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Environmental stress cracking behaviour of urethane methacrylate based resins

Part I *Environmental crazing and cracking under bending conditions*

JIAJUN LI, J. C. ARNOLD, D. H. ISAAC
Department of Materials Engineering, University of Wales Swansea, Swansea SA2 8PP, UK

Two kinds of cross-linked urethane methacrylate resins have been investigated using three-point bend tests to determine their environmental stress cracking (ESC) behaviour in a range of liquids (water, sodium hydroxide, ethylene glycol, acetonitrile, acetic acid, acetone, tetrahydrofuran, toluene, 3,5,5-trimethylhexanol and petrol). The resins were found to undergo ESC in organic liquids only, and the critical strains, ε_c, and critical stresses, σ_c, have been related to the solubility parameters, δ, of the liquid environments. The most severe ESC was observed in solvents with $\delta \simeq 19$–$20\ \mathrm{MPa}^{1/2}$, corresponding to minimum points in the plots of ε_c and σ_c against δ. Generally, the resin with the higher cross-link density had a greater resistance to ESC, but the effect of liquid diffusion complicated the situation and was found to play an important role in the ESC behaviour of these materials. The results confirmed that liquid diffusion into the resins lowered the critical strain (and stress), leading to earlier failure. In the case of the lower cross-link density resin, very fast diffusion was found to cause softening. However, it was noted that liquid diffusion can also blunt crazes and cracks.

1. Introduction

With the increasing use of polymers and polymer-based composites for engineering applications, the mechanical requirements for these materials are becoming more severe. One area that continues to cause a problem for the mechanical stability of polymer-based materials is that of environmental stress cracking (ESC). This is the premature brittle failure caused by the combined action of a stress and an active liquid (most commonly an organic solvent). Such failures are brittle, difficult to predict and can be catastrophic. Although much work has been done in an attempt to understand this problem, realistic methods for predicting or preventing ESC remain some way off.

Environmental cracking of most rigid polymers proceeds by initiation and growth of craze-like zones of cavitation which break down to form cracks [1]. Two particular mechanisms have been proposed to account for the action of crazing and cracking agents in glassy polymers [2], and it is thought that in many cases both mechanisms may apply. One suggestion is that the presence of the liquid lowers the surface energy of the polymer and makes the formation of new surfaces during crazing easier. Another is that the organic liquid penetrates and swells the polymer and lowers its T_g, thus allowing deformation, and hence crazing, to take place at reduced stresses and strains. Once a craze has formed, the active environment is able to diffuse along the craze more easily than through the bulk, plasticize the material at the craze tip and accelerate craze growth.

Attempts to predict the effects of different environments have generally found that there is a critical level of strain below which crazing does not occur. This critical strain decreases as the equilibrium absorption of the liquid in the polymer (and hence the degree of T_g reduction) increases. Indeed, a correlation between the critical strain and the solubility parameter of the liquid has been found [3]: the closer the solubility parameters of polymer and liquid (i.e. the more similar they are chemically), the more severe is the degree of ESC. More detailed measurements [4] have shown that the phenomenon cannot be accounted for in terms of solubility parameters alone, and other effects such as hydrogen-bonding capability should also be taken into account.

Cross-linked thermosetting materials tend to have a better resistance to crazing and chemical attack than thermoplastic polymers due to their limited molecular mobility [5]. However, these materials can still be susceptible to ESC and the mechanism of attack in this case is even less well understood. The present report is part of a wider study into the ESC behaviour of a range of cross-linked urethane methacrylate resins that are being developed by ICI for use as the matrix in filled and fibre-reinforced composites [6, 7]. The

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aims of the work have been to determine the relative hostilities of various environments and to gain a better understanding of the mechanisms of failure.

2. Experimental procedure

2.1. Materials

Although urethane methacrylates can be used in a pure form, it is more common to dissolve the resin in reactive monomer diluents such as methyl methacrylate or styrene. Polymerization is initiated by decomposition of a peroxide, thus generating free radicals. These radicals add to the double bonds associated with the urethane methacrylate or the solvent monomer, resulting in the generation of another radical species and the process continues with the generation of polymeric radicals. Thus, after polymerization, the cross-linked network results from the initial urethane precursor and from copolymerization of the terminal methacrylate unsaturation with the solvent comonomer. By varying the molecular weight of the urethane segment and the average number of comonomer units between methacrylic branch points, the cross-link density can be controlled.

Two experimental urethane methacrylate resins (U/MMA), supplied by ICI, were used in this investigation. They were prepared by free radical polymerization of the liquid resins, followed by post-curing at 115 °C for 40 h. Their typical monotonic mechanical properties are shown in Table I. U/MMA1 has a higher cross-linking density and is stronger and stiffer, but more brittle, than U/MMA2.

