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Effect of preexisting crazes on the dynamic viscoelasticity of poly(methyl methacrylate)

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The effect of preexisting crazes on the storage modulus E' and the loss tangent tan δ was investigated by using two types of pre-crazed specimens of poly(methyl methacrylate) in which plastic deformation by crazing had proceeded to different degrees under a 1-butanol environment. The measurements were conducted both in air under a constant heating rate and in an environment of methanol at room temperature. In air no significant difference can be found between the viscoelastic properties of the pre-crazed and the uncrazed specimens, even when all the pre-crazes entirely heal up above T_g. In methanol two different trends are observed in response to the degree of pre-crazing. In a specimen which is damaged to some degree by crazes, a reduction in E' and an increase in tan δ followed by methanol absorption are suppressed in comparison with the uncrazed specimen. On the other hand, E' and tan δ of a specimen with heavy damage by crazes take almost the same values as those of an uncrazed specimen during exposure to methanol. These observations suggest that in some cases the preexisting crazes act as a rigid second phase to maintain the overall stiffness of the polymer against the plasticization effect of penetrants.

1. Introduction

A craze is known as a crack-shaped region of localized plastic deformation in solid polymers of which the microstructure consists of numerous elongated fibrils and voids. From this structural peculiarity the craze is expected to possess some mechanical properties differing from those of the bulk polymer.

Kambour and Kopp [1] investigated the stress–strain relation of a polycarbonate specimen with thick grown crazes, and educed the quasi-static properties of the craze matter (fibrils and voids) in comparison with those of the bulk polymer without crazes. According to them, the initial modulus of the craze matter is almost the same as that of the bulk polymer, but a remarkable strain hardening after yielding and a large hysteresis loop are characteristic of the craze matter. Lauterwasser and Kramer [2] showed more precisely this severe strain hardening of the craze matter in polystyrene by direct measurements from transmission electron micrographs. Recently Schirrer [3] investigated the dynamic mechanical behaviour of the craze matter in poly(methyl methacrylate) under cyclic loading at 11 Hz, and revealed that a craze generated at high temperature (70° C) is considerably stiffer than that generated at low temperature (−25° C).

These examples suggest that in some cases the craze matter behaves more rigidly than the bulk polymer. Thus a polymer including a number of crazes may be compared to a composite material consisting of ductile matrix and rigid second phase. Then the shape and size, microstructure and volume content of crazes will affect the mechanical properties of this material system. In the experiments described below, the effects of preexisting crazes on the dynamic viscoelasticity represented by the storage modulus and the loss tangent have been investigated on poly(methyl methacrylate) (PMMA) both in air under a constant heating rate and in a methanol environment at room temperature. The dynamic properties of craze matter are inferred from the results by comparing with the above-mentioned examples, particularly with that of Schirrer for PMMA craze.

2. Experimental procedure

The material used was commercially available PMMA sheet, 1 mm in thickness (Mitsubishi Rayon Co., Japan). It was cut into strips 40 mm long by 5 mm wide. Their cut sides were polished with No. 1000 abrasive paper. They then were annealed at 90° C for 2 h to remove residual stresses due to machining and slowly cooled to room temperature in a forced-air oven.

The specimens were pre-crazed under simple tension in an environment of 1-butanol at room temperature (about 26° C) by use of an Instron-type testing machine (Tensiron UTM2.5TW, Orientec Co., Japan) at a crosshead speed of 0.1 mm min^{-1}. 1-butanol was applied to the specimen surfaces through wetted cotton wool. The distance between sample jaws was set to 20 mm. By preliminary tests in several organic fluids, 1-butanol crazes in PMMA were regarded as most suitable for the present investigation with respect to the number of crazes per unit surface area (craze density) and their sizes (length). Two types of pre-crazed specimen were prepared which showed different degrees of plastic deformation by crazes. One is

