Fracture mechanisms of poly(methyl methacrylate) under static torsion in alcohol environments

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Static torsion tests of poly(methyl methacrylate) were conducted in several alcohol environments at room temperature. The critical torsional stress for crazing and/or cracking increased with increasing molar volume of alcohol, and was not correlated with the solubility parameter, nor with equilibrium solubility as reported in previous results on *n*-alkanes. Crazing stresses in alcohols were generally lower than those in alkanes. According to Fourier transform–infrared microscopy of the surface scratch made in several environments, both in ethanol and in 1-butanol, some absorptions were detected at 3450–3650 cm^{-1}, probably due to the hydroxyl group of these alcohols caught by hydrogen bonding to oxygen of the carbonyl group in the side chain, whereas in other environments (1-octanol, *n*-hexane, and air) there were no absorptions in this region of wave number. These results suggest that at a flaw tip strained under stress, penetrating alcohol molecules are chemically adsorbed in a cluster, which breaks a weak bond (e.g. dipole interaction) between the polymer chains and, as a result, facilitates craze formation and breakdown leading to brittle fracture.

1. Introduction

The fracture of glassy polymers is known to be preceded by craze development, which is facilitated in organic liquids environments [1, 2]. The effects of environmental liquids on crazing have been extensively studied, with particular regard to the solubility of the liquid in the polymer [3–7]. A previous investigation [8], however, revealed that the crazing stress in poly(methyl methacrylate) (PMMA) in *n*-alkanes under static torsion cannot be correlated with either the solubility parameter or the equilibrium solubility predicted from the solution theory [9]. It was also shown that the crazing stress is lowered with decreasing molar volume of *n*-alkanes and with increasing loading time, and it was suggested that the time-dependent crazing process is mainly governed by the absorption rate, rather than the solubility of the environmental liquid in the polymer.

In addition to the plasticization effect, depending on the quantity of liquid absorbed under the mechanisms of diffusion or solution, chemical effects, i.e., interactions between the penetrating liquid molecule and the macromolecule, may also be considered. Several investigators have already pointed out the importance of the formation or disruption of hydrogen bonding by the penetrant in the fracture process. Vincent and Raha [5] introduced the hydrogen-bonding parameter into the arrangement of the critical crazing strain measured for PMMA, poly(vinyl chloride), and polysulphone in a wide variety of liquid environments, in order to make the above solubility parameter correlation more comprehensive. According to their two-parameter representation, using both the solubility parameter and the hydrogen-bonding parameter, the liquids are adequately classified to act as solvents, cracking agents, low-strain crazing agents, or high-strain crazing agents for the polymer. Their arrangement, eventually, may be interpreted to explain the effect of hydrogen bonding on crazing and/or cracking from a viewpoint of plasticization under dissolution of the environmental liquid into the polymer. Therefore, in liquids with the same value of hydrogen-bonding parameter, crazing or cracking behaviour is expected to be dominated solely by the solubility parameters of the liquids. However, this expectation is inconsistent with previous results in *n*-alkanes (no hydrogen-bonded liquid), as mentioned above, and with those obtained in alcohols for PMMA under diametral compression [10] and cyclic tension [11]. Thus more direct information on molecular interactions is required to account for the behaviour of environmental fracture. Dunn and Sansom [12] observed the cracking behaviour of biaxially tensed polyamide (PA, nylon 6) films in various inorganic salts. Analyses using infrared and nuclear magnetic resonance (NMR) techniques demonstrated that, under tensile stress, these liquids are linked to the carbonyl oxygen atom of the amide group through complex formation or hydrogen bonding and, as a result, disrupt inter-amide group hydrogen bonding, leading to rapid crack initiation and growth. Subsequently, in the same environments, the simple tensile measurements, the

dynamic viscoelastic measurements, thermal analysis differential scanning calorimetry, and the fracture surface analysis using energy-dispersive X-rays, were performed for nylon 6 and 6,6 to obtain a wider understanding of the fracture mechanism [13, 14].

Similar "mechano-chemical" studies for elucidating the mechanisms of environmental fracture have been made on silica glass exposed to water [15, 16]. In this case, an Si–O–Si bond at the strained crack tip is ruptured to produce a pair of silanol (Si–OH) groups from the adsorbed water, which cleaves to form and disrupt hydrogen bonding.