Samples for the three-point bend tests were cut from "as-received" sheets with a thickness of about 2.5 mm into strips 60 mm × 14 mm. Isotropy in the plaque was confirmed by testing a few samples in a perpendicular direction. The sides of the samples were machined and then polished with 600 and 1200 grit abrasive papers.

Testing was performed in a variety of liquids, including distilled water, sodium hydroxide solution and a range of organic solvents. These are listed with their solubility parameters and hydrogen bonding capabilities in Table II [8]. Dilute solutions were simply prepared by using distilled water as a dilutant (liquid by volume fraction and solid by weight fraction).

2.2. Mechanical testing

Three-point bending tests were employed to determine the degree of crazing and to measure the critical strain in the various different environments. The samples were subjected to flexural deformation across a span length of 40 mm in a three-point bending jig (shown in Fig. 1), followed by immediate immersion in one of the test liquids. After immersion for either 1 or 24 h, samples were examined and measured to determine the separation, b, of the craze boundaries on either side of the fulcrum. The immersion time was determined according to previous test results, making sure that equilibrium crazing was reached at a certain strain (stress) level. Thus an immersion time of 24 h was used in most cases, whilst just 1 h was required for the samples of U/MMA2 in very strong swelling agents.

TABLE I Typical mechanical property data of U/MMA1 and U/MMA2 (data supplied by ICI)

Properties	U/MMA1	U/MMA2
σ_y (plain stress compression) (MPa)	148	91
σ_y (tension) (MPa)	(93)[a]	56
E (measured in flexure (GPa)	3.46	2.3
E (measured in tension) (GPa)	3.62	2.4
K_{IC} (SEN, Flexure) (MPa m$^{1/2}$)	0.6	1.1
T_g (tan δ_{max}) (°C)	150	148

[a] Estimated from σ_y (compression).

TABLE II Solubilities and hydrogen bonding capability for liquids used (from [8])

Liquid	Solubility parameter, δ (MPa$^{1/2}$)	Hydrogen bonding capability
Petrol	15.6	Poor
Toluene	18.2	Poor
Tetrahydrofuran	18.6	Moderate
Acetone	20.2	Moderate
Acetic acid	21.3	Strong
Ethanol	26	Strong
Ethylene glycol	29.9	Strong
Water	47.9	Strong
3,5,5-trimethylhexanol	17.2	Strong
Acetonitrile	24.3	Poor

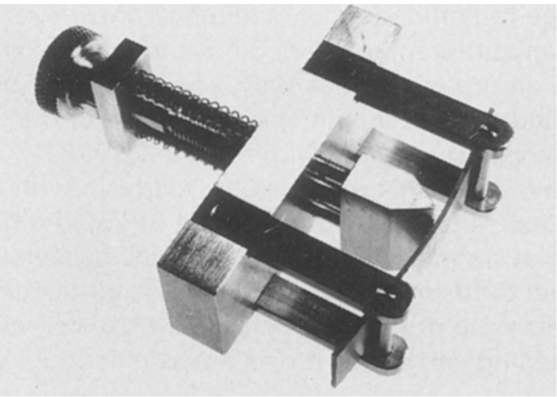

Figure 1 Three-point bending apparatus.

The maximum strain, ε_{max}, at the mid-point of the tensile surface of the three-point bend sample was determined by

$$\varepsilon_{max} = 6\delta d/l^2 \qquad (1)$$

where δ is the deflection, d is the thickness and l is the span length of the three-point bending jig. The critical strain, ε_c, was calculated using

$$\varepsilon_c = (l - b)\varepsilon_{max}/l \qquad (2)$$

where the b is the separation of the points along the length of the sample at which crazing was just visible, determined using an optical microscope with a travelling stage.

In order to check the influence of liquid diffusion on stress crazing and cracking behaviour, some samples were pre-immersed in the liquid for times varying from a few hours to a few months. The thickness and weight changes were then measured using a micrometer and an electronic balance with accuracies of 0.01 mm and 0.01 mg, respectively. Following pre-immersion, samples were immediately subjected to three-point bend testing in the liquid to obtain *b* values.

Crazed samples and fracture surfaces of the samples that failed in the bend tests were examined by optical microscopy and scanning electron microscopy (SEM).

3. Results and discussion

3.1. Effects of different environments

The critical strains of U/MMA1 and U/MMA2, derived from bending tests in various liquid environments, are shown in Table III. This gives a general picture of the effects of different liquids on these two materials.