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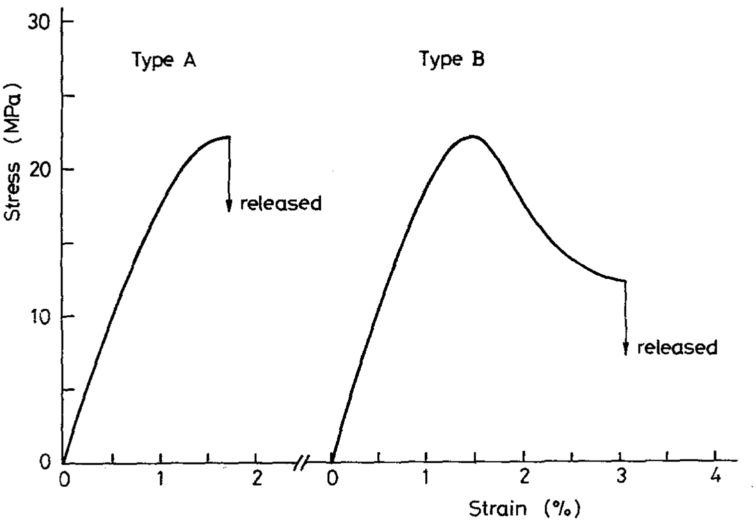

Figure 1 Stress–strain curves showing different degrees of craze yielding in 1-butanol at about 26° C.

a specimen which was quickly removed from the testing machine just after craze yielding (type A), and the other is that which was removed when the stress level was considerably lowered after craze yielding (type B).

Examples of stress–strain curves of these crazed specimens are shown in Fig. 1, in which for convenience the strain is given by dividing the sample elongation by the distance between the jaws (20 mm). Before the measurements of dynamic viscoelasticity, these crazed specimens were dried in forced air at room temperature for about 30 min to evaporate 1-butanol soaked into the crazes, and then their surfaces were photographed through an optical microscope. Fig. 2 shows the crazed surfaces of specimens A and B. It is observed that there is no significant difference in the number and length of crazes between the two specimens. This suggests that the large plastic deformation after craze yielding in specimen B is mainly effected by a thickening process of crazes.

The measurements of the storage modulus E' and the loss tangent tan δ, where δ denotes the phase difference between stress and strain, of the pre-crazed and the uncrazed specimens were carried out by means of a viscoelastic testing machine (Rheovibron DDV-III-EP, Orientec Co., Japan). They were measured at four frequencies of 110, 35, 11 and 3.5 Hz both in air heated at a constant rate of 1.0° C min^{-1} and in a methanol environment at room temperature, as a function of time. The system for measurements in methanol is shown in Fig. 3. Schematic illustrations of the sample jaws and liquid vessel constructed for the experiment are also given in the figure. Methanol was frequently supplied through a funnel during the measurements to keep the specimen immersed completely in it. The temperature of methanol was measured with a chromel–alumel (CA) thermocouple in the vicinity of the specimen, and was about 19° C during the tests. In the case of the measurements in air under a constant heating rate the sample jaws and liquid vessel are removed and then the specimen is completely covered with an adiabatic wall.

Besides the viscoelastic measurements the weight gain of the uncrazed specimen was measured in methanol at 22° C for about 1 week, and was compared with the changes in E' and tan δ measured in this environment.

3. Results and discussion

The dynamic viscoelasticity of the uncrazed PMMA measured in air at four kinds of frequencies is shown as a function of temperature in Fig. 4. As usual, the

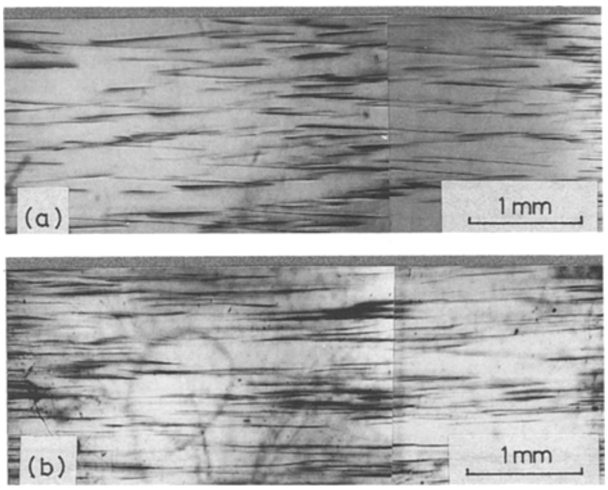

Figure 2 Optical micrographs of crazed specimen surfaces of (a) type A and (b) type B.

