

# The effects of diffusion on environmental stress crack initiation in PMMA

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Slow strain rate tensile tests were conducted on un-notched PMMA samples in a range of liquid environments in order to assess the effects of diffusion on craze formation. The environments were selected to have a spread of diffusion rates and consisted of water, methanol, propan-2-ol, 355 trimethylhexanol and ethylene glycol. Absorption tests in these environments showed that methanol had the fastest diffusion rate and greatest degree of swelling, followed by water. Ethylene glycol and trimethylhexanol showed no weight gain, and propanol caused a steady dissolution of the PMMA. Tensile tests were conducted after the samples had been pre-immersed in the liquid environments for times ranging from 1 minute to 14 days. These were compared with equivalent tests in air, with the point at which the environment curve departed from the air curve being used to establish where crazing commenced. Tests were also conducted in methanol and ethylene glycol at a range of strain rates. It was found that with methanol and to a lesser degree with water and trimethylhexanol, crazing was delayed in tests with longer pre-immersion. This is due to mechanisms of flaw blunting and/or the introduction of surface compressive stresses. Similar effects were seen with the methanol tests at slower testing rates. It was found that these effects can occur very locally to the sample surface, where no weight gain could be measured and in the very early stages of craze development. © 1998 Kluwer Academic Publishers

## 1. Introduction

One of the most common causes of unexpected brittle failure of thermoplastics, especially amorphous materials is Environmental Stress Cracking (ESC). This is a predominantly physical phenomenon where an active (normally organic) liquid can cause craze formation at a much lower stress than would be required in air. It is a process which has attracted considerable research work over recent years, however a complete understanding and ability to predict ESC failure is yet to be produced. The main reason for this lies in the complexity of the process, with chemical compatibility, viscoelastic behaviour, diffusion, swelling, craze formation and crack growth all playing some part. Until a thorough understanding of all of these parameters is gained, predictions will remain little better than the general guidelines in use currently.

The major mechanism of ESC is generally accepted to be one of diffusion of the liquid environment into the material causing plasticisation, a localised reduction in yield strength and hence easier craze formation. Once a craze has formed, this can act as an easy diffusion path and so the process can accelerate. It is therefore clear that the diffusion of the environment into the polymer does play an important part in the process of ESC. The other mechanism proposed is that of surface energy reduction, which has been used to explain ESC when no measurable weight gain through diffusion is seen.

The degree to which the environment is able to swell and hence plasticise the polymer is governed by chemical compatibility. This can be predicted via the use of thermodynamic solubility parameters, with an increased susceptibility to ESC the closer the solubility parameter of the liquid is to that of the polymer [1]. Although the effects of applied stress and hydrogen bonding complicate this picture somewhat, it is an area which has received considerable attention and is reasonably well understood [2, 3]. There has also recently been an improvement in the understanding of the viscoelastic conditions for craze initiation, with the critical relaxed strain criterion proposed by Wright having the ability to be developed into a useful design tool [4, 5]. However, as the understanding gained in both of these areas can be significantly affected by different levels of diffusion, these effects need to be investigated further.

There has been considerable work performed on the effects of diffusion from a fracture mechanics standpoint using notched samples [6–9]. These studies have shown that the effects of ESC are reduced when the crack growth rate is very high due to the inability of the liquid to keep up with the growing craze or crack. At the other extreme, when the crack growth rate is very low, ESC effects can also be reduced due to plasticisation and hence blunting of the crack tip (or the introduction of local compressive stresses).

Less work has been performed using un-notched samples to examine the effects on craze initiation. Previous work in this area using three-point bend tests showed that polystyrene samples “pre-immersed” in ethanol gave a higher value of critical strain to crazing [10]. It was concluded that this was either due to flaw blunting, local compressive stresses due to swelling or a faster stress relaxation during the test. Further work using creep and slow tensile test geometries, where stress relaxation is not an issue, showed that diffusional behaviour can have a range of effects on craze initiation [11]. These effects varied from a delay in craze formation (in some cases to a stress above the tensile stress in air) to the formation of diffuse yielded zones. The purpose of this work is to examine these effects in more detail, using a single material, PMMA, in a range of environments with different diffusional behaviour.

## 2. Experimental

### 2.1. Materials and environments

The material used in this study was an experimental grade of PMMA, of  $M_w = 45,000$ , supplied by ICI in the form of sheet of 2 mm thickness. Dog-bone samples, conforming to ASTM D638, were machined from this and were then annealed between glass plates at 150 °C for two hours to remove any significant residual stresses. In order to avoid any effects of physical ageing affecting the results, the samples were stored at 23 °C for two months prior to testing.

The liquid environments used for this work were chosen to give a range of chemical compatibilities and a range of molecular volumes. The environments are listed in Table I below, together with their solubility parameters and molar volumes [12].

The environments were selected to encompass a range from chemically dissimilar but mobile (water), through increasing chemical compatibility, but also increasing molecular size (methanol, propanol and TMH) to chemically dissimilar and relatively large (ethylene glycol). With this range, it was hoped that all the effects due to different levels of diffusion would be seen.

### 2.2. Absorption testing

The absorption rates for each of the environments were measured by taking rectangular samples of size 3 cm × 2 cm and immersing them in the liquid environment at 23 °C. The weight of each sample was periodically measured

using a Sartorius balance, accurate to  $\pm 0.1$  mg. Before weighing, the excess liquid was removed from the surface of the sample with absorbent tissue. Weight measurements were taken more rapidly during the early stages, and then at decreasing frequency as the tests proceeded.

### 2.3. Tensile testing

Tensile tests were performed using an electromechanical testing machine, operating at a range of crosshead speeds from 10.5 mm/min to 0.001 mm/min, corresponding to strain rates from  $4.9 \times 10^{-3}$  to  $4.6 \times 10^{-8} \text{ s}^{-1}$ . Tests in the liquid environments could be performed by surrounding the entire sample with a cylindrical environmental chamber. In order to eliminate the possibility of failure being initiated at extensometer contact points, the strain was calculated from the machine’s crosshead movement, after appropriate calibration for machine compliance had been taken into account. From each test, a plot of stress against strain was produced.

Two sets of tests were performed. The first investigated the effects of pre-immersion time using all of the liquid environments. For these, samples were pre-immersed in the liquid environment of concern prior to tensile testing at a constant rate of  $1.03 \times 10^{-4} \text{ s}^{-1}$ . These tests were then compared to the behaviour in air at the same strain rate. Pre-immersion times varied from 1 minute (environment introduced immediately before testing commenced) to 14 days.

The second set of tests investigated the effects of testing rate using just two of the environments, methanol and ethylene glycol. For these, a constant pre-immersion time of 1 minute was used, but the applied strain rate varied from  $4.9 \times 10^{-3}$  to  $4.6 \times 10^{-8} \text{ s}^{-1}$ . Again, the results of these tests were compared to those in air (at the appropriate strain rate).

## 3. Absorption results

The liquid absorption results are shown in Fig. 1 for water, ethylene glycol and 355 TMH, in Fig. 2 for methanol and in Fig. 3 for propanol. It is clear from these that there is indeed a wide variation in the diffusional behaviour of the liquids chosen. Water gives a curve that is approximately Fickian, with a weight gain after 1 month of just over 1%. This is the expected behaviour for a liquid of limited chemical compatibility, but of small size that will be fairly mobile, but is unlikely to induce significant swelling.

The TMH shows virtually no weight change, despite the solubility parameter being closer to the PMMA. In this case, the sheer size of the TMH molecule prevents significant diffusion taking place. Ethylene Glycol shows a slight weight decrease initially, presumably due to the dissolution of some mobile component from the PMMA. This stabilises after about a week, with no further weight change being seen. In this case, both the molecular size and chemical dissimilarity preclude any major interaction with the PMMA.