Distilled water and sodium hydroxide solution (1%, 5%, 10%, 20%, 30%, 40%) were found to produce no ESC in U/MMA resins, when using maximum strains of up to 3%. However, it was noticed that large permanent deformations were induced in these samples compared with those tested in air.

Ethylene glycol does not act as a very strong crazing agent to either material. Below a concentration of 40%, no crazes were observed in any of the samples. However, in both 50% and 100% ethylene glycol, crazing was observed at relatively high strains (see Table III). Furthermore, although U/MMA2 did not fail at strains up to 3%, U/MMA1 failed at maximum strains of 2.9% and 2.5% in 50% solutions and pure ethylene glycol, respectively.

Acetic acid is one of the most hostile environments to these U/MMA resins. Fig. 2a shows the relationship between the separation of the craze boundaries, *b*, and the maximum strain for U/MMA2 after samples were tested in different concentrations of acetic acid for 24 h. Fig. 2b illustrates the results for U/MMA1 using the same series of tests. Similar general trends were observed for both materials. It may be seen that the higher the concentration of the solution, the lower the maximum strain at which craze formation begins, that is, the lower the critical strain. Also, *b* values increase with solution concentration for a constant maximum strain. It is clear that U/MMA1 is more susceptible than U/MMA2 to crazing in acetic acid. It was also observed that whilst U/MMA2 tends to undergo less crazing or cracking it is much more susceptible to swelling. This effect is discussed in a later section. It is interesting to note that failure occurs more easily for U/MMA1 in low-concentration acetic acid solutions than in higher concentration solutions. For example, in a 10% solution, almost every sample tested above 2% maximum strain failed, even though crazing was not observed until just below this point. On the other hand, a 50% concentration solution did not cause any fractures even when tested at up to a maximum strain of 2.8%, despite causing crazing below 1%. This effect is also thought to be related to the swelling behaviour and is discussed below. Ethanol and acetonitrile affected the ESC behaviour of U/MMA resins in a similar way to pure acetic acid, that is, both liquids were more aggressive to U/MMA1 than U/MMA2.

TABLE III Critical strains (%) from bending tests

Liquids	Critical strain (%)	
	U/MMA1	U/MMA2
Distilled water	–	–
Sodium hydroxide solutions (1%–40%)	–	–
Ethylene glycol	1.3	1.4
Dilute ethylene glycol (50%)	2.1	2.3
Dilute ethylene glycol (1%–40%)	–	–
Ethanol	0.4	0.7
Acetic acid	0.2	0.5
Dilute acetic acid (50%)	0.8	2.0
(40%)	1.0	2.1
(30%)	1.3	2.4
(20%)	1.4	2.8
(10%)	1.8	–
Acetone	0.01	0.2
Tetrahydrofuran	0.1	0.05
Toluene	1.1	0.7
Petrol	1.2	0.9
3,5,5-trimethylhexanol	1.5	0.9
Acetonitrile	0.4	1.0

Petrol, toluene and 3,5,5-trimethylhexanol behaved more aggressively to U/MMA2 than to U/MMA1. However, samples of U/MMA1 always failed in petrol at maximum strains larger than 2%, while U/MMA2

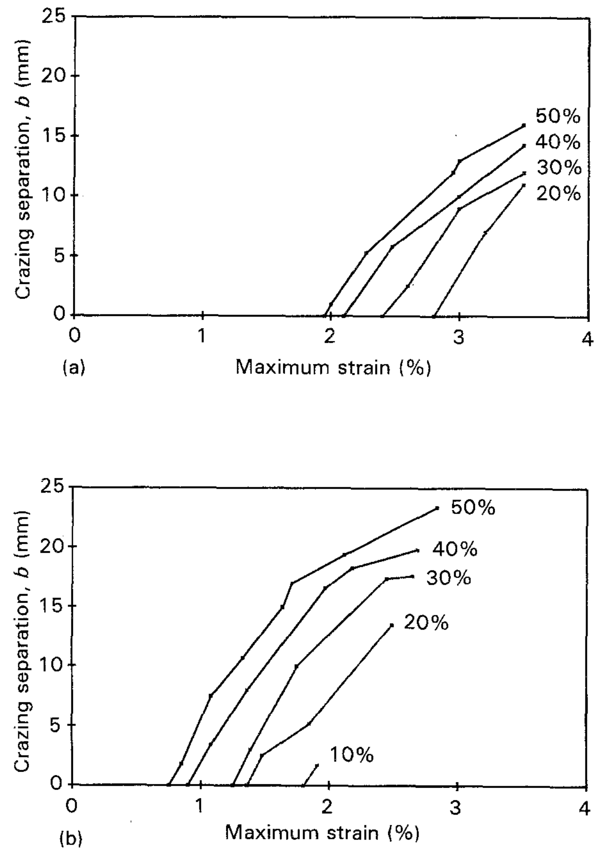

Figure 2 Crazing *b* values plotted against maximum strains of U/MMA resins in dilute acetic acid; (a) U/MMA2 and (b) U/MMA1.

could bear large numbers of crazes without failure, up to a maximum strain of 3.3%.

