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Craze initiation during the environmental stress cracking of polymers

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The environmental stress cracking behaviour of polycarbonate in ethanol was studied with the aim of critically evaluating craze initiation criteria. A combination of constant strain-rate tensile tests and creep tests were conducted in air and ethanol. The onset of crazing was determined by the use of departure points, which were shown to correlate well with the formation of optically visible crazes. Samples with different states of physical ageing and hence different relaxational behaviour were used to test out various initiation criteria. It was found that crazing occurred when the slower α relaxations had accumulated a certain amount of strain, in this case, 0.1%, and that a criterion based on critical inelastic strain was the most appropriate. Post-immersion tests showed that the development of craze precursors occurs independently of the environment.

1. Introduction

Environmental stress cracking (ESC) is still a major cause of failure of polymeric materials. It is generally accepted that it occurs by a process of local plasticization of the polymer due to diffusion of an active environment. This plasticization leads to easier craze formation and growth when subject to stress and can cause unexpected and often catastrophic brittle failure. A large amount of work has been performed in an attempt to predict such failure. This can be split into two main areas. The first has been to determine which combinations of polymers and environments will cause ESC. Much of this work has concentrated on thermodynamic compatibility, through the use of solubility parameters [1–4], and has met with some success, although quantitative predictions remain some way off.

The second area has been to determine what conditions of stress and strain are required for failure to occur through ESC. The aim of this work was to formulate failure criteria. The major problem here is that ESC failure is a very complex process involving craze initiation, craze growth and craze breakdown and so it has proved virtually impossible to formulate failure criteria that successfully encompass all of these features.

A potentially more fruitful approach is to consider just the first stage in this process: craze initiation. Although a criterion based on the time to the initiation of crazing will certainly underestimate the overall lifetime, this may be no bad thing for two reasons. Firstly, it provides an automatic built-in safety factor and, secondly, when dealing with long-term applications, as are more likely to be encountered in service, the majority of the overall lifetime will be taken up by initiation.

Early craze-initiation criteria were based on the use of a critical strain to crazing [5, 6]. It was postulated that there was a minimum value of creep strain below which crazing did not occur. The existence of this asymptotic strain has yet to be proved conclusively, and as such a criterion gives no indication of the relationship between time to crazing and applied stress for conditions above this critical value, it has not become established as a useful criterion.

The critical strain concept is still widely used in conjunction with bend tests in order to determine the severity of ESC for a range of environments [1–4, 7]. In these cases, it has been found that crazing occurs fairly rapidly where the strain is greater than some critical value, ε_{crit}, and does not occur below this, even for very long testing times. The value of ε_{crit} can, therefore, be used as a convenient measure of the hostility of the environment. The reason why the critical strain concept holds for the case of bend tests is that under these conditions of stress relaxation, the applied stress, which is the driving force for crazing, will decay relatively quickly. This is particularly true where swelling and plasticization occur as the environment diffuses into the surface and as crazes open up. Under these situations, a critical strain criterion is a useful approximation.

Under conditions of constant stress, two other criteria have been proposed. The first, proposed by Wright [8], is that crazing occurs when the inelastic strain has reached a critical value. The total strain can then be split up into "elastic" and "inelastic" components

$$\varepsilon_{total} = \varepsilon_{elastic} + \varepsilon_{inelastic} \qquad (1)$$

The short-term "elastic" component can be viewed as the strain due to all relaxations faster then the

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α component (i.e. those not involving main-chain motion) and its value can be obtained from the short-term compliance

$$\varepsilon_{\text{elastic}} = J_0\sigma \qquad (2)$$

The inelastic strain is thus the component due to α relaxations and viscous elements, i.e. those involving main chain motion.

The second criterion, proposed by Bruller [9], is that of critical inelastic strain energy density. That is, when the contribution of strain energy density due to the α relaxations reaches a critical value, crazing occurs.

A comparison of the above criteria was performed by Wright and Gotham [10], who found that the critical inelastic strain criterion was the most successful for solvent crazing under conditions of constant stress and constant strain.

In this paper, the examination of these criteria is taken one stage further by the use of different loading histories (constant stress and constant strain-rate tensile tests) and by the use of prior physical ageing. Physical ageing of amorphous polymers is known to hinder molecular motion due to a decrease in free volume [11]. In particular, it has been found to delay the α relaxations but leave β and faster relaxations unaffected [12]. Therefore, by varying the physical ageing time, it should be possible to alter the relative amounts of "elastic" and "inelastic" strain and so critically evaluate the criteria.

