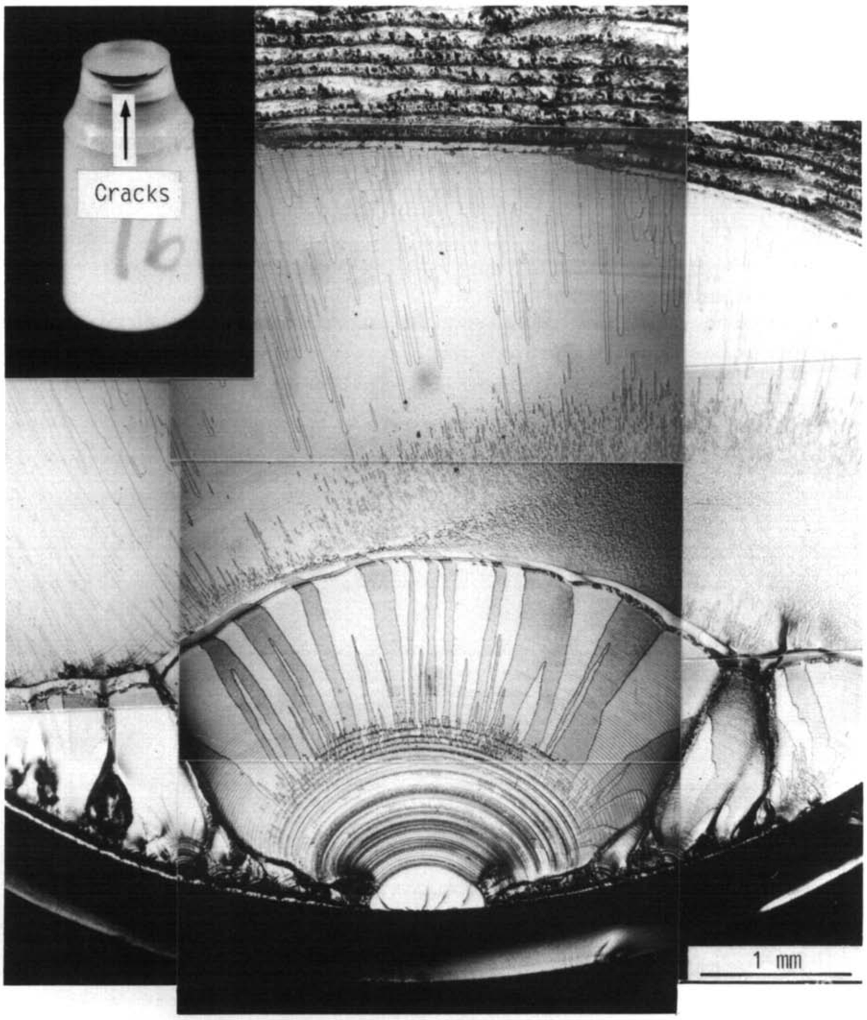

Figure 6 Appearance and fracture surface of the fatigue specimen presoaked in methanol for 120 h. $N_f = 22430$

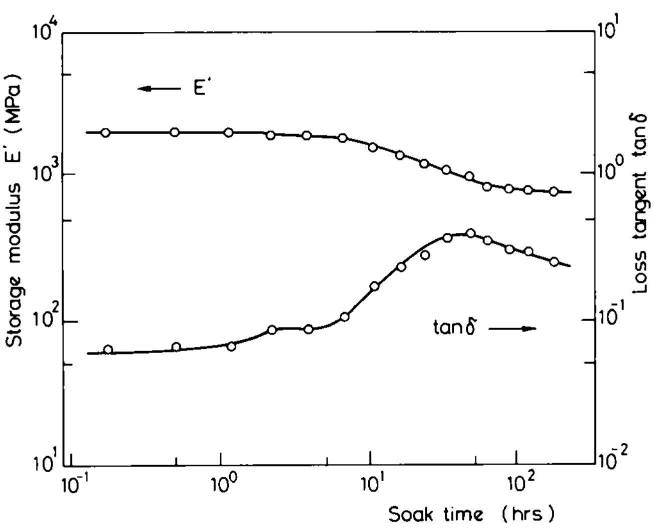

Figure 7 Variations in E' and $\tan\delta$ of PMMA sheet 1 mm thick measured at 11 Hz in methanol at room temperature