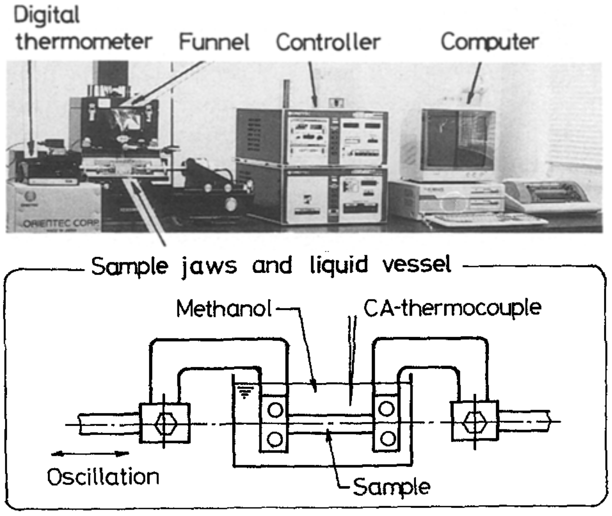

Figure 3 System for measurements of dynamic viscoelasticity in methanol.

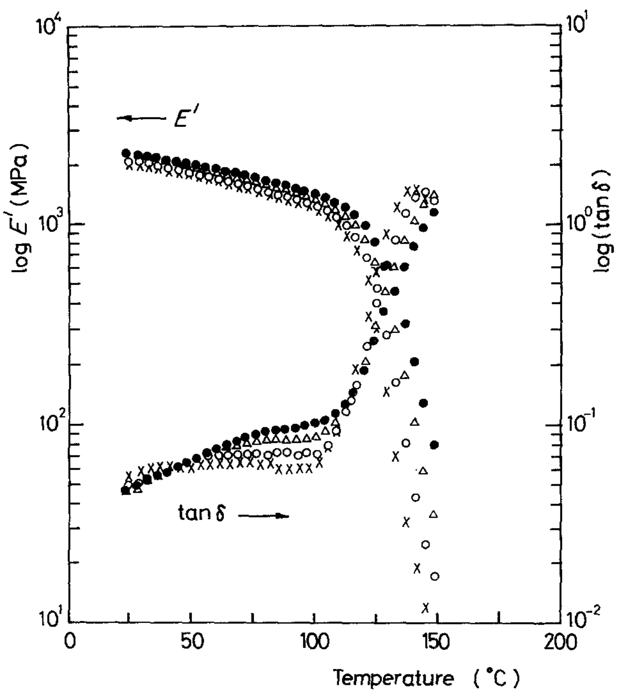

Figure 4 Temperature dependence of storage modulus E' and loss tangent tan δ of uncrazed specimen in air. (●) 110 Hz, (△) 35 Hz, (○) 11 Hz, (x) 3.5 Hz.

storage modulus E' decreases and the loss tangent tan δ increases with rising temperature. The glass transition temperature T_g can be determined as 115° C at 110 Hz from the features of abrupt decrease in E' and an increase in tan δ. T_g tends to shift to lower temperature as the applied frequency is decreased. The observations mentioned above were also entirely true of the pre-crazed specimens irrespective of the difference in the degree of damage by crazes, although after measurements at temperatures above T_g no crazes could ever be found in both the specimens A and B.

This phenomenon of craze healing has already been pointed out by several investigators. Spurr and Niegisch [4] suggested that heating above T_g triggers a contraction in the oriented craze matter and as a result reverts it back to the nearly random state of the bulk polymer. Subsequently, LeGrand [5] confirmed this contraction behaviour of crazes on polycarbonate (PC). Jud *et al.* [6] made compact tension tests using specimens of PMMA and styrene-acrylonitrile copolymer (SAN) in which a crack was previously healed by heating above T_g, and indicated that the fracture toughness increases to the original value with the process of crack healing; the crack healing is attributed to physical links between macromolecular coils across the crack surfaces produced by interdiffusion. Their result at once appears to provide an experimental foundation to the previous suggestion of Spurr and Niegisch on craze healing. As described above, however, no conspicuous variations in the viscoelastic properties accompanied by craze healing could be detected in our pre-crazed specimens.