The methods used in this work were a combination of creep tests (at constant stress) and tensile tests (at constant strain rate) on samples with different physical ageing times. Polycarbonate was chosen as the material of interest, due to its propensity to ESC and its relatively high rate of physical ageing at room temperature [11]. Tests were performed in air and in ethanol as the active ESC agent. The point of craze initiation was determined as the point of departure of the environmental curve compared to the air curve. This method has been used successfully in previous studies [8, 10].

The final part of the work involved an investigation of the processes leading up to craze initiation under ESC conditions. Work by Wellinghof and Baer [13] has established that crazes form gradually from very small voids that form early in the deformation process. As these voids require main-chain motion in order to form, and as crazes form when the amount of voids has reached a critical level, the mechanism lends weight to the idea of a critical inelastic strain criterion. In order to determine the effects of the environment on the process of craze-precursor formation, a series of post-immersion tests was devised where samples were initially loaded in air and then immersed in ethanol at a later point in the loading history.

2. Experimental procedure

2.1. Materials

The material used was "Lexan" polycarbonate, supplied by GE Plastics in the form of sheet of approximately 1 mm thickness. The material was machined into dog-bone-shaped tensile samples of length 36 mm and width 6 mm. The edges were then polished to remove any machining marks. The samples were then annealed between glass sheets at 160 °C for 2 h and subsequently held at room temperature for a specific ageing time. For the constant strain-rate tests, this was 100 h; for the creep tests, this was either 10 000 or 2 h.

2.2. Constant strain-rate tensile tests

Tensile tests at constant strain rate were performed using an electromechanical testing machine. The extension rates varied from 10–0.001 mm min^{-1}, corresponding to strain rates of 5×10^{-3} to 5×10^{-7} s^{-1}. Testing in ethanol was performed using an environmental chamber that allowed the samples to be completely immersed. For each strain rate, tests in air and ethanol were conducted so that a comparison would enable departure points to be determined.

2.3. Creep tests

Creep tests were performed using dead-loaded tensile creep machines with a lever-arm ratio of 5:1. The extension of the samples was measured using transducers to an accuracy of ± 1μm. Measurement commenced 10 s after the load had been applied. Testing in ehtanol was possible using environmental chambers that allowed samples to be completely immersed. Creep tests were performed at a range of stresses (from 20–5 MPa) and for ageing times of 10 000 and 2 h. Both creep testing and constant strain-rate testing were carried out at a constant temperature of 2 °C.

3. Results and discussion

3.1. Constant strain-rate tests

The typical behaviour during the constant strain-rate tests can be seen in Figs 1 and 2 where curves for samples tested in both air and ethanol are shown. It can be seen that initially, the curve for the sample in ethanol follows the air curve exactly. Above a certain point, the curves separate. This is termed the departure point, and is due to the formation of crazes. Once crazes have formed, they will open up to accommodate the strain under a lower stress than the bulk material, thus causing the observed departure. Several samples were tested in ethanol to a point just past departure and were then examined using transmission optical microscopy. In all these cases, very small crazes were visible microscopically, but not with the naked eye. This confirms that the departure points correlate well with the formation of optically visible crazes.

The effect of strain rate can be seen by comparing Fig. 1 (high strain rate) with Fig. 2 (low strain rate). At the high strain rates, the departure points occur at a higher stress and are less abrupt than at low strain rates. This was found to be true for all the samples, except for those at the lowest strain rate used, where departure occurred at a surprisingly high stress. This has been found to be due to diffusional effects and will be discussed in more detail in a future paper.

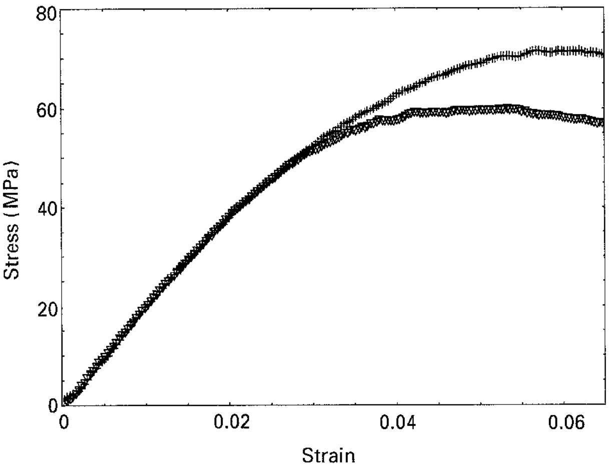

Figure 1 The variation of stress with strain for samples tested in (+) air and (▽) ethanol at a strain rate of 5×10^{-3} s^{-1}.