The present investigation aimed to elucidate the mechanisms of environmental crazing and cracking in PMMA from the mechano-chemical viewpoint. In the experiments described below, the critical crazing stresses in PMMA immersed in alcohols were measured under static torsion. Fourier transform–infrared microscopy of the surface scratch produced in several environments including alcohols was also conducted to obtain additional results under torsion at a molecular level. The present results have been compared with the previous ones [8] in n-alkanes, and examined with reference to the explanation of environmental fracture mentioned above.

2. Experimental procedure

The material used was commercially available PMMA rod, 15 mm diameter (Mitsubishi Rayon Co.). Solid cylindrical specimens with a gauge length of 20 mm were machined from the rods. Detailed dimensions of the specimen were reported previously [8]. The surface of the gauge 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 static torsion tests were performed using an apparatus of our own making [8] in five kinds of alcohols, i.e. methanol, ethanol, 1-butanol, 2-ethyl-1-butanol, and 1-octanol. Their basic properties are given in Table I [5, 17, 18]. For comparison, the properties of n-alkanes used in the previous investigation are also listed. All these reagents are considered to have perfect wettability with the surface of the PMMA specimen because their surface tension is lower than the critical one of PMMA, 39 mN m^{-1} [19]. Just after the specimen was completely immersed in each re-

agent in a vessel, a constant torsional moment was applied for 20 min by means of a pulley and dead-weight loading system. The gauge surface of the specimen was observed using an optical microscope at a magnification of × 100 after unloading and removal from the apparatus. In alcohol environments, the specimens generally tended to fracture in a brittle manner, followed by only a few cracks, in contrast with the previous cases in n-alkanes in which many small crazes were observed. The critical torsional moment required for cracking or crazing was determined as the middle point between the moment levels of cracking and no cracking. All the alcohol were tested at room temperature (21 ± 1 °C).

The infrared absorbance spectra of the surface scratch were measured using Fourier transform–infrared spectroscopy (FT–IR) with a microscope attachment (FT–IR) 8900μ, Japan Spectroscopic Co.) following a similar analysis for silica glass indented in water [20]. The rectangular specimens of PMMA were cut from a sheet 1 mm thick (Mitsubishi Rayon Co.), and their surfaces were scratched by hand using a knife in ethanol, 1-butanol, 1-octanol, n-hexane, and air. After drying in vacuum for 28 h at room temperature, a square region of 30 × 30 μm^2 at the bottom of each scratch was analysed under the reflection mode of infrared rays. 300 scans were conducted.

The weight gains were measured using the rectangular specimens of PMMA in order to assess the rate of absorption in the above five alcohols at 50 °C. The specimens, 40 mm × 5 mm × 1 mm in size, were cut from the same sheet as that used for the FT–IR measurements, and then also annealed at 90 °C for 2 h. They were immersed in the test alcohols, the temperature of which was maintained in a oil bath, and periodically pulled out for weighing with an electronic balance. After weighing, the specimens were immediately returned to the former state.

The surface scratches and the fracture surfaces obtained in the above environments were observed in a scanning electron microscope (SEM) with a field emission gun (Hitachi, S-4000). Before observation in the SEM, the specimen surfaces were sputter-coated with a thin layer of gold.

3. Results and discussion

In Fig. 1 the critical torsional stresses for cracking or crazing are plotted against the molar volume of the