Acetone and tetrahydrofuran were the most aggressive liquids to both materials. A very low strain (stress) level tended to cause crazing on U/MMA1, while for U/MMA2, liquids diffused into the sample so quickly that stressed samples in these environments either failed immediately or were softened thoroughly by swelling.

3.2. Effects of time and temperature

Fig. 3 shows the results of a series of three-point bend tests of U/MMA2 immersed in petrol for various times from 1 min to 115 h. It is clear that the formation of crazes is very rapid provided that the maximum strain is above a critical level (for U/MMA2 in petrol, the critical strain is about 0.9%). Crazes or cracks appear within a few minutes. The larger the maximum strain, the quicker the formation of crazes or cracks, and the shorter the time before the *b* value reaches equilibrium. For maximum strains higher than 1.5%, a large number of crazes occur within 1 min and *b* values reach equilibrium in about 1 h. Samples of U/MMA1 tested in dilute acetic acid for different times showed similar results. These experiments indicate that environmental stress cracking is strongly dependent on not only the stress condition but also the degree of liquid diffusion. When the applied stress was relatively low, it took a long time for crazes to reach a visible size. This is consistent with previous results which have suggested that the frequency of craze nucleation and changes in craze length are a function of time [9], with craze growth being controlled by diffusion of the liquid through the end of the craze [10].

The testing temperature also had a considerable influence on the bend test results for U/MMA2. Samples of U/MMA2 that were tested at room temperature produced crazing or cracking when the concentration of acetic acid was higher than 20%, whilst those tested at 60 °C did not craze or crack at all in any concentration from 10%–50%. It was also found that these samples had an increase in thickness after testing and the retained strain (permanent deformation) was larger than for those samples tested at room temperature. In contrast, samples of U/MMA1 tested at 60 °C and at room temperature showed very similar results in terms of critical strain. However, for some samples which failed in 10% solution at 60 °C, arrest lines were observed on the fracture surface.

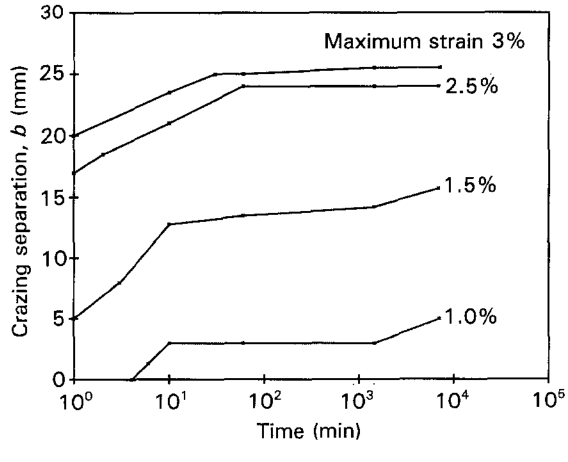

Figure 3 Crazing *b* values plotted against bending time of U/MMA2 in petrol.

3.3. Effects of pre-immersion

The thickness and weight increases of U/MMA2 samples immersed in different concentrations of acetic acid from 10%–100% and for different times from 5 h to 1 month are shown in Fig. 4. They indicate that acetic acid is a very strong swelling agent for U/MMA2 and that this effect depends on the concentration of acetic acid. None of the pre-immersed samples was found to give crazing or cracking after bend testing in 50% acetic acid for 24 h with a maximum strain of up to 3%. However, if these immersed samples were left in air for more than a month to allow acetic acid to diffuse out of the surface, they underwent crazing during bend testing in a similar manner to untreated samples.

For samples of U/MMA2 pre-immersed in petrol for different times, from a few hours to a few months, only slight weight increases were recorded (Fig. 5a). However, the influence of pre-immersion on ESC was distinct, as shown in Fig. 5b, for samples with a maximum strain of 2%. The *b* values of craze separation decreased with increasing pre-immersion time. After pre-immersion for 1 week, no crazing or cracking was found during subsequent bend testing.