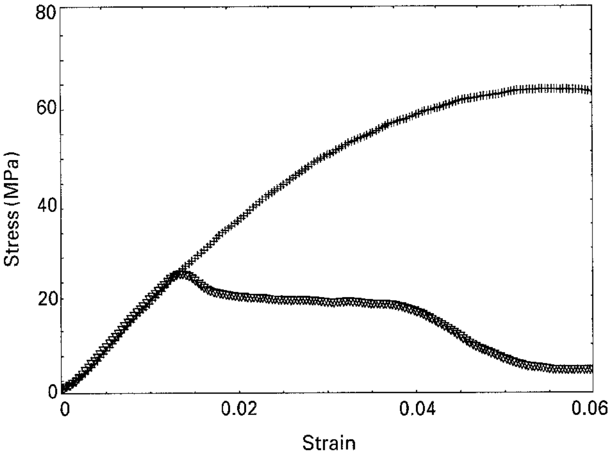

Figure 2 The variation of stress with strain for samples tested in (+) air and (▽) ethanol at a strain rate of 9.2×10^{-6} s^{-1}.

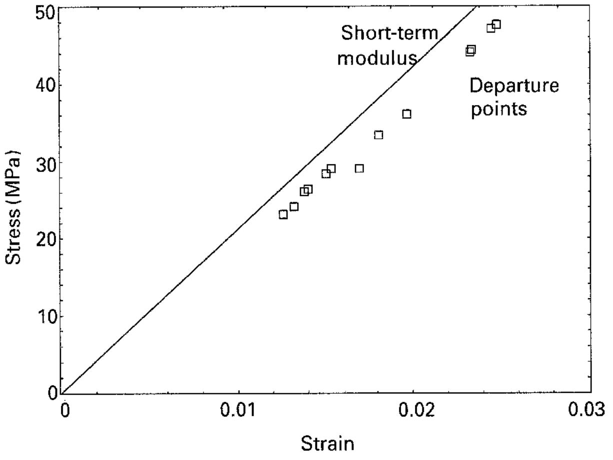

Figure 3 The stresses and strains at departure from the constant strain-rate tensile tests.

Fig. 3 shows the stress and strain at departure for all the samples tested. Also plotted is the short-term modulus, determined from the tests at high strain rate. It can be seen that the departure points lie on a straight line, which has a gradient slightly less than the short-term modulus and is offset from it by about 0.15%. This would seem to hold almost with a critical inelastic strain criterion. If it can be assumed that the short-term strain, often referred to as the "elastic" component, has no contributions from α processes, then initiation should occur when the total strain has exceeded the short-term strain by a certain amount (the critical inelastic strain). This would be represented by a line running parallel to the short-term modulus, but offset by an amount corresponding to the critical inelastic strain. Apart from the slightly lower gradient, which will be discussed below, the experimental situation would fit with this.

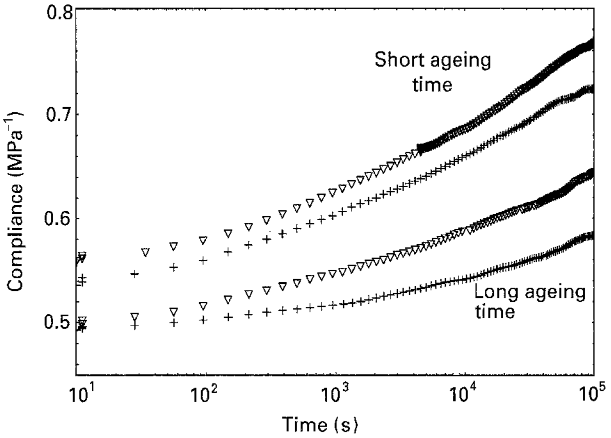

Figure 4 The tensile creep compliance for samples tested in air at stresses of (+) 10 and (▽) 20 MPa with ageing times of 2 and 10000 h.

3.2. Creep tests

To investigate this criterion more fully, creep tests were performed to allow craze initiation at lower stresses and also to investigate the effects of physical ageing. As has been mentioned above, physical ageing alters the relaxational behaviour of polymers. A longer physical ageing time will lead to a reduced free volume, which will hinder and slow down the α relaxations (the "inelastic" component) but has been shown to have little or no effect on the β and faster relaxations (the "elastic" component). Under the same stress, a sample with a long ageing time will, therefore, have a lower overall strain, with a lower proportion of "inelastic" strain than a sample with a short ageing time. By comparing the behaviour of samples with different physical ageing times, it should be possible to examine the effects of having different proportions of "elastic" and "inelastic" strain. The only limitation of this method is that large deformations (particularly the localized ones leading to crazing) effectively wipe out any prior physical ageing and so differences between samples may only be seen during the early part of a test.