TABLE I Physical constants for alcohols and n-alkanes used

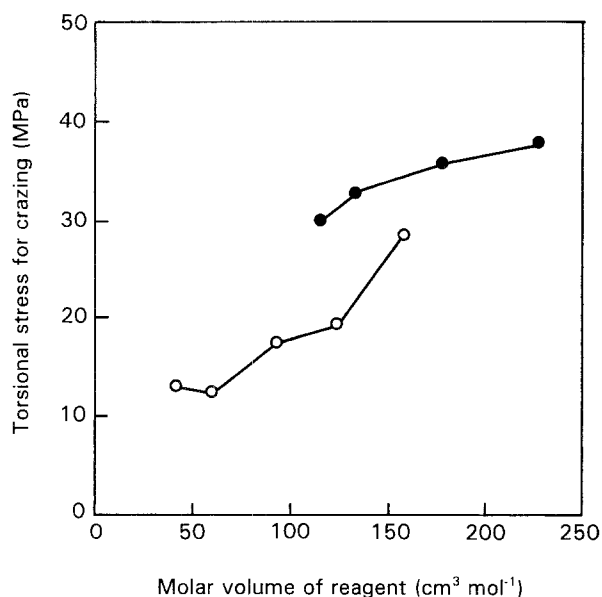|	Molar volume (cm^3 mol^{-1})	Viscosity (mPa s, 20 °C)	Surface tension (mN m^{-1}, 20 °C)	Solubility parameter ((MJ m^{-3})$^{1/2}$)	Hydrogen-bonding parameter
Methanol	40.7	0.59	22.55	29.7	19.8
Ethanol	58.5	1.17	22.27	26.0	17.7
1-Butanol	91.5	2.95	24.60	23.3	18.0
2-Ethyl-1-butanol	123.2	5.63	28.00	21.5	18.7
1-Octanol	157.7	8.93	26.06	21.1	18.7
n-Pentane	116.2	0.23	15.50	14.4	0
n-Hexane	131.6	0.31	17.90	14.9	0
n-Nonane	178.6	0.72	22.92	15.6	0
n-Dodecane	228.6	1.51	25.44	16.2	0

Figure 1 Plot of critical torsional stress for crazing versus molar volume of the reagent in (O) alcohols, and (●) n-alkanes.

environmental reagent. In addition to the present data in alcohols, previous results in n-alkanes [8] are presented for comparison. In both categories of reagent, the cracking or crazing stress generally increases with increasing molar volume of reagent. However, the lowest cracking or crazing stress is not observed in methanol but in ethanol, opposing this trend. Quite similar results were obtained for the fracture loads of PMMA cylindrical specimens under diametral compression in alcohols [10]. One possible explanation is that, even for a short period of loading, the softening and the internal compressive stress are brought about in the surface thin layer by case II diffusion of methanol [21], and that they lower the tensile stress level at the bottom of a surface flaw and, as a result, raise the applied stress required for cracking and/or crazing. More systematic investigations on the effects of case II diffusion on the fracture behaviour of PMMA in methanol have already been reported [22]. The general trend of the critical torsional stress against the molar volume of reagent shown in the figure supposes that cracking and/or crazing are dominated by the diffusion process of the environmental reagent. This problem will be discussed later in detail.

Scanning electron micrographs of the fracture surface obtained in methanol are shown in Fig. 2. The fracture surface was in the direction normal to the maximum principal stress to form a spiral. Despite being under static loading, as shown in Fig. 2a, concentric circular bands were observed to spread from the fracture source, as in fatigue fracture under cyclic loading [11]. Fig. 2b shows a magnified view of a starting region in the fourth band, where well-grown patch marks are clearly seen. It may be concluded that even in methanol, which apparently causes only the crack leading to brittle general fracture, crazes are formed first; then the crack nucleated in the craze advances along the craze–matrix interface, and these processes are repeated. Thus Fig. 1 is interpreted to indicate the critical stresses for crazing.
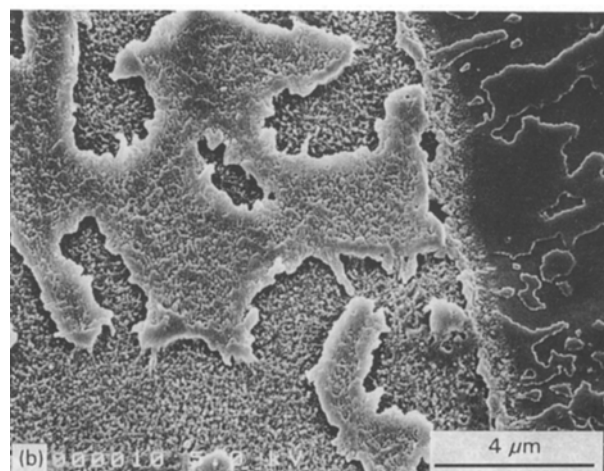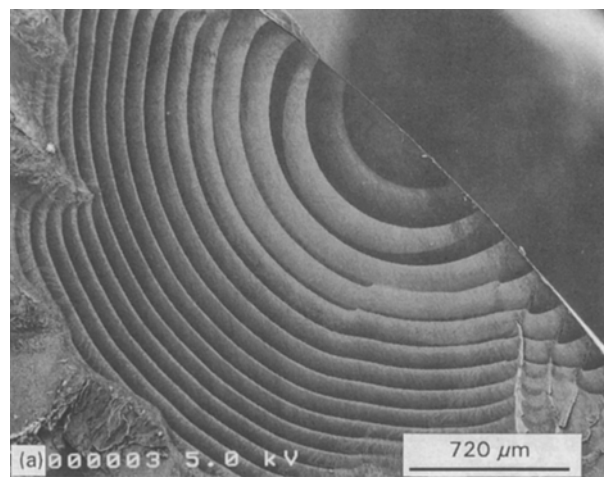