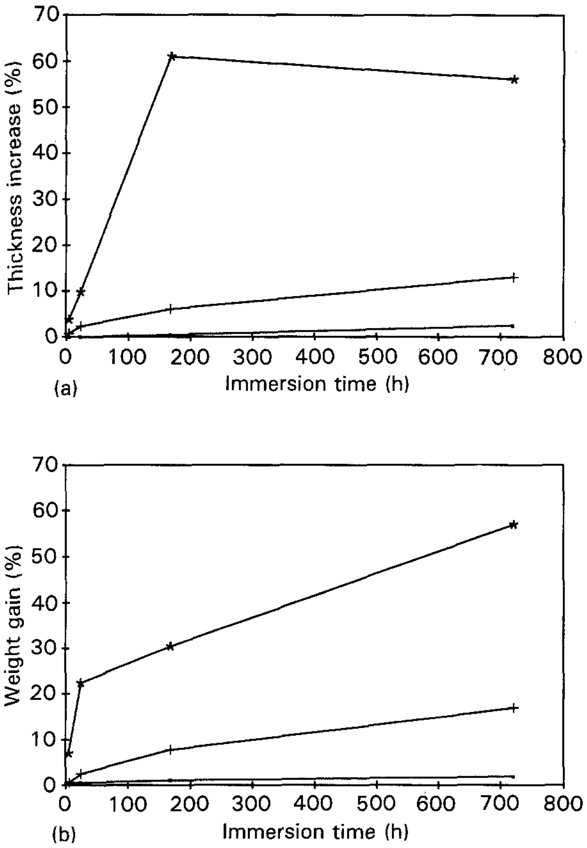

Figure 4 Effect of immersion in dilute acetic acid on (a) thickness, and (b) weight change of U/MMA2 samples. Acetic acid: (✱) 100%, (+) 50%, (-■-) 10%.

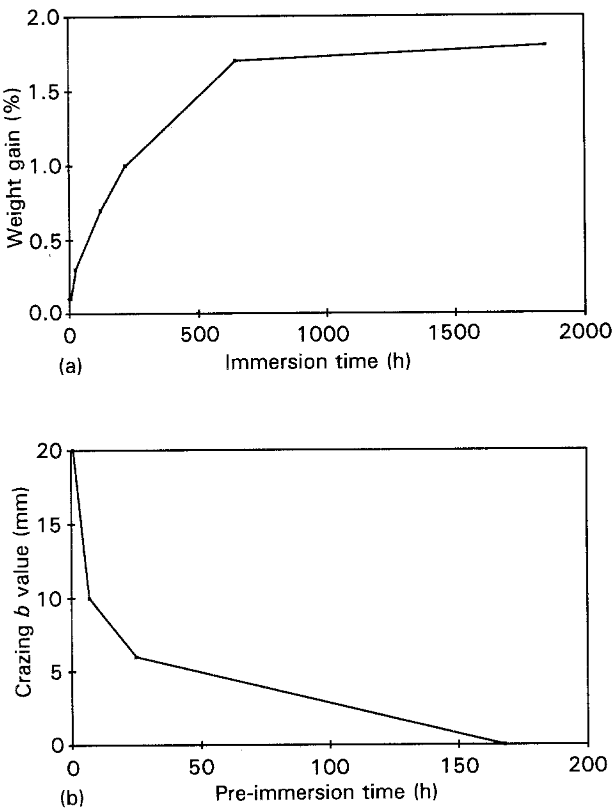

Figure 5 Effect of pre-immersion in petrol on (a) weight, and (b) crazing *b* value (with maximum strain of 2%) of U/MMA2.

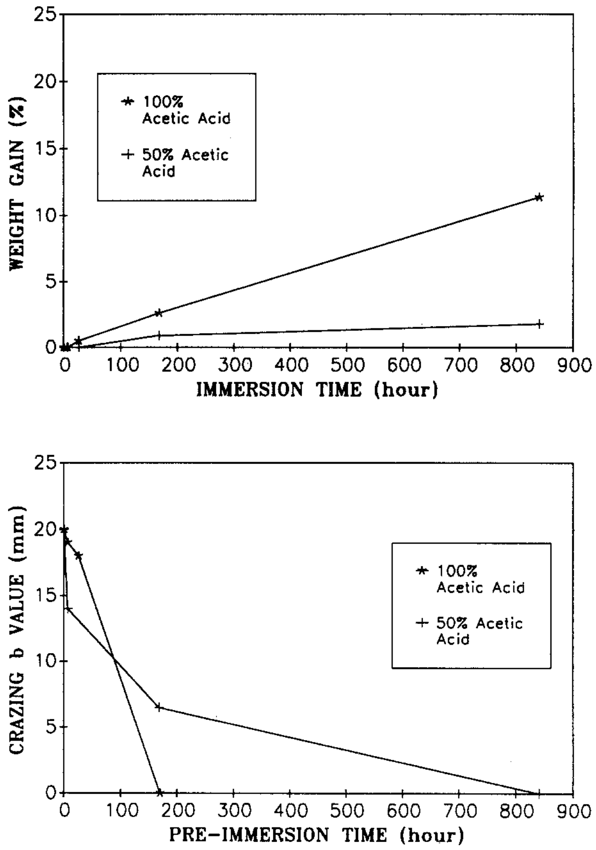

Figure 6 Effect of pre-immersion in acetic acid on (a) weight, and (b) crazing *b* value (with maximum strain of 1.5%) of U/MMA1. Acetic acid: (*) 100%, (+) 50%.

