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Failure of amorphous polystyrene

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The failure behaviour of amorphous polystyrene was studied in methanol and ambient air under constant load and strain rate conditions. The good correlation found between fracture mechanics theory and the test results of both crazing and fracture indicates that fracture mechanics theory can be used in predicting failure of amorphous polystyrene. From the fracture mechanics analysis of the results it is inferred that the kinetics associated with craze initiation and crack propagation are similar and that the inherent flaw responsible for failure first initiates the craze in which a crack is then formed. Both the distribution of inherent flaws and the kinetics of crazing and fracture are dependent on the test environment.

1. Introduction

Amorphous polymers exhibit failure by crazing and cracking in the presence of chemically active environments. It has been found that the crazes and cracks always develop normal to the direction of major principal stress and require some threshold condition of stress and strain for initiation and propagation. Previous studies [1–11] have established that both the threshold conditions of crazing and the propagation velocities of cracks in notched specimens can be described by fracture mechanics theories. However, for unnotched specimens the agreement between fracture mechanics theory and experiment is not good [5]. For these unnotched samples, failure is thought to be due to an "inherent" flaw that is generated during testing by dynamic processes associated with crazing [12]. Unfortunately, these inherent flaws cannot be characterized prior to fracture; hence the lack of success in applying fracture mechanics theory to predicting failure of unnotched samples.

The present investigation was designed as an exploratory study of the failure behaviour of unnotched, amorphous polystyrene under very simple experimental conditions. The time required for a sample to rupture was measured as a function of applied load and the craze initiation stress and fracture strength was measured as a function of strain rate. Fracture mechanics theory was applied to explain this time-dependent fracture behaviour in terms of parameters that can be easily measured. The theory is based on a linear elastic fracture mechanics approach that assumes failure is controlled by slow crack growth.

Amorphous polystyrene was chosen for this initial study because the fracture process in polystyrene has been well characterized [13–15]. These previous studies have shown that fracture is by a sequential process involving formation and growth of a craze, nucleation and slow propagation of a crack within the craze by coalescence of cavities, and finally rapid fracture of the remaining cross-section. Methanol was used as the test environment since both the crazing and fracture processes are accelerated in this environment [16].

2. Experimental

All test specimens were commercial tensile test specimens* made of Carinex GP polystyrene. The samples were injection moulded and had a nominal thickness of 3.18 mm, width of 12.70 mm, and gauge length of 106.10 mm.

The tensile tests at a fixed strain rate were carried out in an Instron testing machine that was fitted with an environmental chamber to allow testing in a methanol environment. The fracture

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*Tecquipment, Inc., Acton, MA 01720, USA.

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strength and craze initiation stress was measured at five different strain rates. The self-tightening tensile grips had sand blasted faces for gripping the samples and were connected to the Instron through a hook and ring arrangement that allowed for self-aligning of the tensile sample. No evidence of slippage in the grips was seen and only rarely was a failure in the grips observed. Test data were discarded when samples failed in the grips.

Ten stress rupture stations were constructed to permit testing of the samples in methanol under a constant applied load. The tensile grips were identical to those used in the strain-rate tests and were attached to the base plate and lever arm of the stress-rupture test machine by a hook and ring arrangement. The load was applied at the end of a 10:1 mechanical advantage lever arm. To prevent accidental shock to other specimens when a sample failed, the loading arm of each station was caught by a rubber bumper after a specimen failed.

3. Results

Load–displacement plots indicated that the deviation from linear behaviour of polystyrene tensile samples in methanol test environment occurred at about 70% the final fracture stress and that the actual deviation was less than 5%. This non-linear behaviour was observed to coincide with the onset of crazing. Permanent strain after fracture was less than 1%. Because this non-linear behaviour was small, it was assumed for the stress calculations that the strain rate was directly proportional to the stressing rate. In the stress rupture tests, less than 1% creep occurred during the duration of the tests.