Figure 2 Scanning electron micrographs of the fracture surface in methanol: (a) a region near the fracture source, and (b) a magnified view of the starting region in the fourth circular band.

In Fig. 3 the critical stresses are plotted against the solubility parameter of the reagents. The solubility parameter of PMMA is in the range represented by the hatched lines. The trend of the critical crazing stress is completely opposed to those of the critical crazing strain measured for various combinations of polymer and reagent under fixed deflection [3–6]. In alcohol environments, the effect of hydrogen bonding should also be considered [5]. The hydrogen-bonding parameters of five test alcohols, however, show almost the same value, as presented in Table I. Therefore, the order of the critical crazing stress seems to be uninfluenced by the hydrogen bonding of these alcohols, although lower crazing stresses in alcohols than in n-alkanes are probably due to hydrogen bonding, as discussed later. Thus no reasonable explanation may be provided for the plot in Fig. 3.

Fig. 4 presents the results of weight-gain measurements in five alcohols. The absorption rate, which is defined here as an initial slope of each curve, clearly increases with decreasing molar volume of alcohol. Andrews et al. [23] have already investigated the behaviour of diffusion and solution of several alcohols in PMMA over a wide range of temperature. They revealed that the absorption rate of alcohol with smaller volume is greater than that with a larger one,
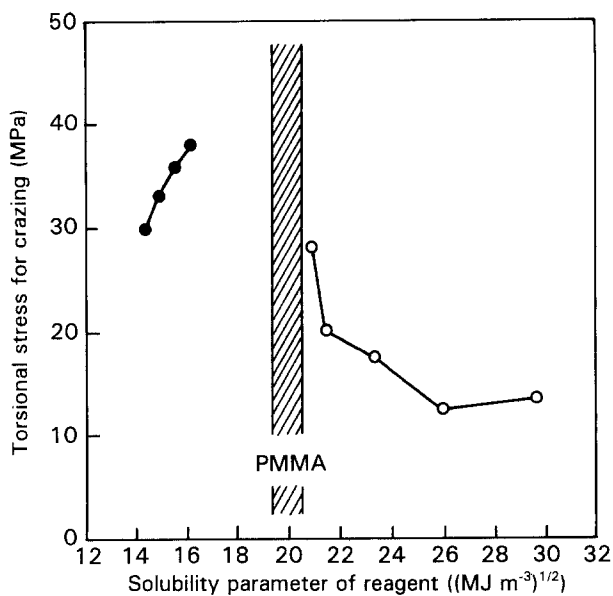
Figure 3 Relation of torsional crazing stress to solubility parameter of the reagent in (○) alcohols, and (●) n-alkanes.
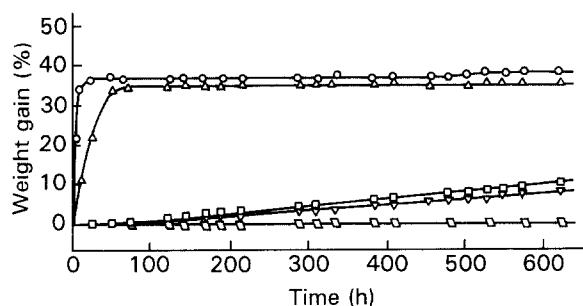