TABLE I The liquid environments used, with solubility parameters and molar volumes

Environment	Solubility parameter (MPa <sup>1/2</sup> )	Molar volume (cm <sup>3</sup> /mol)
Water	48	18
Ethylene Glycol	34.8	56
Methanol	29.7	41
Propan-2-ol	23.5	75
355-Trimethylhexanol	17.2	174
PMMA	20.0	—

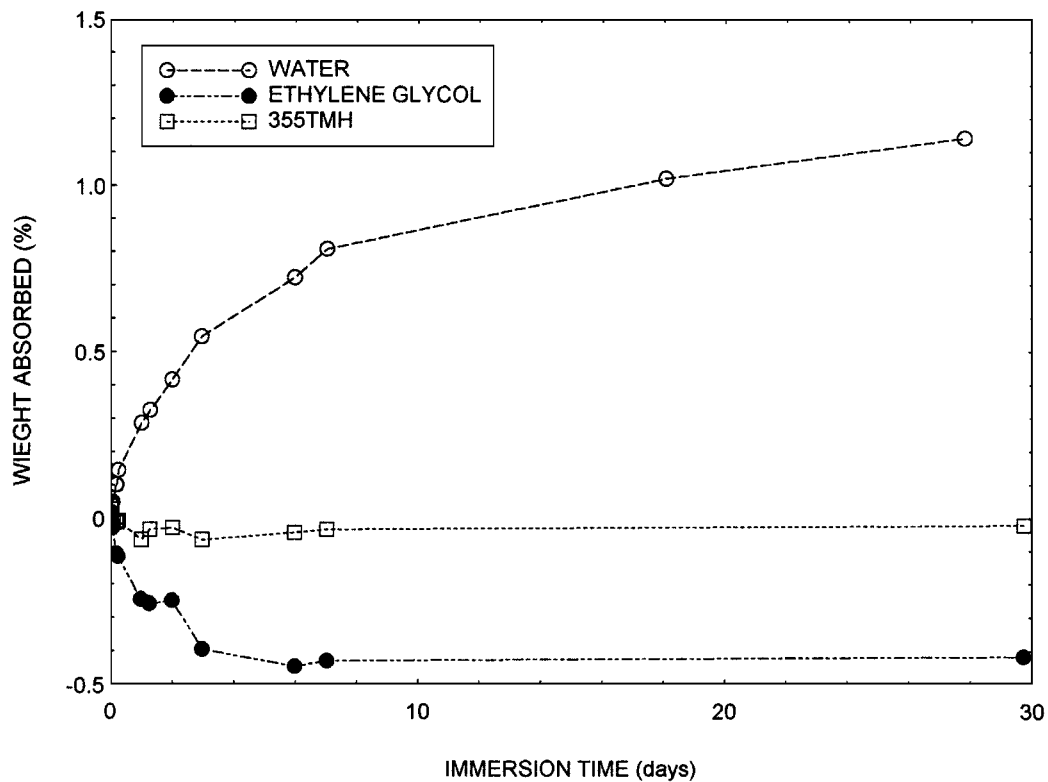


Figure 1 The weight change versus time behaviour for immersion in water, ethylene glycol and 355 TMH.

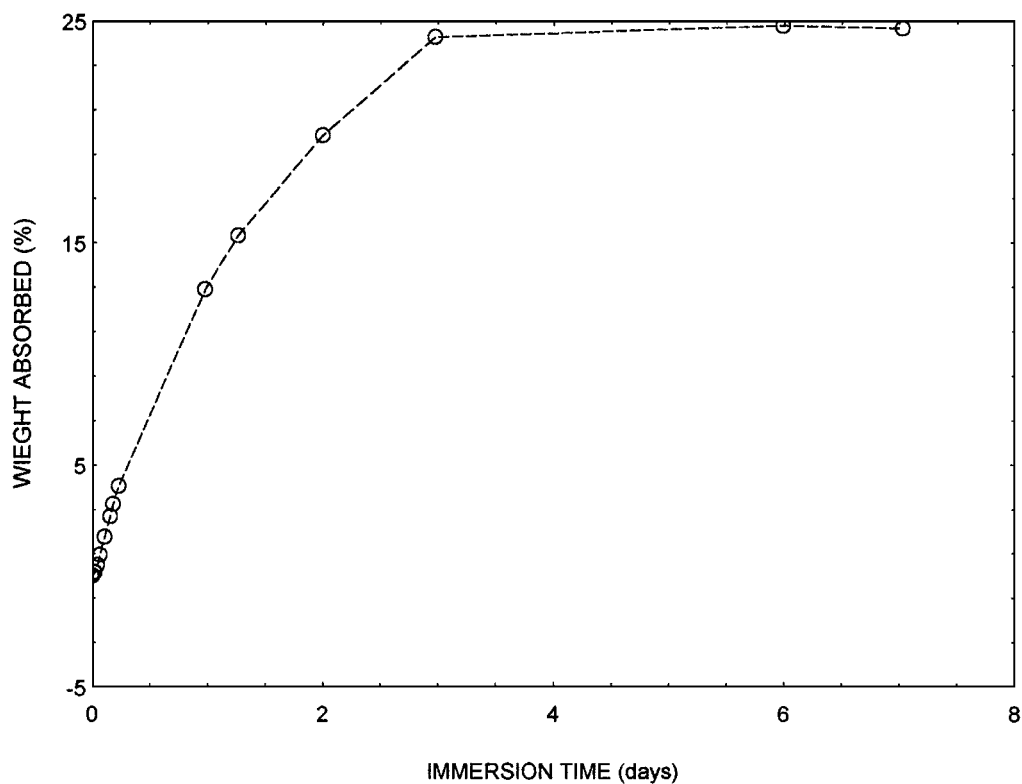


Figure 2 The weight change versus time behaviour for immersion in methanol.

In methanol (Fig. 2), the largest weight gain is seen, with a diffusion profile that is close to Case II diffusion, as has been seen in previous work [13]. Here, the weight increases to an equilibrium value of about 24% during the first three days, with a fairly sharp diffusion front being visible during this time. Considerable swelling occurs, with a noticeable softening of the polymer.

Propanol (Fig. 3) causes rapid dissolution of the PMMA, with over half the sample dissolving within the first week. In this case, the better chemical match than is seen with methanol causes total dissolution, but it is interesting to observe that both the weight and thickness decreased in a nearly linear manner, with a very sharp dissolution front and no noticeable swelling.