The influence of pre-immersion in acetic acid on ESC of U/MMA1 is shown in Fig. 6. The weight increase when immersed in pure acetic acid was much higher than in the 50% solution (Fig. 6a). The *b* values of pre-immersed samples, tested in 50% acetic acid with a maximum strain of 1.5%, decreased with the increase of immersion time (Fig. 6b). It is interesting to note that samples pre-immersed for a relatively short time were less affected by pure acetic acid than by 50% solution. This is possibly because, during bend testing with 50% acetic acid, acetic acid desorbs from the surface of the sample which was pre-immersed in pure acetic acid. An increase in weight (of about 2.6%) was found after pre-immersion in pure acetic acid for 7 days (168 h), and a distinct swollen layer (Fig. 7) existed on the sample surfaces. After pre-immersion in pure acetic acid for 35 days, the surfaces of the sample were highly swollen and softened, with an increase in weight of about 11.4%, and no crazes or cracks were found during bend testing. Samples of U/MMA1 after pre-immersion in acetic acid were found to fail much more easily when stressed compared with non-immersed specimens. Furthermore, for those samples pre-immersed in acetic acid, shear-yielded zones were always seen ahead of the crack/craze tips after bend testing.

Samples of U/MMA1 pre-immersed in petrol exhibited a different behaviour. Neither the weight nor *b* values were found to change with pre-immersion, even for times up to 35 days. However, as in the case of pre-immersion in acetic acid, samples of U/MMA1 pre-immersed in petrol were also found to fail more readily at lower strains than non-immersed samples.

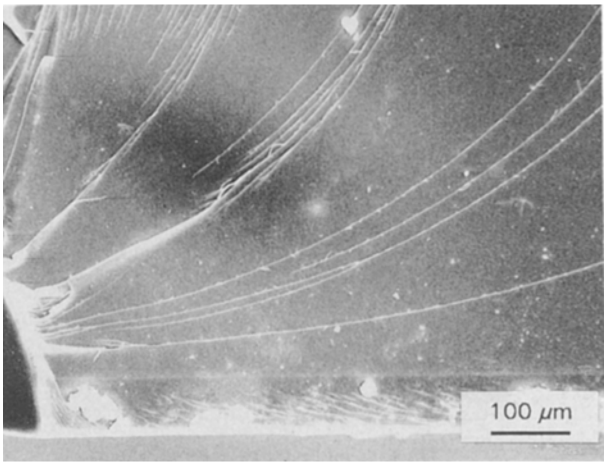

Figure 7 Fracture surface of a U/MMA1 three-point bend sample which had been pre-immersed in acetic acid for 7 days, showing the swollen layer on the sample surface.

It is clear from the above results that the process of liquid diffusion plays a very important role in the ESC behaviour of these materials. In the case of U/MMA2 in strong swelling agents, liquid diffusion into the sample was so fast that the swollen and softened surface layer of material allowed the relaxation of applied stress and a reduction in the likelihood of crazing. Sometimes pre-existing crazes were closed by swelling. Indeed, it was observed that for samples of U/MMA2 bent in pure acetic acid for a few minutes, a large number of crazes occurred. When the testing time was longer than a few hours, the crazes became