Figure 4 Absorption of various alcohols by a PMMA sheet, 1 mm thick, at 50 °C. (○) Methanol, (△) ethanol, (□) 1-butanol, (▽) 2-ethyl-1-butanol, (◇) 1-octanol.

and, in addition, that the equilibrium solubility is affected by the solubility parameter in accordance with the solution theory, but only a slight effect is observed. Although the equilibrium solubilities cannot be compared with their results because our measurements are restricted in time, the order of the absorption rate is clearly identical to them. Supposing this relation to be maintained at lower temperature, a good correlation may be obtained between the critical crazing stress and the absorption rate of the reagent.

From the above discussions, it is concluded that the crazing processes of PMMA in alcohols and probably also in n-alkanes, are dominated by the absorption rate rather than the equilibrium solubility of the reagent, as has been previously pointed out [8, 11].

Next, why the critical crazing stresses were lowered in alcohols compared with in n-alkanes, was examined. Fig. 5 shows the infrared absorbance spectra of the surface scratches produced in several environments. Both in ethanol and in 1-butanol, clear absorption bands are observed in the regions of 2870–3000 cm^{-1} and 3450–3650 cm^{-1}. The former and the latter absorption bands are supposed to arise from the methyl and the hydroxyl groups, respectively
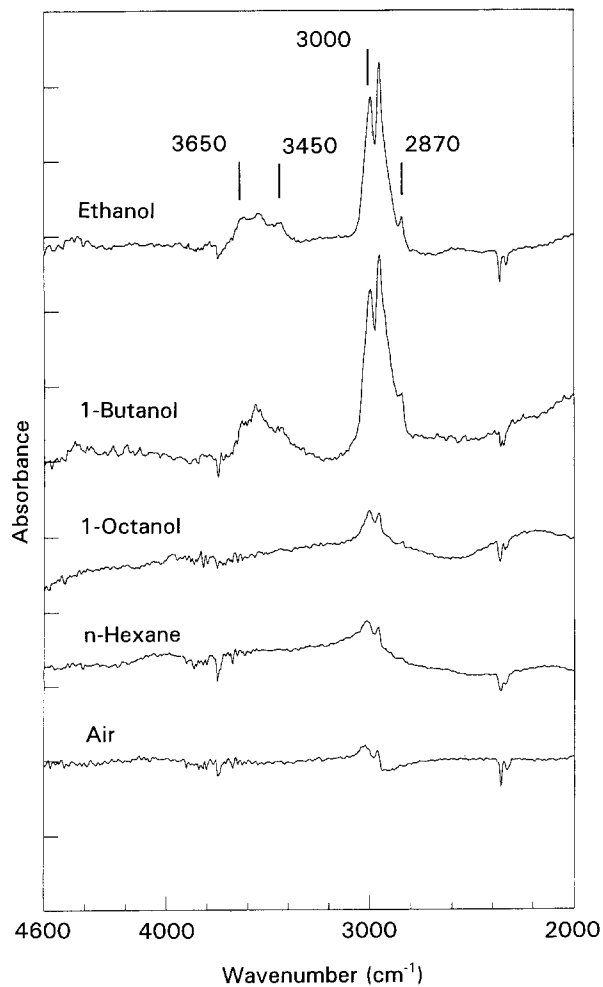

Figure 5 Infrared absorbance spectra of a surface scratch in a PMMA sheet produced in several environments.

[24]. The latter band, ranging to a low wave number of 3450 cm^{-1}, implies the effect of intermolecular hydrogen bonding. In 1-octanol, the former absorption can be weakly seen, but the latter is not observed. For the scratches made in n-hexane and in air, only weak peaks may be found at 2960 and 3000 cm^{-1}. These signals are the same in wave number and intensity as those for a flat surface of PMMA measured in air under the reflection mode. In this connection, the spectra obtained for the flat region surrounding the scratch are also the same, irrespective of environments. From the above observations of the infrared spectra, it is speculated that the molecules of ethanol and 1-butanol are chemically adsorbed on to the virgin surfaces generated during the scratching process in these alcohols.