Figure 5 shows the variations in E' and tan δ of the uncrazed specimen which were measured in a methanol environment at room temperature at four frequencies. The value of E' keeps constant at first for about 5 h, and then gradually decreases and settles down to the minimum value after about 60 h. Conversely tan δ increases with increasing time and attains a peak value at the corresponding time. These variations in E' and tan δ with time observed in methanol resemble those in air heated at a constant rate shown in Fig. 4. Comparison between these features suggests a plasticization effect of absorbed methanol on the polymer.

The weight gain of the uncrazed specimen immersed in methanol is shown in Fig. 6. After an induction time of about 5 h the weight gain begins to increase at an approximately constant rate, and then after about 70 h the rate of weight increase is gradually reduced. From a comparison with Fig. 5, it is noted that there exists a rough correspondence between the periods when the trends of E' or tan δ and the weight gain begin to vary. It has already been indicated [7] that a large quantity of methanol can diffuse into PMMA with characteristics of (i) a sharp boundary which separates an inner glassy core from an outer swollen layer advancing at a constant velocity, and (ii) the swollen gel which is almost in equilibrium behind the advancing front of penetration. A diffusion process like this is called Case II diffusion [7, 8]. As Case II

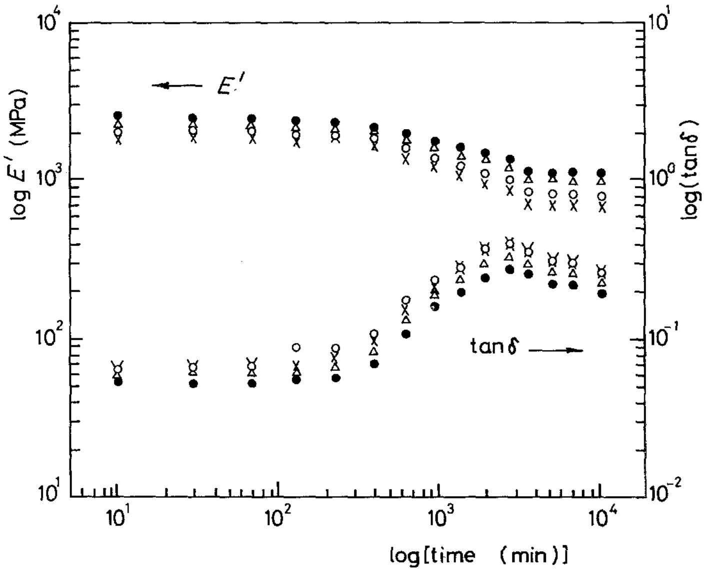

Figure 5 Variations in storage modulus E' and loss tangent tan δ of uncrazed specimen in methanol at about 19° C. (●) 110 Hz, (△) 35 Hz, (○) 11 Hz, (x) 3.5 Hz.

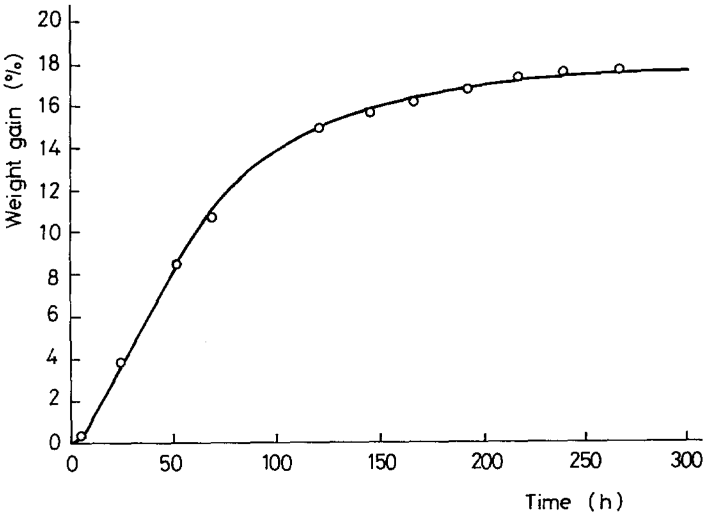

Figure 6 Weight gain against time for uncrazed specimen immersed in methanol at 22° C.