Young's modulus (the slope of the linear portion of the stress–strain curve) in air was determined as a function of strain rate and the results are shown in Fig. 1. The modulus values given in Fig. 1 represent an average of the measurements obtained on 3 separate samples. Modulus was essentially constant from strain rates of 7.25×10^{-6} to $7.85 \times 10^{-4}\ \text{sec}^{-1}$ and then exhibited a small increase at a strain rate of $1.57 \times 10^{-3}\ \text{sec}^{-1}$. These modulus values were used in calculating the stressing rate associated with a given strain rate.

The results of the constant strain rate tests are summarized in Fig. 2 where the craze initiation stress is compared with the fracture stress as a function of stressing rate. The similarity of the dependence of these two stresses with stressing rate emphasizes the importance of crazing in determing fracture behaviour. Regression analysis of the median craze initiation stress ($\bar{S}_c$) and the fracture stress ($\bar{S}_f$) as a function of stressing rate ($\dot{\sigma}$) yields

$$\ln \bar{S}_c = 3.150 + 0.115 \ln \dot{\sigma} \qquad r^2 = 0.97 \tag{1}$$

$$\ln \bar{S}_f = 3.538 + 0.127 \ln \dot{\sigma} \qquad r^2 = 0.98, \tag{2}$$

where r is the correlation coefficient to a straight line.

The constant applied stress data is summarized in Fig. 3. A regression analysis of the median time-to-failure ($\bar{t}_f$) as a function of the applied stress (σ_a) gives:

$$\ln \bar{t}_f = 28.213 - 7.074 \ln \sigma_a \qquad r^2 = 0.97. \tag{3}$$

For the high applied stresses (>20 MPa) crazes formed during the initial application of the load and for the low stresses (>20 MPa) crazes formed within a few seconds.

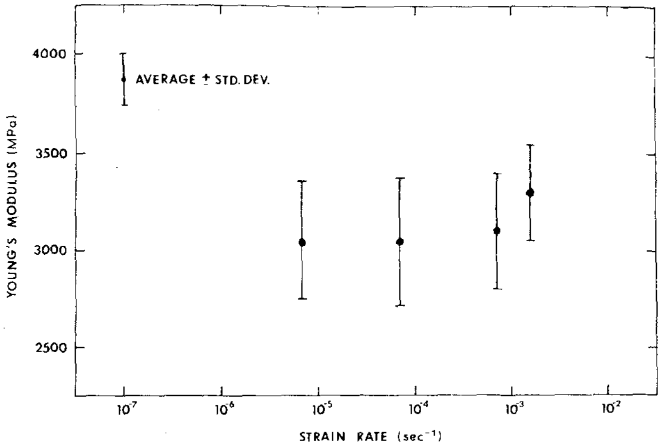

Figure 1 Young's modulus of amorphous polystyrene in air as a function of strain rate.