The scanning electron micrographs of the bottoms of surface scratches obtained in ethanol and in air are shown in Fig. 6, where the direction of scratching is always from left to right, as denoted by arrows. It is of interest that in both the environments the scaly marks are observed to line up in a direction opposite to the scratching direction. These marks are probably produced by a mechanism similar to that in cutting of brittle materials such as ceramics, in which, as an elemental process, a crack unstably extends downwards from the region near the tool tip, being governed by the maximum principal stress [25]. Magnifying
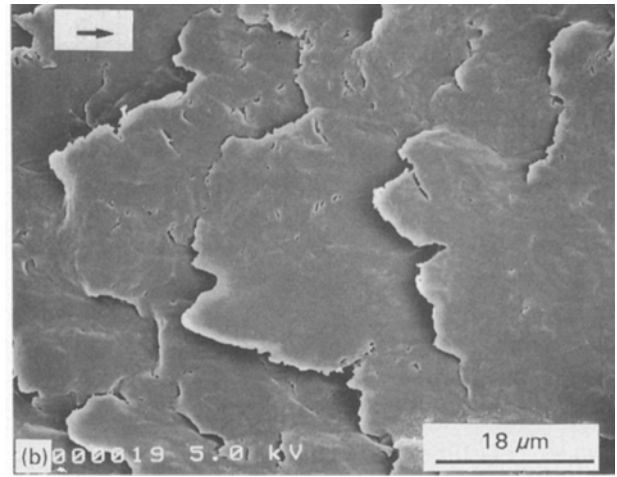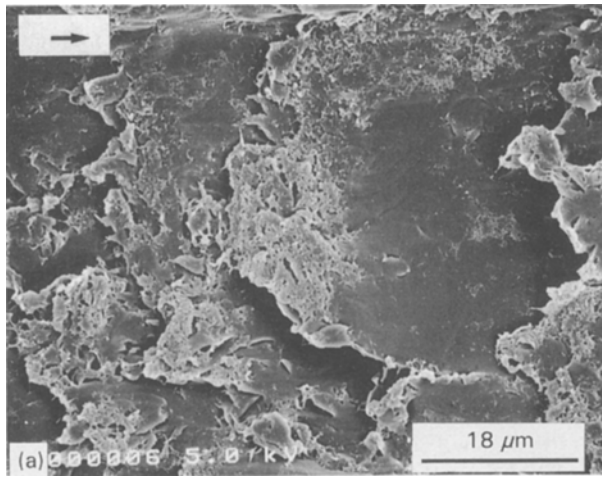
Figure 6 Scanning electron micrographs of the bottom of a surface scratch in (a) ethanol and (b) air. Arrows denote the scratching direction.
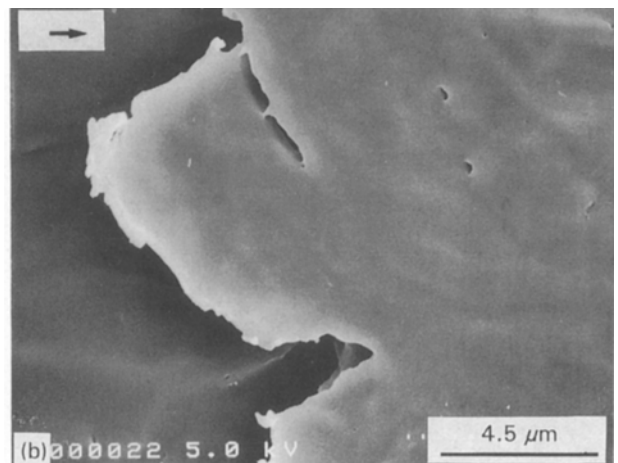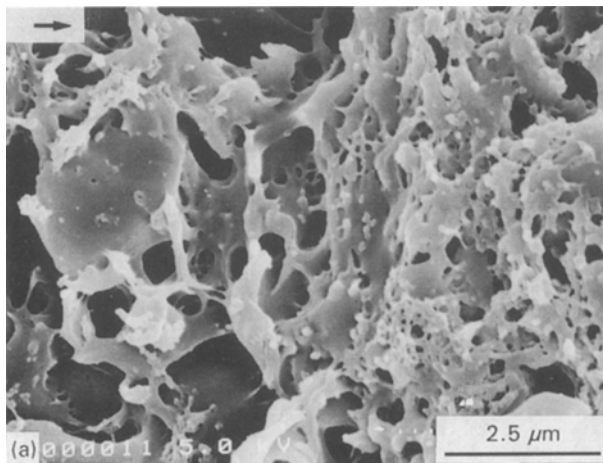