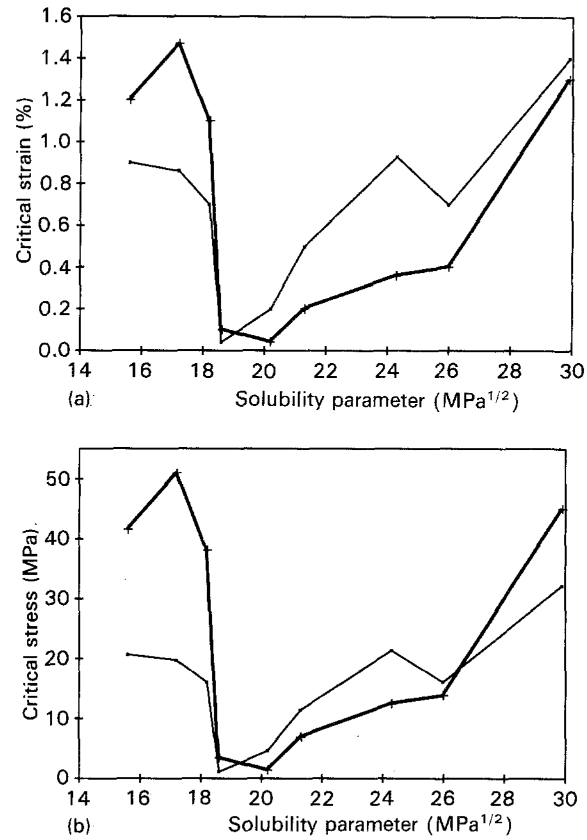

Figure 8 Solubility parameter, δ, of crazing liquids plotted against (a) critical strain, and (b) critical stress of U/MMA resins: (-■-) U/MMA2, (- + -) U/MMA1.

invisible. Higher temperatures accelerated the speed of liquid diffusion into the samples. For U/MMA1, it is suggested that liquid could only penetrate and swell the sample at preferential sites of stress concentration such as surface flaws, and lower the T_g in localized areas, allowing deformation and crazing to take place much more easily. This mechanism has been suggested by many authors for various resin and liquid combinations [2]. On the other hand, environmental diffusion into the sample, resulting in plasticization, could blunt the crack tip. For example, U/MMA1 crazed in 50% acetic acid at strains above 0.8%, whereas failures were not observed until the strain reached 2.8%. This suggests that, once formed, the crazes were relatively stable, which could be explained by the blunting of cracks due to the liquid ingress. With more dilute solutions, crazes did not form until higher strain levels (1.8% strain in 10% acetic acid), and yet failures occurred more easily (at 2% strain in 10% acetic acid). This is thought to be due to the reduction in the amount of craze tip blunting. In addition, arrest lines, which were found in the samples tested at 60 °C and in those that had been pre-immersed, are believed to be related to the reduction in yield stress due to plastic deformation during crack propagation [11]. The fact that shear yielding zones were found ahead of crack tips is further evidence that crack tips are blunted by plastic deformation in pre-immersed samples. However, when U/MMA1 was pre-immersed in a swelling liquid, such as acetic acid, for a long enough time (say 1 month), the surfaces of the sample swelled and were softened thoroughly by the liquid, in a similar manner to U/MMA2.

3.4. Effects of solubility parameter

When critical strains (obtained from the three-point bend tests) or critical stresses (derived from critical strain and flexural modulus) are plotted against the solubility parameters of the liquids tested, as shown in Fig. 8, it can be seen that there is a minimum point in each curve. This general behaviour is similar to that found in previous studies [12]. The trend of changes in critical strain (and stress) with solubility parameter for these two materials with different cross-link densities (and slight differences in chemical composition) is almost the same.

The solubility parameters of liquid environments have been considered in relation to ESC of glassy polymers by earlier workers [3]. A liquid will act as a solvent when its solubility parameter is identical to that of the polymer. When the difference between the two solubility parameters is small, the liquid will promote cracking. When the difference is larger, the liquid will be a crazing agent [4]. The minimum point in the curves of Fig. 8 corresponds to the liquid in which these materials have the highest solubility, and occurs when the values of δ for the material and the solvent are similar. It shows again that crazing in these U/MMA resins is due principally to the reduction in T_g, caused by swelling, a mechanism suggested by previous researchers [2].

Examination of the critical strain to crazing as a function of solubility parameter (Fig. 8a) shows that for liquids with a solubility parameter of less than about 19 MPa$^{1/2}$, U/MMA2 is more susceptible to ESC than U/MMA1. For liquids with solubility parameters greater than ~ 19 MPa$^{1/2}$, the situation is reversed. A higher cross-link density would be expected to confer greater resistance to ESC (due to the higher inherent strength and reduced liquid diffusion and solubility) [13], and this is indeed the case with liquids of low solubility parameter. For the more surprising results, observed with high solubility parameter liquids, the effects of hydrogen bonding were initially considered as a possible explanation, because strong hydrogen bonding and high solubility parameter normally occur together. However, liquids with low solubility parameter and strong hydrogen bonding and vice versa were found to produce the same general behaviour, and so this could not be the main cause.