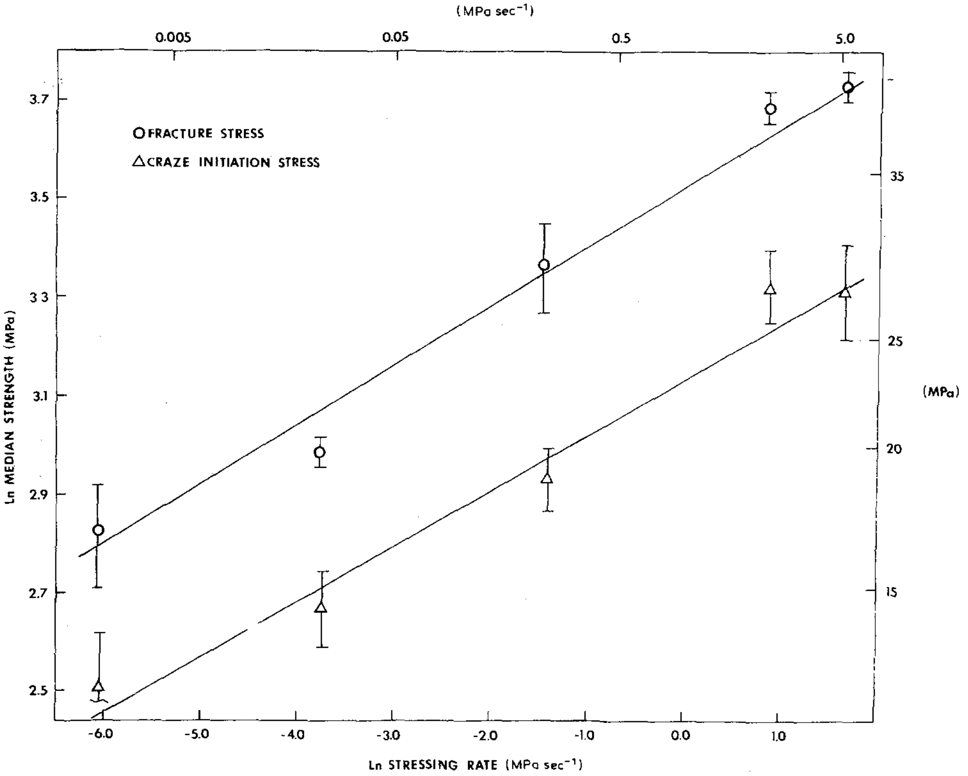

Figure 2 Median fracture strength and craze initiation stress of amorphous polystyrene in methanol as a function of stressing rate. Brackets indicate ± one standard deviation.

Observations of the fracture surface was generally supportive of previous studies [12–15]. The fracture surface could be divided into two main regions: the mirror region associated with the propagation of a crack within a pre-existing craze and the hackle (rough) region associated with crack growth beyond the original craze boundary. The observed micromorphological details of the mirror region showed areas that could be identfied with crack initiation and subcritical crack growth. Although there were differences in the size, shape, and location of the mirror region, these differences were not a simple function of strain rate or the applied stress.

The density of surface crazes in the region close to the fracture was observed to be strongly dependent on the fracture stress. At high stresses for both the constant stress and strain rate tests, the samples were heavily crazed. Conversely, at low stresses the samples had few and in some cases only one craze from which fracture ensued.

4. Discussion

Failure of amorphous polymeric materials involve two time-sensitive processes:

(1) Craze initiation that occurs after a stress-dependent time delay.

(2) Flaw propagation which is the stress-dependent growth to fracture of a flaw within a craze.

The lifetime of a component can, therefore, be considered as the sum of the times for completion of these two stages of failure. When the craze initiation time is much shorter than the time associated with flaw propagation and when the flaw growth rate can be expressed as a power function of the stress intensity factor ($V = AK_{\mathrm{I}}^n$), the time-to-failure (t_{f}) under a constant applied stress (σ_{a}) is [6]:

$$t_{\mathrm{f}} = \frac{2K_{\mathrm{Ii}}^{n-2}}{[(n-2)AY^2\sigma_{\mathrm{a}}^2]} \qquad (4)$$

where K_{Ii} is the initial stress intensity factor at the flaw tip, Y is a geometric constant, and A, n are constants related to the flaw growth rate. The initial stress intensity factor is related to the critical stress intensity factor (K_{IC}) by:

$$K_{\mathrm{Ii}} = (\sigma_{\mathrm{a}}/S_{\mathrm{i}})K_{\mathrm{IC}} \qquad (5)$$