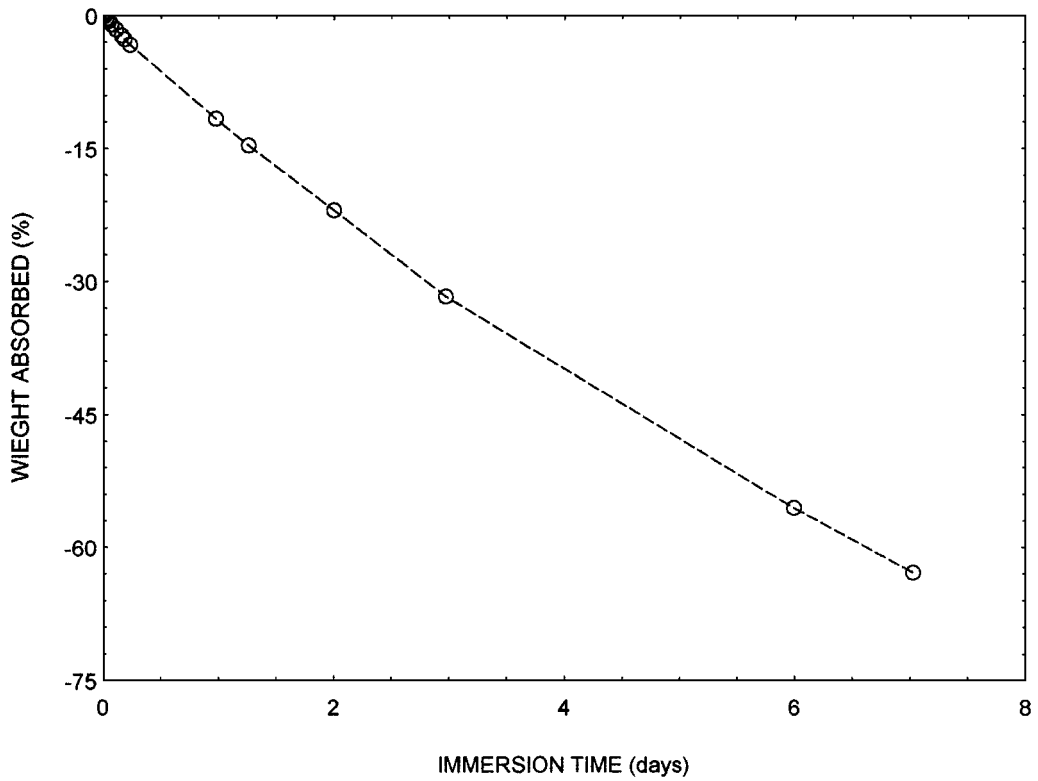


Figure 3 The weight change versus time behaviour for immersion in propanol.

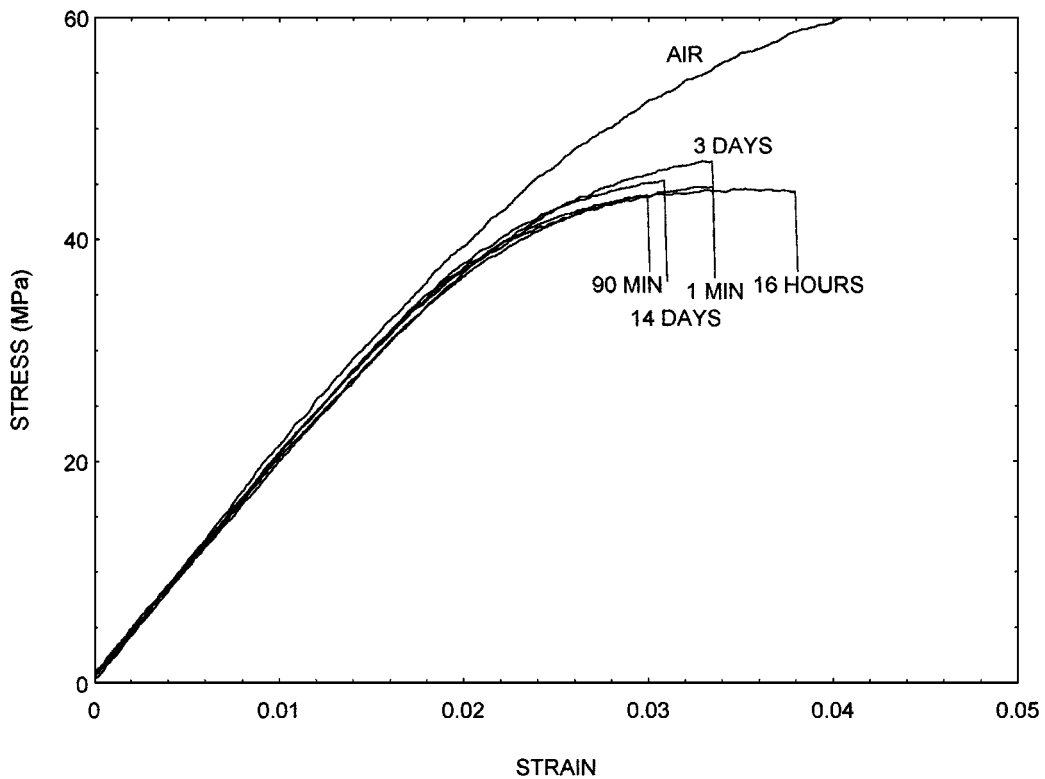


Figure 4 The stress/strain behaviour of samples pre-immersed in ethylene glycol for the times indicated and then tested at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ .

#### 4. ESC in ethylene glycol

Ethylene Glycol will be considered first as it is typical of many of the liquid environments that cause most unexpected ESC failure. Its solubility parameter is quite well removed from that of PMMA, absorption tests show no measurable diffusion occurring and yet under certain circumstances, it can produce severe ESC.

The stress/strain curves for the pre-immersion tests are shown in Fig. 4. Here, the results of tests conducted in ethylene glycol at pre-immersion times of 1 min, 90 mins, 16 hours, 3 days and 14 days are shown, along with the results obtained for a test conducted in air. The curve in air continued to a maximum value of 63 MPa, before yielding slightly and failing at a strain of about

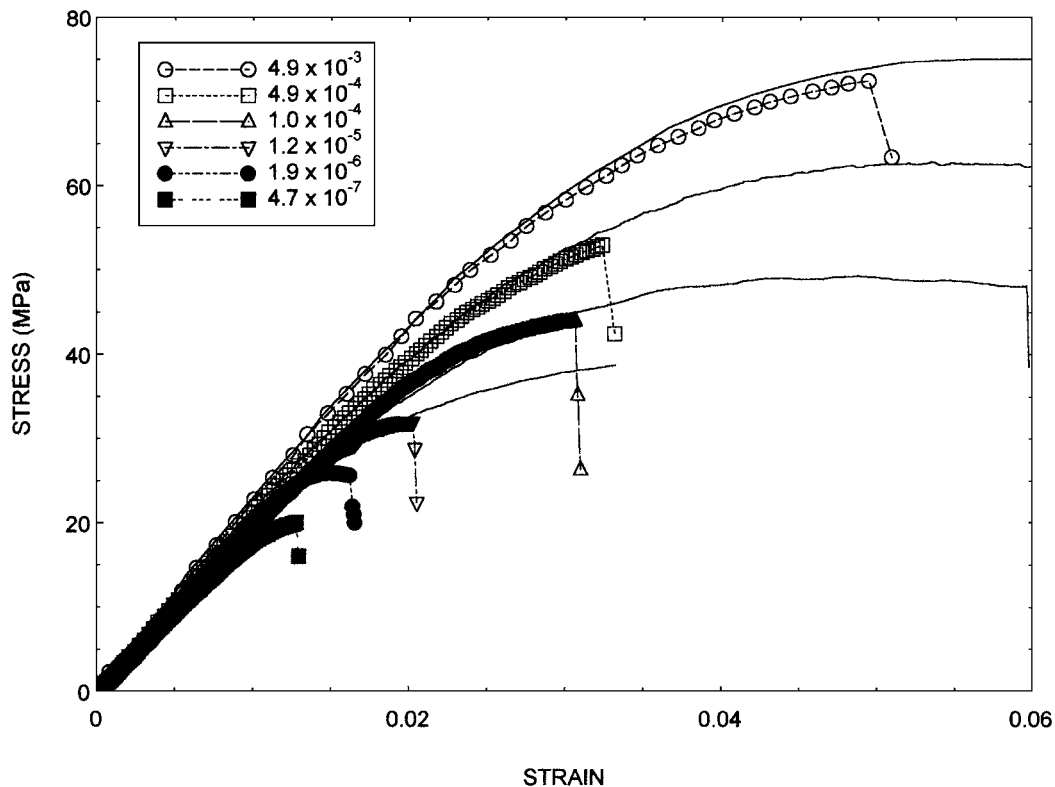


Figure 5 The stress/strain behaviour of samples tested in ethylene glycol at the strain rates indicated with a pre-immersion time of 1 minute. The appropriate curves for samples in air are shown with solid lines. Air curves for the two lowest rates are omitted for clarity.