The behaviour of samples tested in air is shown in Fig. 4. The compliance (ε/σ) is plotted against time for samples with ageing times of 2 and 10 000 h at stresses of 10 and 20 MPa. The following points can be seen from this:

(a) the samples with a short ageing time have higher initial compliances;

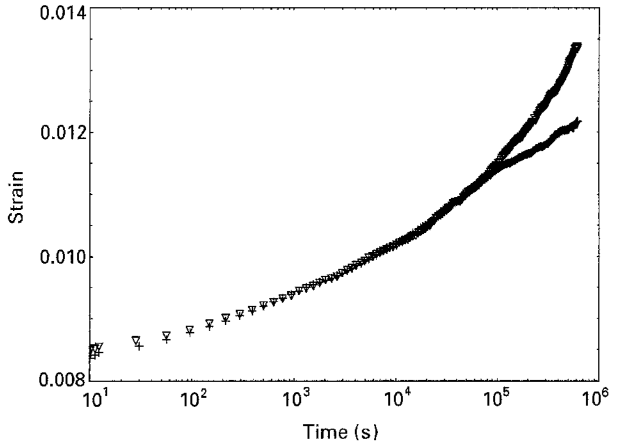

Figure 5 A typical departure point seen with a creep test in (+) air and (▽) ethanol. The applied stress was 15 MPa and the ageing time 2 h.

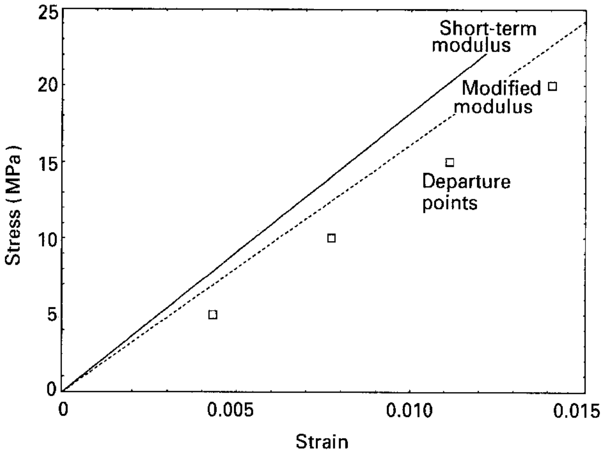

Figure 7 The stresses and strains at departure for the creep tests with a prior ageing time of 2 h. Also plotted is the short-term (10 s) modulus and the "modified" modulus (including the rapid α relaxations).

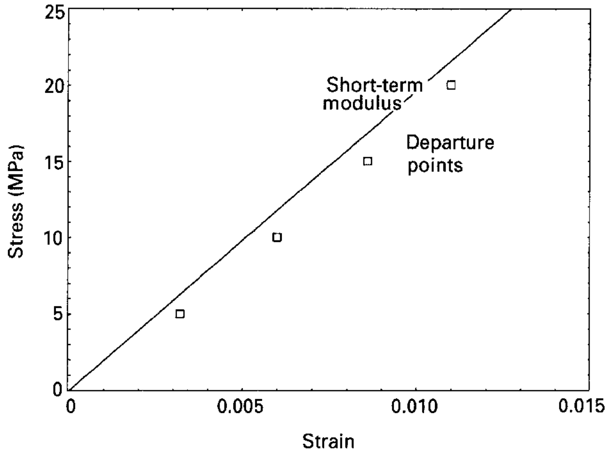

Figure 6 The stresses and strains at departure for the creep tests with a prior ageing time of 10 000 h. Also plotted is the short-term (10 s) modulus.

(b) the creep rates are initially higher for the samples with a short ageing time;

(c) at long times, the creep rates become independent of ageing time, a feature that occurs earlier with higher stresses.

The increase in initial compliance with the short ageing time is due to greater movement of the rapid α relaxations that occur in the first 10 s of testing, before the strain is recorded. The increased molecular mobility with short ageing time also accounts for the higher initial creep rate; however, with long times and large strains, the prior ageing becomes erased and the behaviour becomes independent of ageing time. Owing to the larger amounts of deformation, this happens sooner with the higher stress.