The more probable explanation is that diffusion effects are important. If the results are presented in terms of critical stress (as in Fig. 8b), rather than critical strain, it would appear that U/MMA2 is more susceptible to ESC for all liquids except those in the central region. These liquids are generally the strongest swelling agents with the fastest diffusion rates and so craze initiation in U/MMA2 could be delayed by the blunting of flaws and the introduction of a surface compressive layer. This is particularly likely for U/MMA2 in acetonitrile (solubility parameter of 24.3), which has a very high diffusion rate and also a surprisingly high value of critical stress.

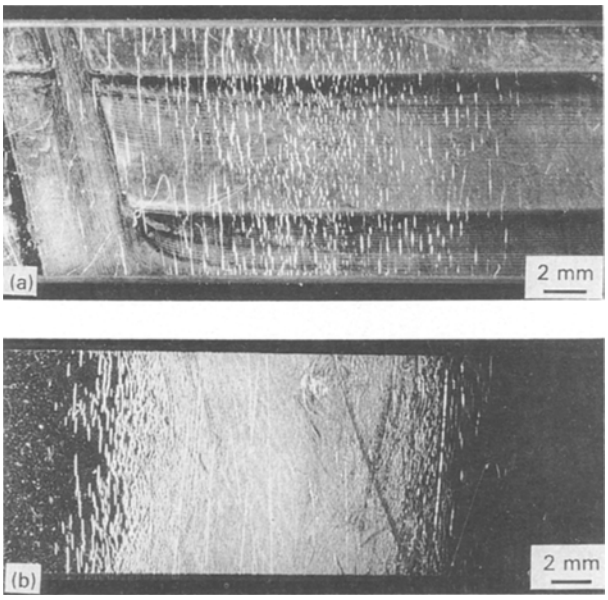

Figure 9 Surfaces of crazed specimens of U/MMA1 in (a) pure acetic acid with a maximum strain of 0.4% or stress of 14 MPa ($b = 20$ mm), and (b) 50% acetic acid with a maximum strain of 1.1% or stress of 3 MPa ($b = 19.4$ mm).

3.5. Effects of liquid concentrations

Fig. 9 shows the general features of crazed samples of U/MMA1 after testing in acetic acid. Samples tested in pure acetic acid (Fig. 9a) yielded a b value of 20 mm with a maximum strain of 0.4% (corresponding to a stress of 14 MPa), while a similar b value was obtained in 50% acetic acid (Fig. 9b) with a higher maximum strain of 1.1% (stress of 38 MPa). The fact that the lower concentration solution produces a greater density of crazes is due to the higher applied strain. Crazes will open up until the bending stress is relaxed to a point where no further crazing occurs.

These results, together with the data of Fig. 2, clearly show that higher concentrations cause a more severe ESC effect than dilute solutions. If the solubility parameters of dilute acetic acid and ethylene glycol are calculated using a simple "law of mixtures" approach [8], the results do not fit with the behaviour seen in Fig. 8. Dilute solutions have a more severe effect than such calculated solubility parameters would suggest, and further experimentation is being performed to develop an understanding and to model this behaviour.

The solution concentration also influences craze stability. In pure acetic acid, the diffusion rate and degree of swelling are high enough to allow craze blunting and thus no failures were observed in bend tests. In dilute solutions, however, this effect is much weaker, and so failures were observed, even though crazes did not form as easily.

4. Conclusion

Urethane methacrylate resins suffer crazing and cracking in organic liquids above a critical stress level. Water and dilute alkali solution were found not to cause ESC of U/MMA resins.

The hostilities of the organic liquids can be related to their solubility parameters. Acetone and tetrahydrofuran with solubility parameters $\sim$ 19–20 MPa$^{1/2}$ are the strongest swelling and most hostile solvents for both U/MMA materials. Liquids with solubility parameters above or below these values behave less aggressively. The higher cross-linked U/MMA1 resin has a greater resistance to environmental stress crazing than U/MMA2, except in liquids with solubility parameters in the range of $\sim$ 20–27 MPa$^{1/2}$, such as acetic acid, acetonitrile and ethanol, where strong swelling affects U/MMA2 much more than U/MMA1. Dilute solutions have a more severe effect than would be suggested by a simple "law of mixtures" calculation of their solubility parameters.

The effects of liquid diffusion play a very large part in the ESC behaviour of these materials. Liquid diffusion commonly softens U/MMA2 (with its lower cross-link density) and reduces or eliminates crazing, because the diffusion rates of the environments can be very high and large degrees of swelling can occur in short times. However, the softening caused by swelling is likely to impose serious limitations on this material. For U/MMA1, with a higher cross-link density, liquid diffusion is slower and failure is more likely to be by crazing and cracking.

All the results suggest that the mechanisms of ESC are very complex, with several factors (plasticization, chemical composition, swelling and the complex stress states associated with this) all having an influence on the crazing and cracking behaviour.

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