0.09. The curves for tests in ethylene glycol initially follow the air curve, but then depart from it before failure occurs at a considerably reduced stress and strain (about 45 MPa and 0.035). Although there is a small degree of scatter, it can be seen that the different lengths of pre-immersion had no significant effect on the failure stress or strain.

The effects of varying the testing rate are shown in Fig. 5. Here it can be seen that the curves again depart from the behaviour seen in air, with failure then occurring soon after. Here, there is a dramatic effect of strain rate, with the departure point, as well as the stress and strain at failure all decreasing as the strain rate decreases.

The appearance of the failed samples is also of interest and is shown in Figs 6 and 7. All the pre-immersed samples had a similar appearance, as illustrated in Fig. 6 for samples tested with pre-immersion times of 1 minute and 3 days, both of which show similar features with very many small crazes present. Variation of the testing rate does, however produce differences in failure appearance as is seen in Fig. 7. Here, the fastest test produced just one single craze/crack (not shown). With intermediate rates, many small crazes were seen and then with slower rates, the number of crazes reduced and they became generally coarser.

The behaviour in ethylene glycol can be explained as follows. As no effect of pre-immersion was seen, either on the stress at failure or on the number and size of crazes formed, it can reasonably be concluded that diffusion prior to testing plays no part in ESC with this combination. Failure will occur by the ethylene glycol at the surface facilitating craze formation. Whether this is caused by an immeasurably small amount of liquid

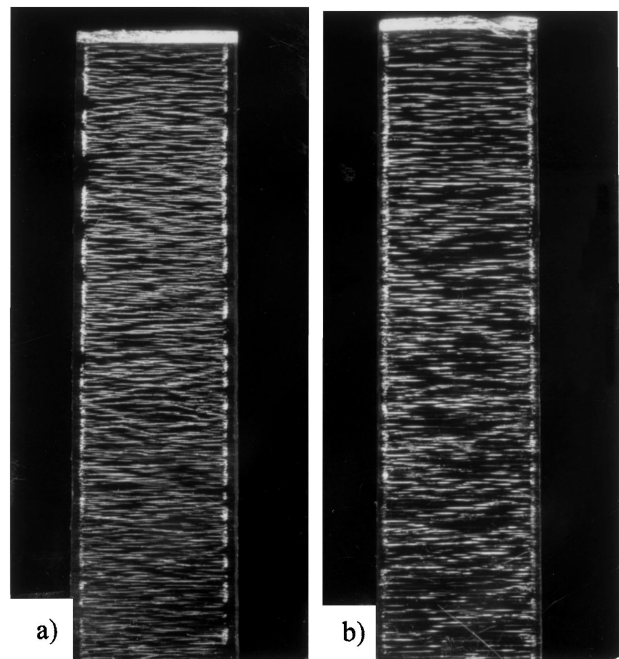


Figure 6 The appearance of samples tested in ethylene glycol at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ , with pre-immersion times of (a) 1 minute and (b) 3 days.

diffusing into the near surface layer (or voids once they have formed during testing), or by a purely surface energy effect is impossible to say; at this level, the two mechanisms probably overlap to such an extent that it makes little difference.

The effects of testing rate are more dramatic as here there is a definite effect of timescale, both on the stress at failure, and on the number and size of crazes/cracks.

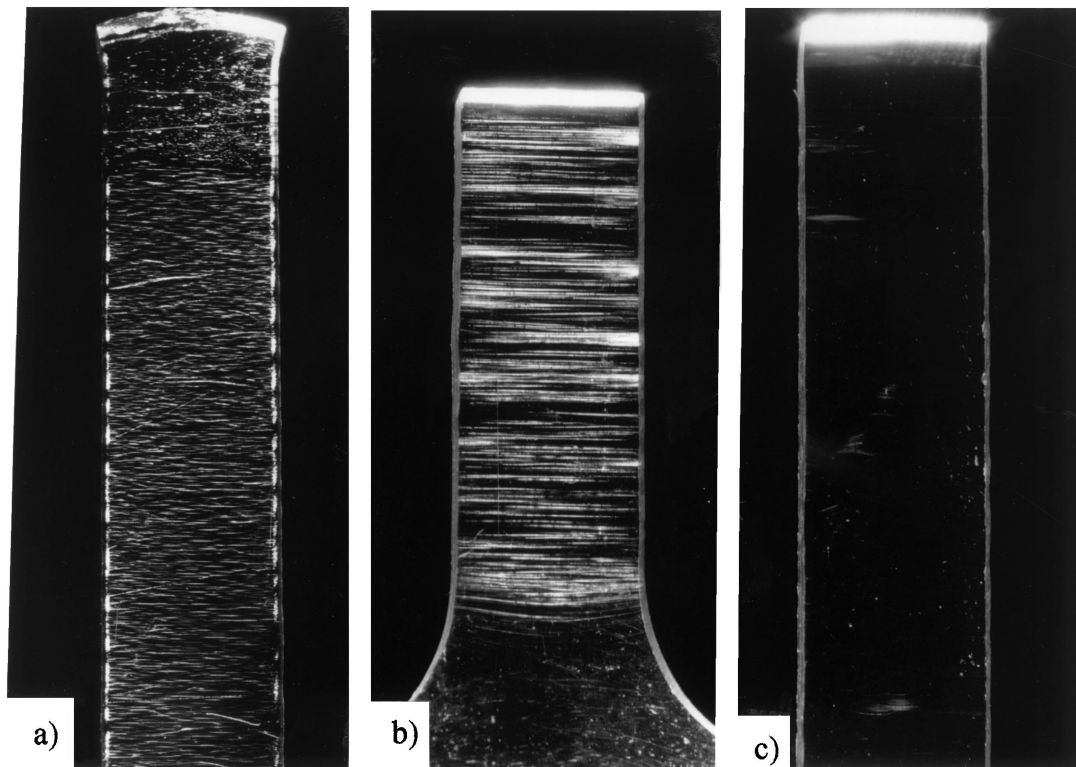


Figure 7 The appearance of samples tested in ethylene glycol with a pre-immersion time of 1 minute at strain rates of (a)  $4.9 \times 10^{-4}$ , (b)  $1.2 \times 10^{-5}$  and (c)  $4.7 \times 10^{-7} \text{ s}^{-1}$ .

The stress at failure will be predominantly determined by the ease of craze formation. This can be concluded from the fact that there is little difference between the stress where departure from the air curve occurs (corresponding to craze formation) and the final failure stress. The variation of this stress with testing rate can be explained by two time-dependant phenomena.

(i) Limited penetration of ethylene glycol. At the faster testing rates, there may not be enough time for the ethylene glycol to enter the craze precursors and exhibit its full ESC effect. This is most likely to be the case with the fastest tests, but with the slower ones, this trend is still seen, and yet it could be argued that there is now ample time for the liquid to penetrate the voided region adjacent to the surface. In this case, the second explanation will be more important.

(ii) Relaxation dependent craze formation. It has been demonstrated that a certain amount of anelastic deformation needs to occur prior to craze formation, an idea which forms the basis of Wright's critical relaxed strain criterion. As the test speed decreases, there will be more time for anelastic deformation, leading to craze formation before the stress has risen to the levels seen with faster tests.