As before, comparison with samples tested in ethanol show departure points (Fig. 5) although as this is a constant load test rather than a constant strain-rate test, the ethanol curve increases away from the air curve. The departure points for a range of stresses from 5–20 MPa are plotted in Fig. 6 for the long ageing time and in Fig. 7 for the short ageing time. The departure points in Fig. 6 show a similar trend to the constant strain-rate tests, with the departure points lying parallel to the short-term modulus (the 10 s value) and offset by about 0.1%. These results would appear to hold very well with a critical inelastic strain criterion. For the short ageing time tests, however, the departure points have a significantly lower gradient and are offset to a greater degree, giving considerably higher overall strains to crazing. This is similar to the behaviour seen with the constant strain-rate tests, but to a greater extent.

For samples with a long ageing time, the faster α relaxations are hindered due to reduced free volume and molecular mobility. The slower α relaxations are much less affected, because by that stage, the imposed stresses have re-generated free volume.

For samples with a short ageing time, a larger amount of the strain has come from the fast α relaxations. As departure occurs at larger strains in samples with a short ageing time, and as most of this extra strain is from fast α relaxations, it would seem that these make little contribution to the crazing process. This leads to the idea that it is only the slower α relaxations that contribute to crazing, and that crazing occurs once these have reached a critical strain value.

A check on this can be made by subtracting the rapid α components of strain in the short ageing time tests. This is the additional strain accumulated in the early portion of the creep test. If this component is put into the "elastic" strain (i.e. that component that does not contribute to crazing) then the "elastic" modulus is reduced and now runs parallel to the departure points with an offset of 0.1%. This is shown as the dotted line in Fig. 7.

In summary, it seems that for polycarbonate in ethanol, crazing occurs when the slower α contributions have reached a strain value of 0.1%. This is a similar criterion to that of critical inelastic strain, except that the term "inelastic" needs some redefinition. The effect of a short ageing time is that the extra free volume allows more strain to accumulate from the rapid α relaxations that do not contribute to crazing and so higher values of strain to crazing are recorded.

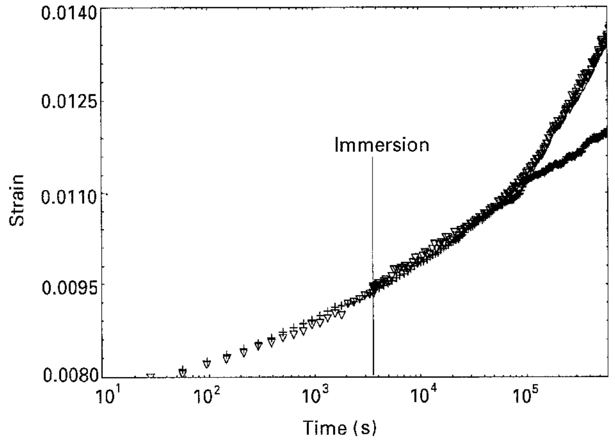

Figure 8. The tensile creep behaviour seen during a post-immersion test in (+) air and (∇) ethanol with an applied stress of 15 MPa and an ageing time of 2 h. The ethanol sample was immersed after 3600 s.

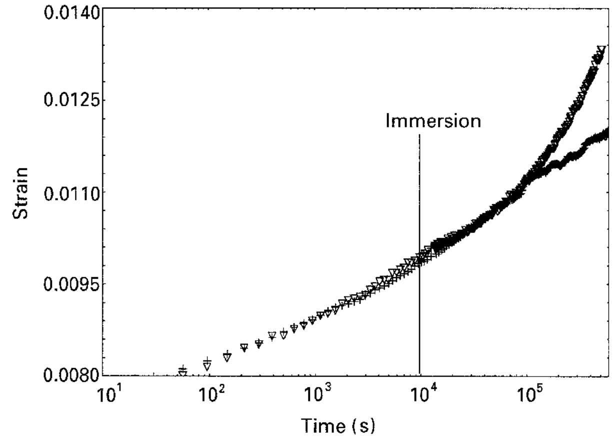

Figure 9 As Fig. 8, but with a post-immersion time of 10 000 s.

3.3. Post-immersion tests

A series of experiments was then devised to determine the effect of the environment on the formation and development of craze precursors before they become crazes. This was done by performing creep tests at a stress of 15 MPa. Tests were performed in air, in ethanol and where the samples were immersed in ethanol a certain time after being loaded in air (termed post-immersion tests). Thus a test with a post-immersion time of 10 000 s would be loaded in air and after 10 000 s would be immersed in ethanol (without interruption of the load). Tests were performed with post-immersion times of 0, 3600, 10 000, 86 400 and 500 000 s.