Figure 7 Magnified views of the edge region of a scaly mark in (a) ethanol and (b) air. Arrows denote the scratching direction.

the edge regions of the scaly marks reveals that in ethanol the fibrous and voided structure of the craze is highly developed, in contrast with the case in air, as shown in Fig. 7. It is thus suggested that ethanol penetrating into a localized region near the tool tip, which is strained by the maximum principal stress under the above mechanism, facilitates plasticization, leading to craze formation and breakdown during the scratching process.

Based on the above discussions, the lower crazing stresses measured in alcohols presented in Fig. 1 may be interpreted as the effect of diffusion and adsorption of alcohols as follows. At the bottom of a surface flaw, where both the tensile and the deviatoric components of applied stress (the product of which is required to attain a critical value for craze initiation [26]) are concentrated, the alcohol molecules with smaller volume can easily penetrate, and are chemically adsorbed to the polymer chains. The chemical adsorption may take place between the hydroxyl hydrogen atom of alcohol and the carbonyl oxygen atom of the ester group of the PMMA side chain through hydrogen bonding. At this time the alcohol molecules break a weak bond as dipole interaction between the polymer
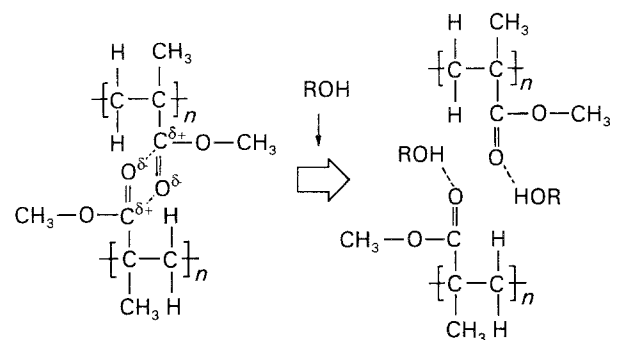

Figure 8 Representation of a proposed mechanism of chemical adsorption of alcohol on to PMMA during fracture.

chains. This situation is represented schematically in Fig. 8, for the analogous cases of nylon 6 and 6,6 fractured in various inorganic salts [12–14], and for silica glass fractured in water [15, 16]. In addition, the alcohol molecules are in a cluster, which may act as a filler particle leading to stress concentration, rather than as a plasticizer, and thus lowers the applied stress for crazing, as was pointed out by Shen *et al.* in their

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results on the tensile properties of PMMA in water environment [27].

4. Conclusions

The effects of environmental alcohol on crazing in PMMA were investigated under static torsion at room temperature. As has been previously observed, the crazing stresses increase with increasing molar volume of alcohol, and are not correlated with the solubility parameter. Their order corresponds to the rate of absorption in the test alcohols measured at 50 °C. From these results, it may be concluded that crazing in alcohols and also in n-alkanes is the effect of localized plasticization facilitated by the diffusion, not by the solution, of the reagent.

The FT–IR analyses through a microscope of the surface scratches on the PMMA sheets produced in several environments, suggest that the chemical adsorption of the alcohol can take place on to the polymer chains by hydrogen bonding in a stressed region. It is supposed that the alcohol molecules penetrating the polymer are chemically adsorbed by hydrogen bonding, with breaking of the weak bonds between the polymer chains, and in addition are in a cluster which act as a filler particle causing stress concentration, rather than as a plasticizer.

In alcohol environments, the chemical adsorption of the alcohol on to PMMA under the action of stress may weaken the interaction between the polymer chains to promote their mobility, leading to craze nucleation accompanied by the plasticization effect, which is substantial in reagents with no hydrogen bonds, such as n-alkanes.

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