The number of crazes seen on the sample is a function of the competition between craze formation and growth. At fast rates, craze formation is hindered, as described above, and yet when the first craze does form, the stress on the sample is of such a size as to cause rapid failure, even without ESC activity along the growing craze. At the other extreme, the craze growth rate is high due to ESC activity continually at the craze tip (there being

enough time for the ethylene glycol to keep up with the growing craze). The growth of the first craze can then accommodate the increasing applied strain and so the stress on the sample will not rise to levels high enough to initiate more crazes. At both of these extremes, where the craze growth rate is high compared to the craze formation rate, few but large crazes are seen. In the intermediate range, the stress on a craze once formed will not be high enough to cause fracture in air, and yet the ethylene glycol is not fully able to keep up with the growing craze front. In this case, as the craze formation rate is moderate, many smaller, more stable crazes will be formed.

To summarise the behaviour in ethylene glycol, it is a combination where no measurable diffusion occurs, and so there is no effect of pre-immersion. As the testing rate decreases, there is more chance of ESC failure, due to the environment being able to fully penetrate growing craze pre-cursors (at fast rates) and to more time for relaxationally-controlled craze formation (at low rates). At the extremes of testing rate, the crazes are least stable; due to high applied stresses at fast rates, and to complete ESC action at the growing craze front with low rates. With intermediate rates, neither of these effects are as dominant and so the crazes are more stable. This can be classed as "standard ESC action", which accounts for most failures in service and is most catastrophic with long loading times.

## 5. ESC in methanol

At the other extreme of behaviour is methanol. With this environment, high rates of diffusion and considerable bulk plasticisation are seen in relatively short

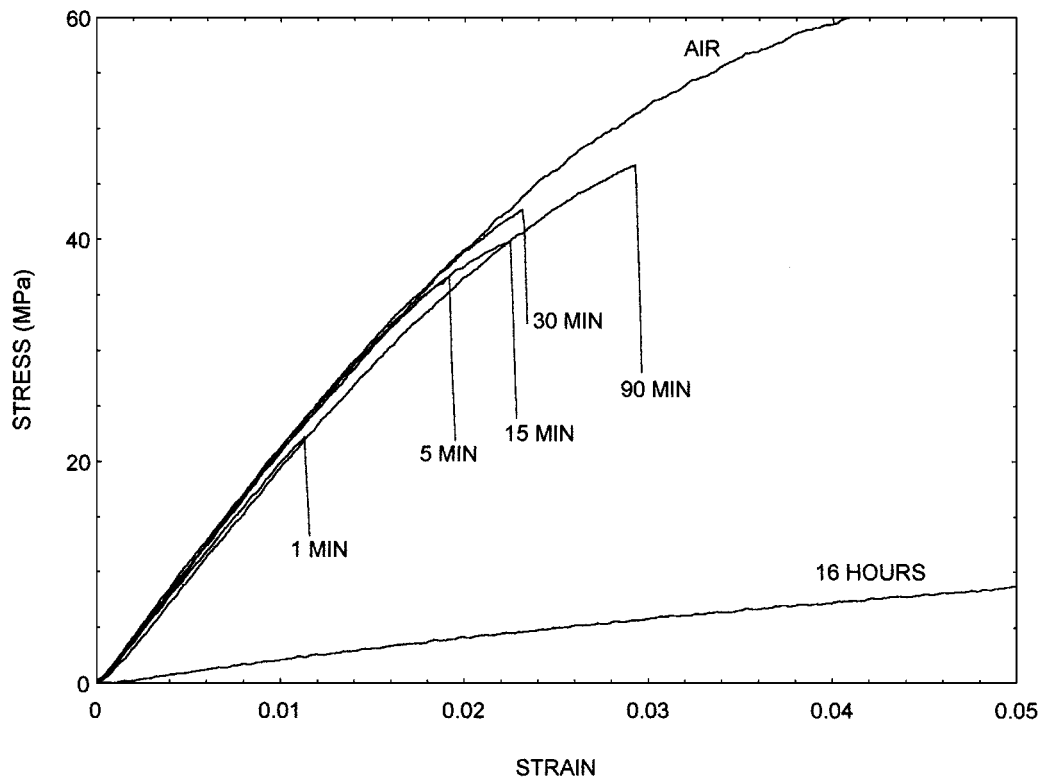


Figure 8 The stress/strain behaviour of samples pre-immersed in methanol for the times indicated and then tested at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ .

times. Indeed, in real applications, this combination would not be used due to the swelling effects rather than ESC potential. The effects of pre-immersion are shown in Fig. 8. As the pre-immersion time increases from 1 to 30 minutes, there is a dramatic increase in the failure stress. This continues to some extent with the 90 minute test, but by this point, the modulus is lower throughout the test, showing that considerable softening is occurring. By 16 hours, large scale bulk

softening had occurred. The failed samples are shown in Fig. 9. These show that with the shortest pre-immersion time, a single catastrophic craze is formed. As the pre-immersion time increases, this changes to a larger number of smaller crazes before the failure mode changes to one of yielding with no crazing with the softened samples after longer pre-immersion.

The variation in behaviour with testing rate is shown in Fig. 10. With the fastest rate, the departure (and

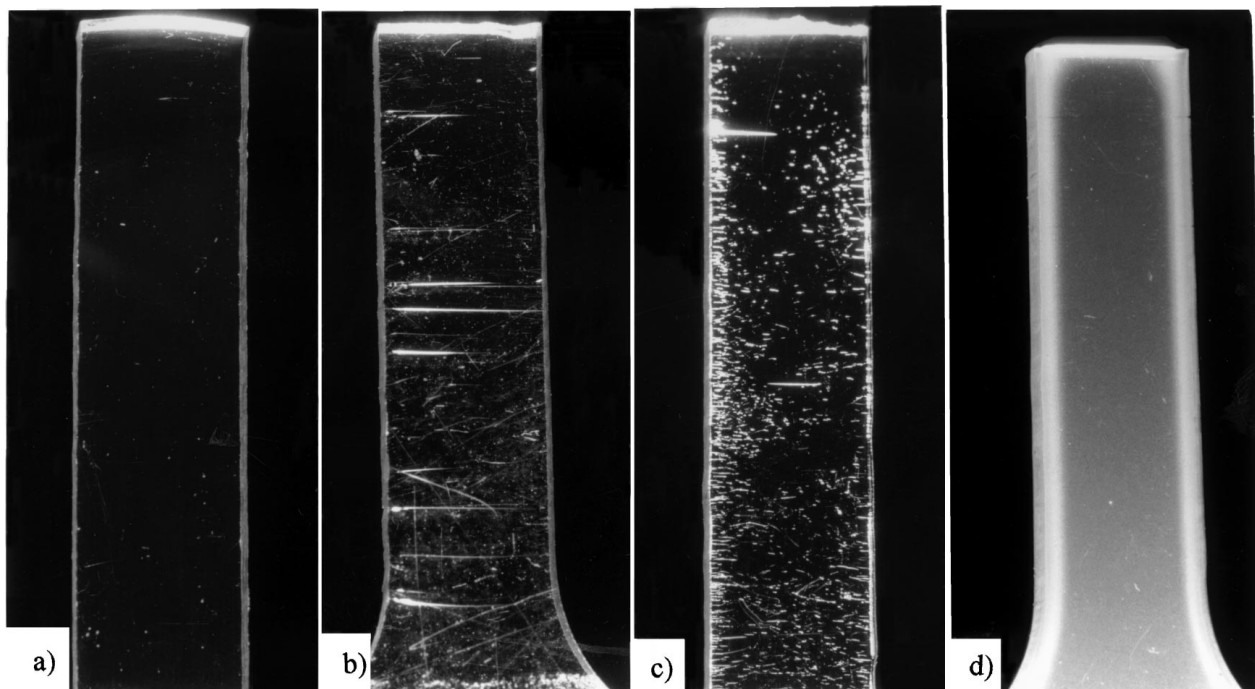


Figure 9 The appearance of samples tested in methanol at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ , with pre-immersion times of (a) 1 minute, (b) 15 minutes, (c) 90 minutes and (d) 16 hours.