The behaviour of some of these tests is shown in Figs 8–10 for post-immersion times of 3600, 10 000 and 86 400 s. These can be compared with the standard ethanol test shown in Fig. 5. The departure times for all the tests are plotted against post-immersion time in Fig. 11. It was found that departure occurred at the same time (and strain) regardless of when the sample was immersed in ethanol. For the sample with a post-immersion time longer than the normal departure time, departure occurred immediately upon immersion.

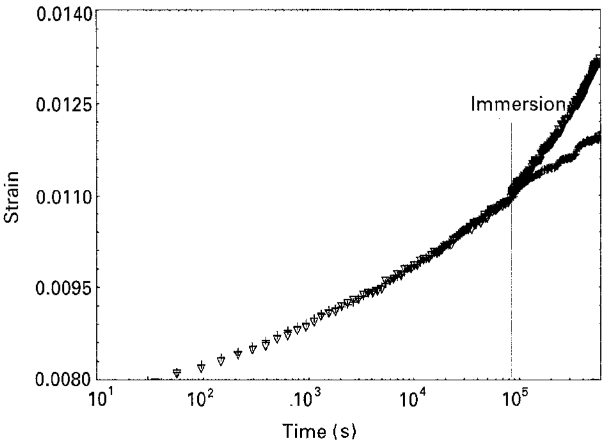

Figure 10 As Fig. 8, but with a post-immersion time of 86 400 s.

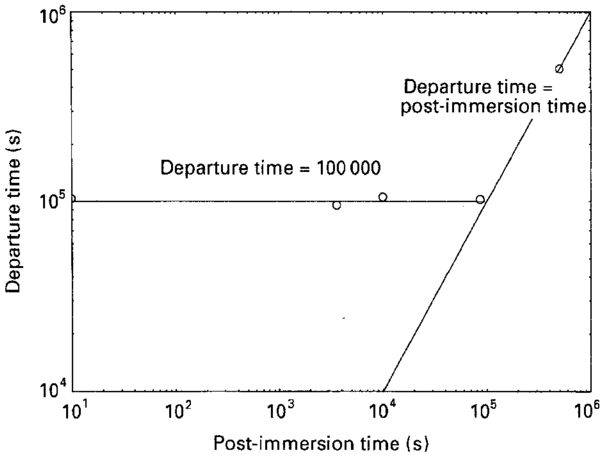

Figure 11 The departure times plotted against post-immersion time for the post-immersion tests.

These results show conclusively that in the stages leading up to craze formation, where very small craze precursors are developing and growing, the environment has no influence; craze precursor growth is the same in air as in the environment. It is only when craze precursors have grown to a particular size (which will be dependent on the particular polymer/environment combination) will crazing occur and the environment take an active role.

3.4. Implications for craze initiation criteria

From the above results, it can be concluded that environmental crazing occurs when the strain contributed by the slower α relaxations has reached a critical value. This critical value will almost certainly vary with polymer/environment combination, though the development of craze precursors up to the point of crazing is independent of the environment. This could well form the basis of a failure initiation criterion as the critical value of strain could be measured for various polymer/environment combinations. The only problem then is determining what proportion of the α relaxations contribute to crazing. To do this rigorously would require a sizeable amount of testing for every polymer. The simplest method would be to use the total a contribution, i.e. to use the inelastic strain criterion as discussed earlier. This would include a built-in safety factor of the early α relaxations that do not contribute to crazing; however, as these become less important as the ageing time increases, the discrepancy is likely to be small for long service lifetimes.

4. Conclusions

1. Departure points give a good indication of the formation of optically visible crazes in both constant strain-rate tests and in creep tests.

2. For constant strain-rate tests and for creep tests with a long ageing time, the departure points lie parallel to the short-term modulus, offset by about 0.1% strain.

3. For creep tests with a short ageing time, the departure strains are higher. Most of this extra strain results from rapid α relaxations that do not contribute to crazing.

4. Crazing occurs when the slower α relaxations have accumulated a certain amount of strain, in this case 0.1%.

5. Post-immersion tests have shown that the development and growth of craze precursors occurs independently of the environment.

6. A craze initiation criterion of critical inelastic strain works well, incorporating the built-in safety factor of the fast α relaxations that do not contribute to crazing.

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