where S_{i} is the strength of the component under

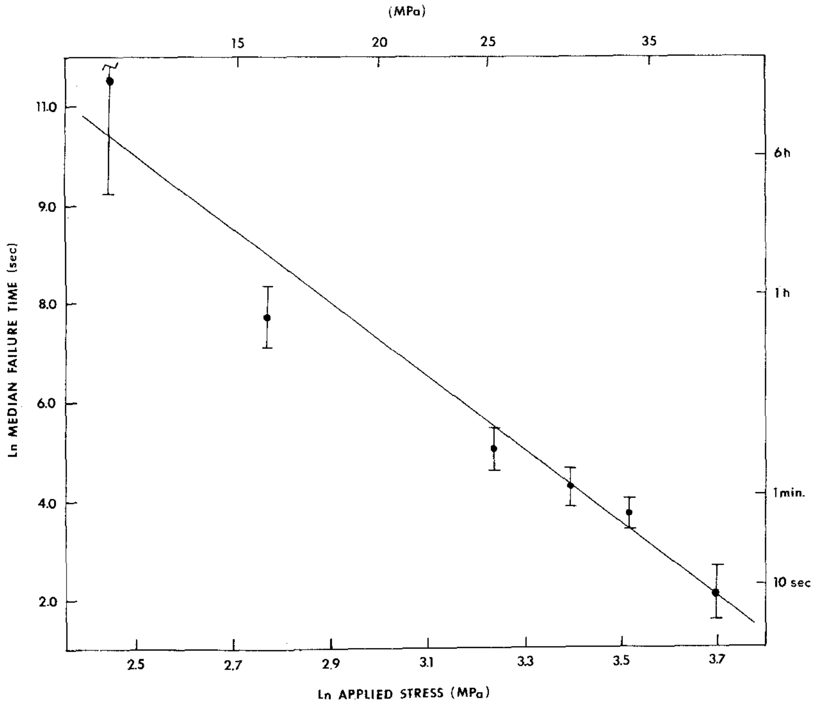

Figure 3 Median time-to-failure of amorphous polystyrene in methanol as a function of applied stress. Brackets indicate ± one standard deviation.

conditions where flaw growth does not occur and is a measure of the initial flaw severity. Substituting Equation 5 into Equation 1:

$$t_f = \left[\frac{2K_{IC}^{n-2}}{(n-2)AY^2}\right] S_i^{n-2}\sigma_a^{-n} = BS_i^{n-2}\sigma_a^{-n} \qquad (6)$$

where B is a constant equal to the term in brackets. By making similar assumptions as above, it can be derived that the fracture strength (S) measured at a constant stress rate ($\dot{\sigma}$) is given by [17]:

$$S = [B(n+1)S_i^{n-2}\dot{\sigma}]^{1/n+1} \qquad (7)$$

It is evident from the regression results of the fatigue data in Figs. 2 and 3 that the data can be well represented by Equations 6 and 7. This agreement tends to support the fracture mechanics approach to time-dependent failure of polystyrene where it is assumed that the time for flaw initiation is neglible with respect to the time for flaw propagation and that a simple power law relationship exists between subcritical flaw growth and stress intensity. By comparing Equations 6 and 7 with Equations 2 and 3, values of the flaw propagation parameter n can be determined to be 6.87 based on the constant strain rate tests, and 7.07 based on the stress rupture tests. This excellent agreement indicates that the kinetics of flaw growth under constant load is the same as under constant displacement rate, which agrees with crack velocity measurements on Perspex [6]. Also, the similarity of the dependence of craze initiation stress and fracture strength (Fig. 2) emphasizes the important effect of crazing in determining fracture behaviour. In fact, an equation of the functional form of Equation 7 can be used to represent the craze initiation stress data, although the physical meaning of S_i in this case is not clearly defined. Using Equation 6 the value of "n" for craze initiation can be determed from Equation 1 to be 7.70. This close agreement in "n" between fracture and craze initiation implies that the kinetics involved with craze initiation and fracture are similar as could be implied from previous observations [12, 15, 16] on microcrazing ahead of the crack tip.

Since fracture of these unnotched polystyrene samples is from flaws that are generated during testing, it is not possible to determine the inherent strength (S_i) of the samples. Without such measurements the fatigue constant B cannot be determined and fracture mechanics theory cannot be fully utilized in making failure predictions. However, the present authors have recently proposed a data analysis technique that gives information about the inherent strength distribution as well as about the flaw growth parameteres [18]. This technique assumes that the inherent strength is given by a two-parameter Weibull distribution:

$$\ln \ln (1/1-F) = m \ln (S_i/S_0) \tag{8}$$

where F is the cumulative failure probability and m and S_0 are constants. Substituting Equation 8 into Equations 6 and 7 gives:

$$\ln t_f = \ln B_0 + \frac{(n-2)}{m} \ln \ln (1/1-F) - n \ln \sigma_a \tag{9}$$

$$\ln S = \frac{1}{n+1} \left[\ln B_0(n+1) + \frac{(n-2)}{m} \ln \ln (1/1-F) + \ln \dot{\sigma} \right] \tag{10}$$