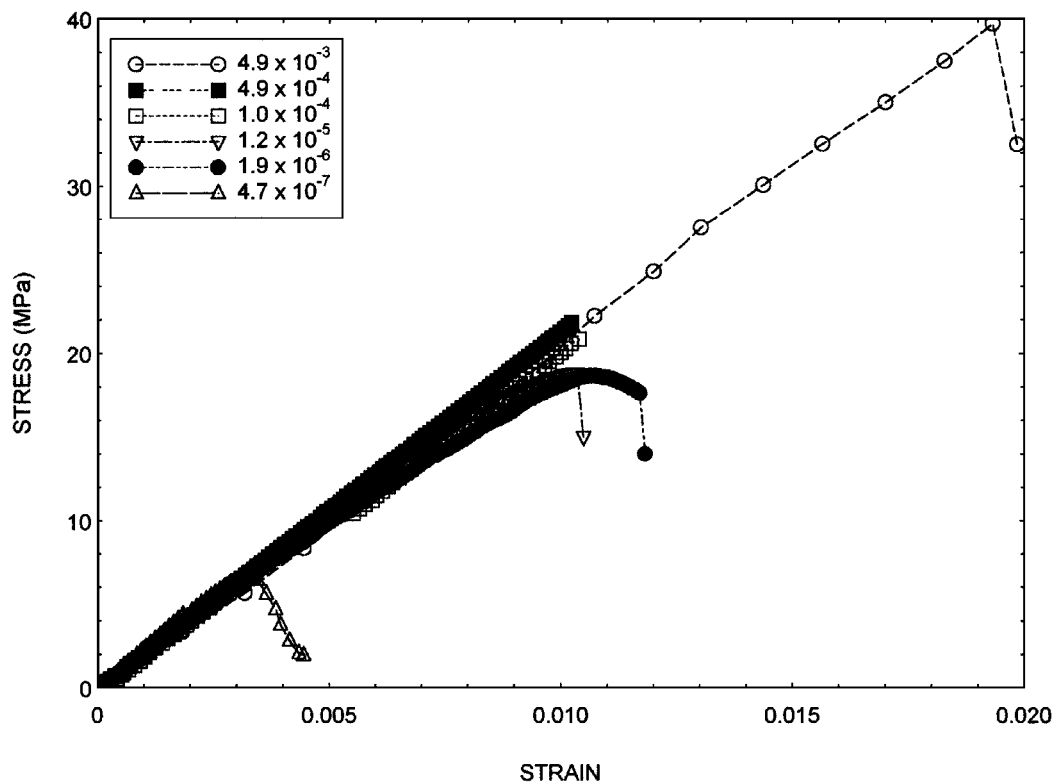


Figure 10 The stress/strain behaviour of samples tested in methanol at the strain rates indicated with a pre-immersion time of 1 minute.

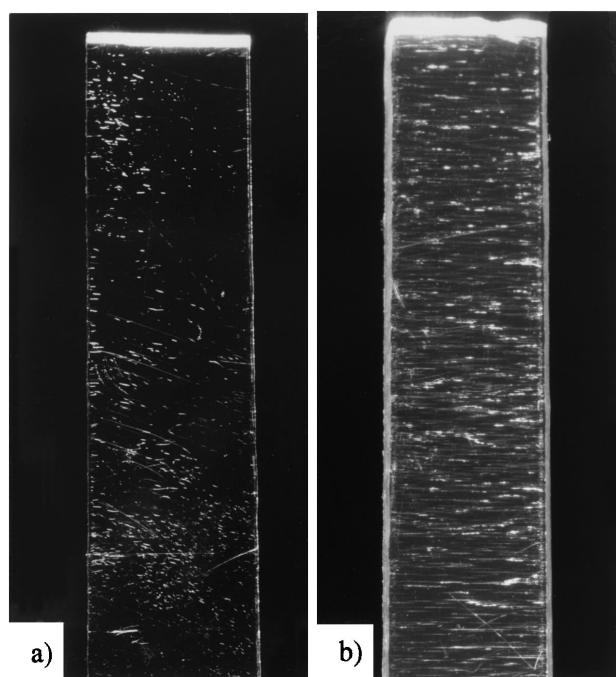


Figure 11 The appearance of samples tested in methanol with a pre-immersion time of 1 minute at strain rates of (a)  $1.2 \times 10^{-5}$  and (b)  $1.9 \times 10^{-6} \text{ s}^{-1}$ .

failure) stress is fairly high, at about 40 MPa. This is reduced to about 20 MPa for all of the rates from 1.05 mm/min to 0.004 mm/min, with very little difference. With the slowest rate, however, the stress drops dramatically again to about 7 MPa. The failed samples were seen to exhibit just a single crack for the three fastest rates, whilst several crazes were produced with the slower rates (Fig. 11).

It can be seen that methanol is quite a severe ESC agent, with the stress to failure after a short time of environmental contact being about 1/3 the value in air, over quite a range of testing rates. The effects of pre-immersion and testing rate are significantly different to those seen with ethylene glycol. These effects are predominantly due to the methanol being able to fully diffuse into and around growing crazes and their precursors and so hinder the ESC action. With the pre-immersion tests, the lowest failure stress is seen with the 1 minute pre-immersion time. In this case, during the test, there is enough time for the methanol to keep up with the developing and growing craze, however, there has not been sufficient time for the methanol to diffuse into the surface significantly. With longer pre-immersion times of 5, 15 and 30 minutes, the diffusion of methanol into the surface of the sample delays the formation of crazes, presumably by a mechanism of either flaw blunting or the introduction of compressive stresses due to swelling. In these cases, dramatic increases in failure stress are seen. With the 90 minute pre-immersion time, the effects of global softening are starting to be seen, which are dramatic for the sample pre-immersed for 16 hours.

The appearance of the samples backs up this idea. As the pre-immersion time increases, the effective toughening caused by diffusion leads to more stable crazes, and so a larger number of them are seen.

With the tests at different rates, there is the same underlying behaviour as seen with the ethylene glycol; the failure stress decreases as the rate decreases, due to the environment not keeping up with the growing craze at high rates (less likely with the more mobile and less viscous methanol) and by the greater time available for anelastic strain development at low rates. This trend



is however affected by some toughening mechanism at intermediate rates whereby methanol diffusion can hinder the development of craze precursors by the mechanisms mentioned above. As the testing rate decreases, there is more time for these toughening mechanisms to occur, and so the underlying reduction in failure stress is masked by an increase in toughening, giving effectively little variation of failure stress with rate. The failed samples' appearance again supports this, with more stable (and hence more numerous) crazes formed at the slower rates. With the slowest test (which takes about 2 hours), appreciable bulk softening is again taking place, leading to a dramatic reduction in failure stress.

## 6. ESC in water

Water has limited chemical compatibility with PMMA, but yet due to its small molecular size, there is a significant weight gain on immersion. The behaviour of samples with different pre-immersion times in water is shown in Fig. 12. Here it can be seen that the water gives a similar reduction in failure stress to that seen with the Ethylene Glycol. In this case, however, there is an effect of the pre-immersion time. The stress to failure increases as the pre-immersion time increases, but the effect is not as noticeable as seen with methanol. The effect also seems to take longer than seen with methanol, with the largest change occurring between 15 minutes and 3 days. All the samples failed with a single craze propagating rapidly across the sample.