diffusion takes place, the weight gain of the specimen is expected to vary proportionally to the immersing time, contradicting Fick's laws, and then attain an upper limiting value corresponding to the equilibrium state of the whole specimen. The present result shown in the figure also appears to represent this trend. As a consequence, Fig. 5 indicates variations in the viscoelastic properties of PMMA following by Case II diffusion of methanol.

In addition, a comparison, between Figs 4, 5 and 6 reveal that the minimum value of E' and the peak value of tan δ for the immersing time of about 60 h, when the increase rate of weight gain begins to be reduced, are nearly equal to those in air at about 115° C, i.e. T_g. Thus it is supposed that after immersion for 60 to 70 h the outer swollen layer grows sufficiently thick and it is in a rubbery state, and conversely the inner glassy core becomes thinner and no longer contributes to the mechanical properties of the whole specimen.

To these phenomena, he provided an explanation that re-entanglement (welding) occurs between craze fibrils during the relaxation process and when the craze is produced at higher temperature. This explanation seems to have substantially the same content as that of Jud *et al.* [6] for crack healing in air above T_g and is thus also consistent with the suggestion of Spurr and Niegisch [4] on craze healing mechanism. Although the phenomenon of craze healing is not always evident in our specimen A, Schirrer's explanation may also be applicable to the inhibitory effect of preexisting crazes on the stiffness reduction of PMMA during methanol absorption, because the T_g of a swollen surface layer with preexisting crazes is supposed to be lowered near room temperature.

In Fig. 9 for specimen B in which considerable plastic deformation was allowed to continue after craze yielding, in opposition to the trends of specimen A shown in Fig. 7 the ratio of E' of the pre-crazed specimen to that of the uncrazed specimen is slightly reduced below 1.0 under long-time immersion. The ratio of tan δ maintains a constant value of 1.0 during the test except for a broad peak at about 300 min.

Fig. 10 shows an optical micrograph of the specimen surface after measurements in methanol. The surface is swollen to a great extent, and crazes are so distorted as to be almost indistinguishable from each other. The features clearly indicate that a large amount of methanol was absorbed in the specimen not only through the sound surface but also through the pre-

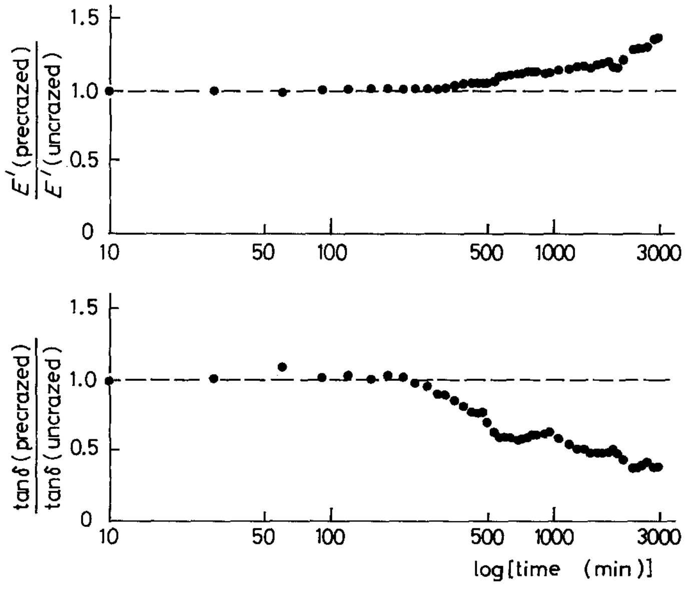

Figure 7 Variations in ratios of storage modulus E' and loss tangent tan δ of pre-crazed specimen of type A to those of uncrazed one measured in methanol at 110 Hz.