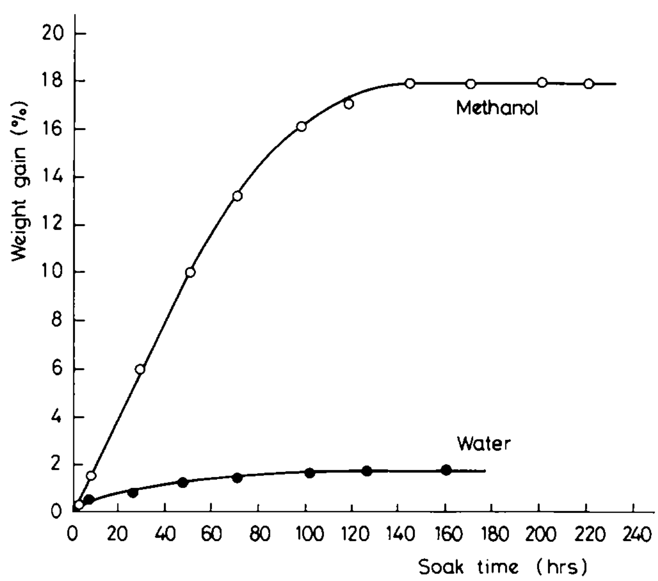

Figure 8 Absorption of methanol and water by PMMA sheet of 1 mm thickness at room temperature

by the induced compressive stress, and consequently enhances the torsional moment for crazing and prolongs the fatigue life. The nucleation and growth of many crazes entailing shear flow at their tips will also contribute to the fatigue life increase (*Figure 10b*). After presoaking for longer times the surface layer is well softened, shear flow is improved and as a result cracks may grow slowly following shear flow at their tips. Furthermore in this case the generation site of the internal compressive stress

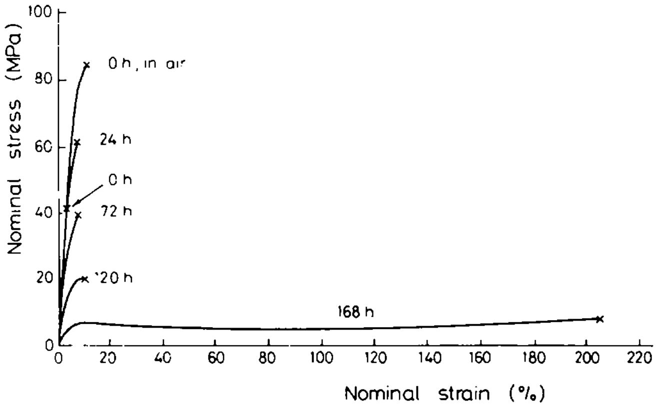

Figure 9 Nominal stress–strain curves of PMMA sheets of 1 mm thickness in methanol at room temperature for different presoak times in methanol: ×, fracture

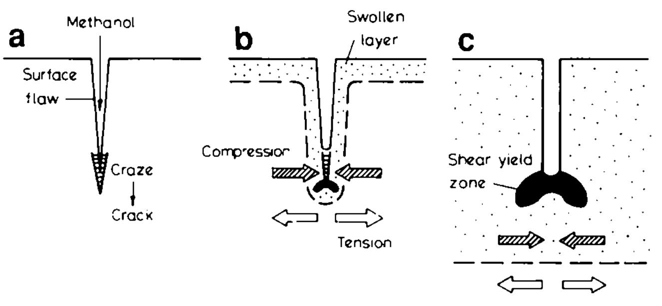

Figure 10 Models for environmental fracture following case II diffusion: (a) no presoaking; (b) presoaking for short times; (c) presoaking for long times

advances to a greater depth far from the surface flaws. Consequently the manner of deformation becomes more ductile, and the fatigue life increases to a lesser extent (*Figure 10c*).

In order to provide a more exact explanation, it will be necessary to evaluate the internal compressive and tensile stresses, and also to examine the possibility of shear flow or fracture occurring under these stresses near the boundary formed by case II diffusion.

CONCLUSIONS

The effects of case II diffusion on crazing and fatigue behaviours were investigated on PMMA in methanol. Although the precise mechanism remains to be explained, it is concluded that the case II diffusion of methanol greatly contributes to the strength of PMMA in methanol, particularly to the fatigue lifetime, and there exists an optimum presoak time to bring about the greatest effect. If the swollen surface layer is maintained stably, even under dry conditions, it will be available as a mechanism to toughen brittle polymers.

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