The delayed onset of ESC initiation with longer pre-immersion times can again be attributed to flaw blunting or the presence of surface compressive stress, although

of lower magnitude than seen with methanol. The important point to highlight here is the fact that the water does not seem to have a toughening effect on the growing crazes once they have formed, as all the samples failed suddenly with only one single catastrophic flaw. This shows that at certain levels of diffusion, these toughening mechanisms can only be effective on the early stages of craze formation and so would not be seen with any form of notched samples.

## 7. ESC in 355 trimethylhexanol

Of the environments tested, trimethylhexanol (TMH) is probably the most chemically compatible with PMMA, however, its large physical size prevents any measurable weight gain to occur. The results for pre-immersion in TMH are shown in Fig. 13. From these it can be seen that TMH is of similar ESC severity to water and ethylene glycol. As with methanol and water, the stress to failure increases as the pre-immersion time increases, at a slightly faster rate than seen with water as the effects are significant after 16 hours pre-immersion. The failed samples are shown in Fig. 14, where it can be seen that a large number of small crazes are visible in all the samples. This demonstrates that the crazes are more stable than those formed in air, possibly due to a greater degree of blunting at the craze tip, but more probably due to an environment that is less able to rapidly diffuse to the growing craze tip.

## 8. ESC in propanol

The results in propanol are totally overshadowed by the fact that the material dissolves in this environment. The

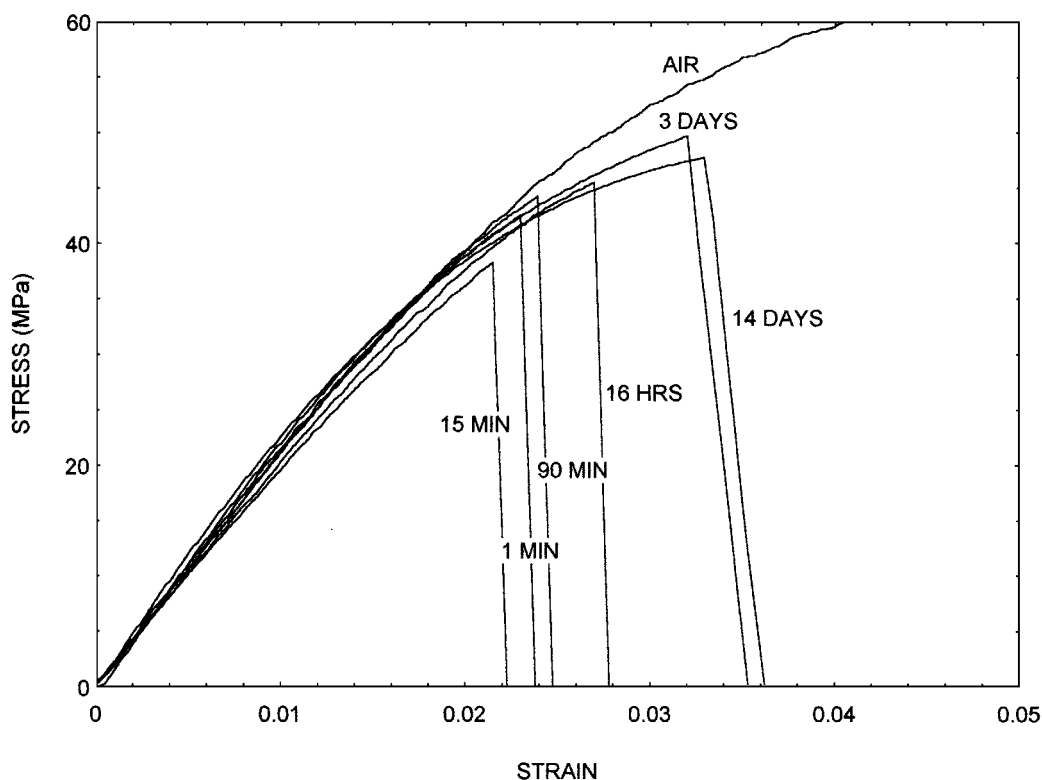


Figure 12 The stress/strain behaviour of samples pre-immersed in water for the times indicated and then tested at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ .

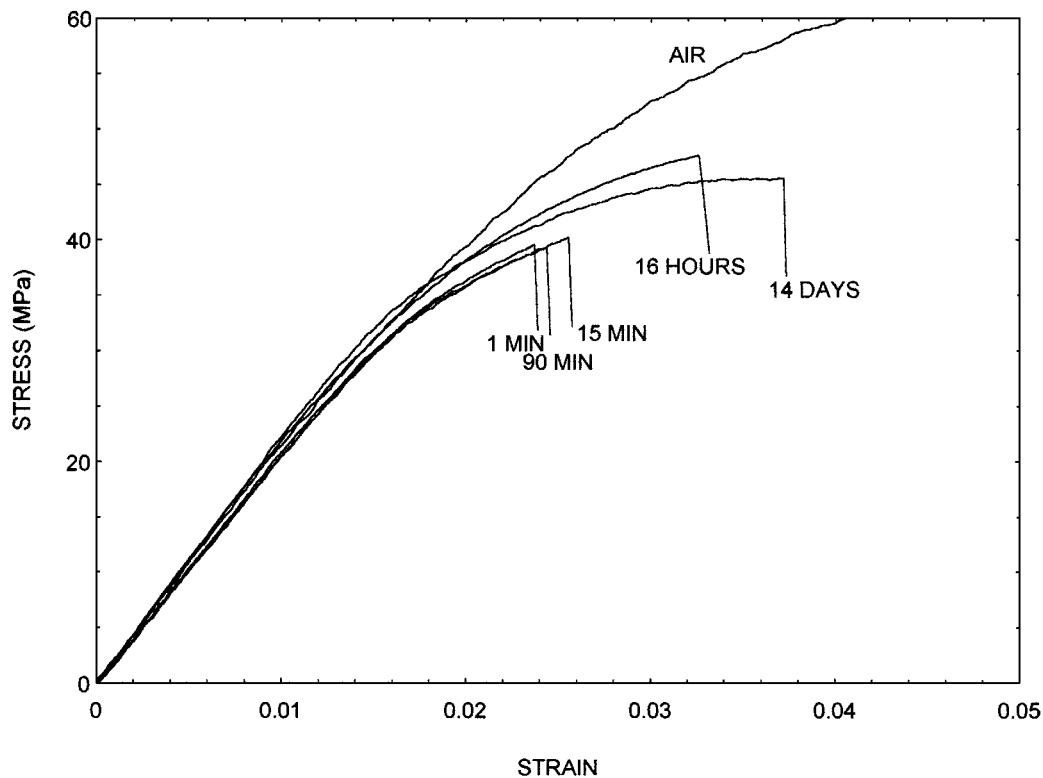


Figure 13 The stress/strain behaviour of samples pre-immersed in 355 TMH for the times indicated and then tested at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ .

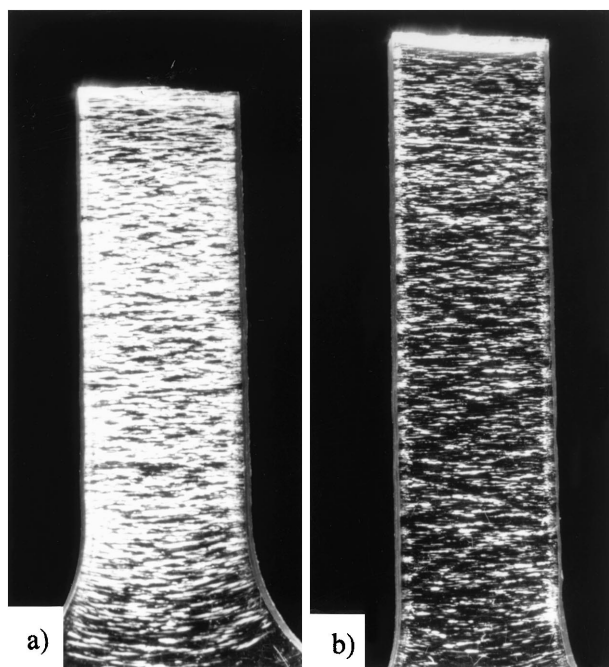


Figure 14 The appearance of samples tested in 355 TMH at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ , with pre-immersion times of (a) 1 minute and (b) 16 hours.

nature of dissolution, with a very sharp front is rather unusual, and presumably only occurs with very specific combinations of chemical compatibility, molecular size and polymer molecular weight, whereby the environment diffuses into the polymer and dissolves out polymer chains at a similar rate.

The ESC behaviour of PMMA in propanol is shown in Fig. 15, where it can be seen that this is the most aggressive environment studied, and that pre-immersion

has little effect. The only difference seen is with the longer pre-immersion times, where a reduction in apparent modulus is seen which is entirely due to removal of material by dissolution (the cross-sectional area of the sample was measured before immersion). The failed samples exhibited only a few crazes, showing that the craze growth is relatively rapid.

## 9. Discussion

It is clear from the above results that the different amounts of diffusion occurring prior to and during a test can have significant effects on the results. Where there is effectively no bulk diffusion occurring (with ethylene glycol), there are no effects of pre-immersion and the stress required for crazing decreases as the testing rate decreases, due to the time required for anelastic strain accumulation prior to crazing.

As the amount of diffusion increases, this can delay the onset of crazing, as seen in methanol (after 5 minutes pre-immersion), TMH (after 16 hours) and water (after 3 days). Tests in methanol at different rates also showed that toughening occurred with lower strain rates, thereby offsetting the decrease in crazing stress that would otherwise be expected. This effective toughening will arise by a combination of the blunting of flaws (craze pre-cursors) and the introduction of compressive stresses. Although similar effects have been seen during craze growth in notched samples, an important conclusion from this work is that these mechanisms also apply in the very early stages of craze development. This can be seen from the results in TMH, where toughening occurs despite no measureable weight gain, and from the results in water, where initiation is delayed, but craze propagation is always rapid (sudden failure with

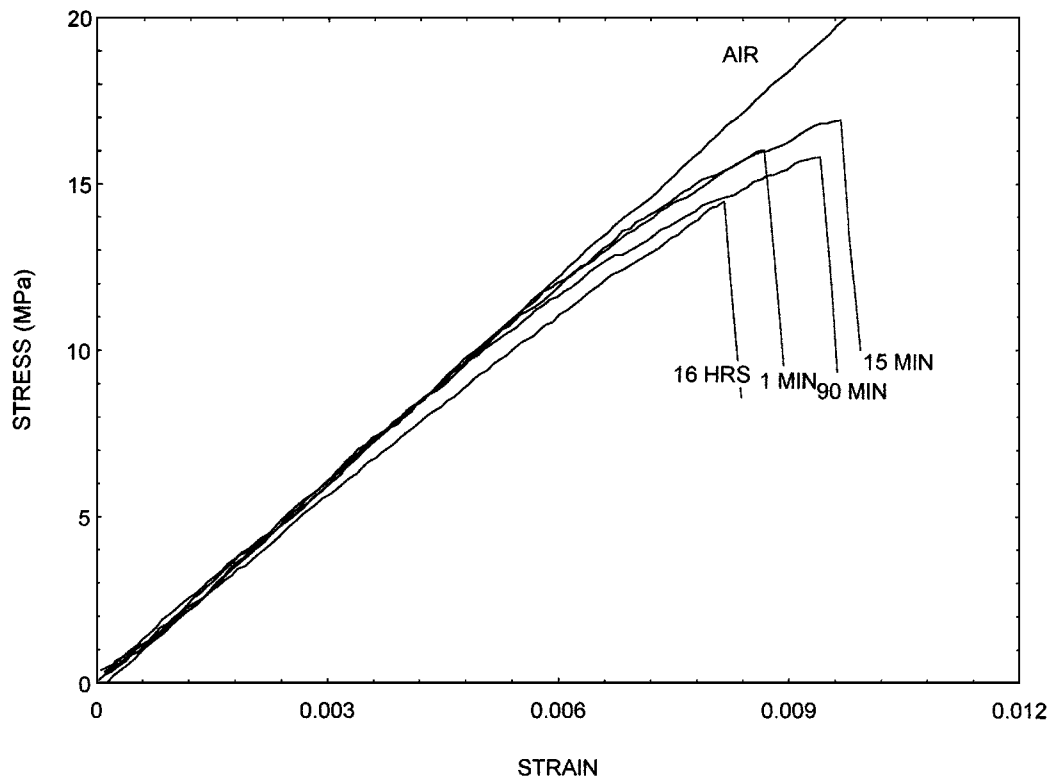


Figure 15 The stress/strain behaviour of samples pre-immersed in propanol for the times indicated and then tested at a strain rate of  $1.0 \times 10^{-4} \text{ s}^{-1}$ .

TABLE II The stability of crazes after different amounts of diffusion

Ratio of diffusion rate/testing rate	Craze stability	No. of crazes	Mechanism	Example
Lowest	Low	1	Single craze nucleates at high stress: environment can't keep up-rapid failure	Ethylene Glycol at fastest test rate
Low/medium	High	Many	Many nucleate (at lower stress). Environment can't keep up	Ethylene Glycol at slower rates and TMH.
Medium	Low	Few	Environment keeps up with first craze to form (but does not toughen) Rapid craze growth	Water, propanol at middle rates. Methanol at faster rates with short pre-immersion
Medium/high	High	Many	Environment keeps up with growing crazes and toughens them	Methanol at slower rates/longer pre-immersion times
High	—	—	Overall softening or dissolution	Methanol at slowest rates and longest pre-immersion times, Propanol at long times

a single crack). With even larger amounts of diffusion, these effects are overshadowed by global softening or even dissolution, as seen in some cases with methanol and with propanol.

Although the aim of this study was to focus more on craze initiation than growth, some interesting conclusions can be drawn from the appearance of the failed samples, which give an indication of the craze stability. These are shown schematically in Table II, below where the craze stability is indicated against the ratio of diffusion rate to testing rate. This ratio is chosen to illustrate the effects seen when the amount of diffusion that can occur during a test increases (either by a higher diffusion rate or a lower test speed).

All of these proposed mechanisms were seen with the test samples, and just go to indicate the overall complexity of the ESC process when craze initiation and growth are combined. Despite this, the above results have qualitatively shown the range of diffusional effects that can be seen with un-notched samples, and provide a basis for the future incorporation of these effects into quantitative models.

## 10. Conclusions

1. Slow strain rate tensile tests of PMMA in a range of liquid environments have shown that diffusional effects play an important part in craze formation.

2. With pre-immersion in several of the environments, the onset of crazing can be delayed, due to a mechanism of flaw blunting and/or the introduction of surface compressive stresses.

3. These effects were seen with TMH, an environment where no measureable weight gain occurred, showing that these effects can be very localised to the sample surface.

4. Tests at slower strain rates with no pre-immersion can also lead to delayed craze formation, by the same mechanisms.

5. Under conditions where the greatest amount of diffusion occurred, global softening or dissolution takes over.

6. Although the final appearance of the failed samples, which indicates craze stability, shows a complex variation with degree of diffusion and testing rate, these effects can be explained with an understanding of how diffusion affects both craze formation and growth.

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