where $\ln B_0 = \ln B + (n-2) \ln S_0$. By assuming an initial value for n, the stress rupture data is ranked in terms of $[\ln t_f + n \ln \sigma_a]$ and the stress rate data in terms of $[\ln S + \ln \dot{\sigma}/(n+1)]$. A trivariant, regression analysis of the data is then carried out using Equations 9 and 10 to determine the constants n, $\ln B_0$, and m. This "regressed" value of n is now used to recalculate and rerank the data and the trivariant regression is reiterated until convergance on n is obtained. Therefore, this iterative, trivariant analysis not only determines the flaw growth parameter n but also the Weibull parameter m which represents the spread in the inherent strength distribution, i.e. severity.

Table I summarizes the results of the trivariant analysis. An excellent fit of the data was obtained as shown for constant stress rate in Fig. 4. This excellent agreement of the data with Equations 9 and 10 gives additional justification of the applicability of linear fracture mechanics concepts to the failure of polystyrene. Also this agreement of the data with Equations 9 and 10 indicates that the inherent strength distribution of these samples can be represented by a two-parameter Weibull distribution. The values for n agree quite well with those found previously from Figs. 2 and 3. The agreement between the values of m between the constant stress and strain rate tests implies that the distributions of the inherent flaws that form in the two tests are similar. The obtained values of m

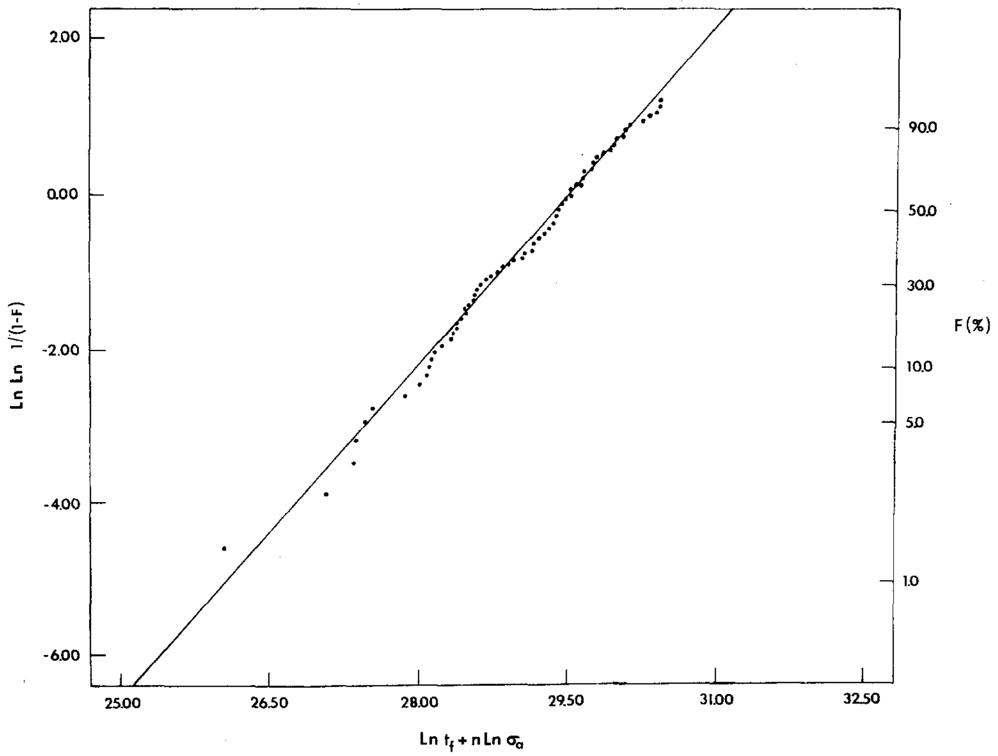

Figure 4 Results of iterative, trivariant analysis of constant stressing data for amorphous polystyrene in methanol. For clarity not all data points are shown.