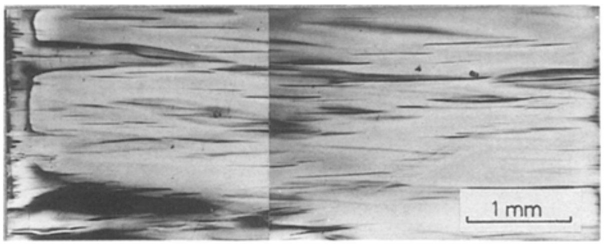

Figure 8 Optical micrograph of pre-crazed specimen surface of type A after measurements in methanol.

existing crazes. As already shown in Fig. 2, crazes in specimen B are thicker than those in specimen A. According to Kramer [10], two distinct mechanisms are possible for craze thickening. One is a surface drawing mechanism in which new fibrils are drawn from the surrounding bulk polymer at the craze/bulk polymer interface, and the other is a fibril creep mechanism in which the existing fibrils are further elongated plastically.

Next, the effects of preexisting crazes on the dynamic viscoelasticity under the environment of methanol are examined. The ratios of E' and $\tan\delta$ of the pre-crazed specimens at a frequency of 110 Hz to those of the uncrazed specimen given in Fig. 6 are plotted against the immersing time in Figs 7 and 9. In Fig. 7 for specimen A from which the applied load was removed just after craze yielding, it should be noted that in comparison with the uncrazed specimen E' and $\tan\delta$ of the pre-crazed specimen are raised and conversely lowered, respectively, as the immersing time increases. This result, broadly speaking, means that the stiffness reduction of the whole specimen accompanying methanol absorption is suppressed in the specimen pre-crazed to some degree, compared with the uncrazed specimen. As mentioned already, the craze matter is characterized by severe strain hardening. Strain hardening will make the craze matter more stable and resistant to solvent penetration than the bulk polymer in which the macromolecular chains are in a random arrangement. Thus the preexisting crazes are expected to impede the stiffness reduction of the whole specimen caused by solvent absorption.

An optical micrograph of the pre-crazed specimen A taken after viscoelastic measurements in methanol is shown in Fig. 8. Before taking the photograph, the specimen surface was softly wiped with tissue paper and then dried in air. Comparison of this picture with that in Fig. 2 taken before the measurements indicates that during the immersion in methanol the number and the length of crazes apparently decrease and the fringe of each craze becomes obscurer. These changes in craze appearance may be caused by two distinct mechanisms of (i) craze healing and (ii) similarity between the refractive indices of the craze matter and the surrounding polymer following methanol absorption.

With regard to the former case Spurr and Niegisch [4] have already pointed this out in their observations on PMMA, polystyrene (PS) and PC in an atmosphere of chloroform vapour at room temperature. According to them, although craze healing behaviour in such a solvent is not always as rapid or as complete as that in air at elevated temperature above T_g, the healing mechanism is still suggested to be the contraction of the oriented craze matter through the T_g reduction induced by the dissolved solvent. On the other hand, Kefalas and Argon [9] recently observed the phenomenon corresponding to the latter case for crazes of PS wetted with water. In the present result, however, since the photograph was taken after drying the crazed surface, the latter mechanism seems to make only a slight contribution.

In his investigation on the dynamic mechanical behaviour of the craze matter of PMMA in air Schirrer [3] revealed that a craze produced at 70° C is ten times stiffer than a craze produced at −25° C, and a relaxed craze is also stiffer than a non-relaxed one.

It has been observed that air crazes are thickened by the former mechanism to give a microstructure consisting of a dense fibril network, while the latter mechanism is appropriate to environmental crazes and makes their structure have a lower fibril volume fraction. Thus, in specimen B which was considerably deformed after craze yielding, it is inferred that craze fibrils are thinner and ruptured in places, and further-

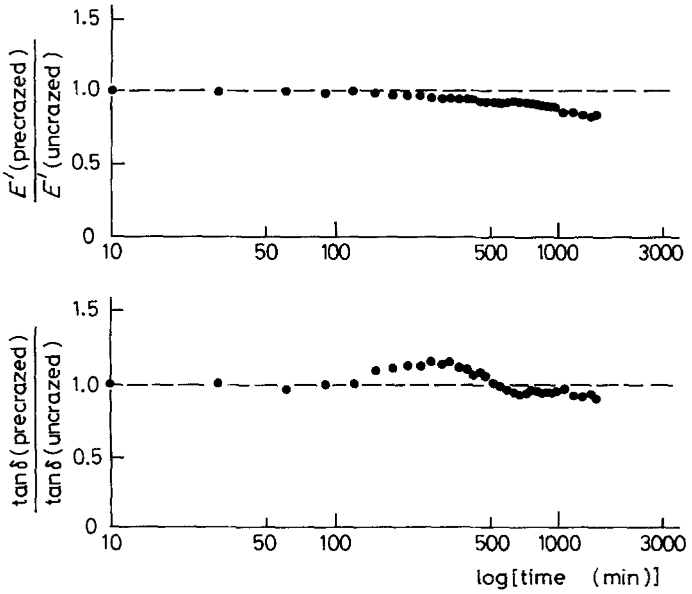

Figure 9 Variations in ratios of storage modulus E' and loss tangent $\tan\delta$ of pre-crazed specimen of type B to those of uncrazed one measured in methanol at 110 Hz.

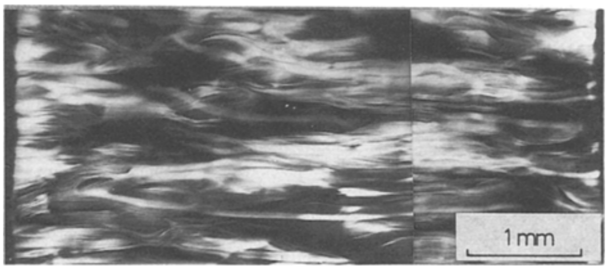

Figure 10 Optical micrograph of pre-crazed specimen surface of type B after measurements in methanol.

more that this craze microstructure with a higher void content allows a large amount of environmental liquid to penetrate into the polymer at the craze surface. As a result the effect of preexisting crazes to suppress the stiffness reduction of the whole specimen accompanied by liquid penetration is no longer expected, and specimen B is swollen to a great extent.

The above-mentioned results at 110 Hz hold true at other frequencies of 35, 11 and 3.5 Hz.

From the above discussion, it may be concluded that preexisting crazes, which cause damage to a certain extent to the specimen, act as a rigid second phase to maintain the overall stiffness against swelling. However, this action will at the same time give some brittleness to the crazes, and will also affect the fatigue failure under cyclic loading in liquid environments.

4. Concluding remarks

Dynamic viscoelastic measurements have been made both in air under a constant heating rate and in an environment of methanol at room temperature using two types of pre-crazed specimens of PMMA in which plastic deformation by crazing had proceeded to different degrees in 1-butanol.

In air no significant difference can be found in the storage modulus E' and the loss tangent tan δ between the precrazed and the uncrazed specimens, although craze healing is clearly observed during heating up to above T_g. In methanol two distinct trends in the viscoelastic properties of the precrazed specimen are observed in response to the degree of precrazing. In the specimen which was quickly unloaded just after craze yielding, a reduction in E' and an increase in tan δ followed by methanol absorption are suppressed in comparison with the uncrazed specimen. On the other hand, in the specimen which was unloaded after a considerable plastic deformation was allowed to continue after craze yielding, E' becomes slightly lower than that of the uncrazed specimen for long-time immersion, and tan δ holds approximately the same value as that of the uncrazed specimen except for a temporary increase.

From these observations and the comparison between the optical micrographs taken before and after the measurements in methanol it is supposed that in some cases the preexisting crazes act as a rigid second phase in polymers by their strain-hardened fibrils supressing the stiffness reduction of the whole specimen following by liquid penetration, but crazes grown thicker by the fibril creep mechanism allow a large quantity of liquid to penetrate into the specimen through their structure with a higher void content, and as a result facilitate swelling of the specimen.

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