TABLE I Summary of the results from the iterative, trivariant analysis of the constant stress and stressing rate data for amorphous polystyrene in methanol

Parameter	Constant stress	Constant stressing rate	
		Fracture strength	Craze initiation stress
m	8.00	8.37	7.53
n	7.43	7.52	7.66
$\ln B_0$	29.50	38.35	35.63
r^2	0.99 +	0.99 +	0.99 +

appear quite reasonable in comparision with values found for inorganic glass and ceramic materials [19]. However, there appears to be a real difference in the values of $\ln B_0$ as determined by the two tests. The parameter B_0 depends upon the crack propagation parameter B and the inherent strength parameter S_0. Fracture mechanics tests on Perspex [6] indicate that the crack propagation parameters A, n, and K_{IC}, which determine B, are independent of whether they are measured in a constant load or a constant displacement test. Thus, it is believed that the difference in B_0 as determined by the two strength tests is due to S_0, with a larger value of B_0 corresponding to a larger value of S_0. Since a large value of S_0 represents a higher inherent strength, i.e. a smaller initial flaw, the differences in the B_0 values imply that the severity of the flaw formed during testing is larger under constant load conditions than under constant stress rate conditions.

The similarity between crazing and fracture can again be demonstrated by assuming that an equation of the functional form of Equation 10 can be used to represent the craze initiation stress data. The application of Equation 10 to the craze initiation stress data implies that crazes form from inherent flaws that have a Weibull distribution. The results of this iterative, trivariant analysis yielded values of $n = 7.66$, $m = 7.53$, and $\ln B_0 = 35.63$ with an $r^2 = 0.99+$. These values are shown in Table 1. The similarity in the values of n determined from the craze and fracture data by the iterative, trivariant analysis gives strong support to the idea that the kinetics involved with craze initiation are similar to those of crack propagation. The correspondance in the values of m supports the concept that the inherent flaw responsible for failure first initiates the craze in which a crack is then formed.

TABLE II Summary of the results from the iterative, trivariant analysis of the constant stressing rate data for amorphous polystyrene in ambient air

Parameter	Fracture strength	Craze initiation stress
m	35.79	25.76
n	24.25	25.35
$\ln B_0$	99.78	102.478
r^2	0.99 +	0.99 +

To illustrate further the usefulness of the iterative, trivariant analysis, strain rate data for a limited number of polystyrene samples tested in ambient air was also analysed. The craze initiation stress and fracture strength of several samples were determined at each of five different strain rates. The results of the iterative, trivariant analysis are summarized in Table II. As with the results in the methanol test environment, it is seen that values of n and m as determined from craze and fracture data are similar. However, on comparing these results with those determined in the methanol test enviornment, it is evidence that the test environment effects not only the kinetics of crazing and fracture (n) but also the distribution of inherent flaws (m).

The excellent fit of the constant load and strain rate data with the iterative, trivariant analysis indicates that fracture mechanics theory can be used in predicting the failure of amorphous polystyrene. For example, suppose that polystyrene components are expected to survive 1 year under a constant applied stress of $4\,\text{MN}\,\text{m}^{-2}$, using the above determined values for n, m, and $\ln B_0$ from the constant stress data, the probability of failure under these service conditions is 5.6%. By decreasing the applied stress to $2\,\text{MN}\,\text{m}^{-2}$ for the same 1 year lifetime, the failure probability is reduced to 3×10^{-7} per cent, a vanishingly small number. Similar failure predictions could be made for either craze initiation stress or fracture strength under constant strain rate conditions. It should be noted that these failure probabilities are based on laboratory samples and have not been scaled for the fact that the test samples may be much smaller than actual polystyrene components. The reduction in allowable stress to account for scaling effects can be estimated from Weibull statistics [19].

5. Summary

The results of constant stress and stress rate tests on amorphous polystyrene in methanol and ambient air environments indicate that fracture mechanics can be used to predict the onset of crazing and fracture. In a given test environment good correlation was found between the results of the two loading modes in terms of the fatigue parameter, n, and the inherent flaw distribution parameter, m. Also, these parameters were quite similar to those for craze initiation, giving evidence to the postulate that crazing and slow crack growth in polystyrene are governed by a similar mechanism. The lack of correlation found between the values of the fatigue parameter B_0 as determined from the constant stress and stressing rate tests is believed to be due to the differences in the severity of the initial flaw formed under the two types of loading conditions.

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