Creep Fracture in Polymers: Technique and Data Handling for a Statistical Characterization

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SUMMARY

In this paper the need for a more thorough statistical characterization of creep fracture in polymers than is usually made is stressed. Then an automatic recording apparatus that can test a hundred specimens simultaneously is described. An example of data acquisition and handling is given for notched poly(methyl methacrylate). The results show a high degree of experimental scatter even for propagation-controlled creep fracture.

1. INTRODUCTION

Since polymers are used more and more in demanding engineering applications involving load-bearing, weather-resisting or deformable components, there is a need for more extensive data on these materials as well as for reliable design criteria and methodologies applicable to this class of materials.

It has been said that "the highest expression of engineering is in the use of incomplete information in designing and making useful, economical, safe and reliable structures" [1]. As regards materials, information is lacking on their in-service performance, and this is due to both the many uncertainties or variability of the service conditions and the inadequacy of the characterization customarily made. (The many standard test data available from handbooks and the supplier's technical bulletins have a limited or no predictive value of the probable performance in service.) While there cannot be any general remedy for the lack of information on in-service performance, there is no reason why more adequate and complete methods of characterization of the behaviour of materials should not have been developed and applied, at least under laboratory conditions.

This paper originates from such a pragmatic engineering motivation which applies to both the deformation and the failure behaviour of polymeric materials. There is one important difference between deformational properties and failure properties, however, which is relevant to their characterization, *i.e.* the statistical variability of failure properties. Experimentally determined characteristics such as the strength, the time to failure and the concentration of free radicals always show a wide scatter of values; they are stochastic variables [2]. This attribute stems from the highly localized nature of the failure phenomenon; the variability of the experimental results is thus inherent in this class of mechanical properties.

Since the variability of the measured values is an inherent characteristic of failure properties, proper characterization of failure behaviour should take it into account and accommodate its statistical aspects rather than circumvent them, as has already been pointed out [3]. The usual creep fracture testing of polymers is generally inadequate in this respect for two reasons: (i) the attention of the experimenter is almost always directed towards average values of the measured properties and (ii) statistical sample sizes are almost always too small for any statistical analysis.

The aim of this paper is to stress the need for a more thorough statistical characterization of creep fracture in polymers. An automatic recording apparatus that can test a hundred specimens simultaneously has been developed, and methods of data acquisition and handling are described.

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2. STATISTICAL ANNOTATIONS

The dynamic variables that we have to deal with are essentially time-dependent probabilities. The collection, organization and analysis of data or data "samples" on the basis of the laws of probability form the body of statistics. Even a brief recollection of the basic concepts of statistics would be outside the scope of this paper; reference is made to standard texts, *e.g.* refs. 4 and 5. Specific application of the statistical methodology to the design of fatigue experiments is treated in ref. 6. We shall therefore limit ourselves to a few remarks pertaining to the discussion to follow.

We shall regard the time t_f to fracture after loading as a real continuous random variable [4], and the *probability* $\mathscr{P}(t)$ *of the fracture after a lapse of time* t since loading as a non-increasing monotonic function of t, normalized so as to have the limiting values $\mathscr{P}(0) = 1$ and $\mathscr{P}(\infty) = 0$. It is also advisable to consider the *probability* $p(t)\,\mathrm{d}t$ *of fracture between* t *and* $t + \mathrm{d}t$ and the *unbroken-broken specimen transition probability* $K(t)$ which are related to $\mathscr{P}(t)$ by the following simple equalities:

$$p(t) = -\frac{\mathrm{d}}{\mathrm{d}t}\{\mathscr{P}(t)\} \tag{1}$$

$$K(t) = -\frac{\mathrm{d}}{\mathrm{d}t}[\ln\{\mathscr{P}(t)\}] \tag{2}$$

According to eqn. (2), the phenomenon is described as a decay process, with K representing the "instantaneous" decay rate. $\mathscr{P}(t)$ and $p(t)$ are also commonly referred to as the cumulative probability distribution and the probability density function respectively.

The main task of the statistical characterization of creep fracture is the evaluation of the above probabilities by means of a limited number of experimental determinations on a finite number of specimens, *i.e.* a statistical sample. If N is the number of statistically equal specimens forming the sample, which are separately loaded under identical test conditions and are such that all rupture events are independent, the probability $P_{m,N}(t)$ that m out of N specimens are unbroken at t will follow the binomial distribution

$$P_{m,N}(t) = \binom{N}{m}\mathscr{P}(t)^m\{1-\mathscr{P}(t)\}^{N-m} \tag{3}$$

Hence the fraction $n(t)/N$ of specimens *actually* unbroken at an instant t will fluctuate around the mean value $\mathscr{P}(t)$ with a standard deviation [4, 5]

$$\Delta\mathscr{P}(t) = \left[\frac{\mathscr{P}(t)\{1-\mathscr{P}(t)\}}{N}\right]^{1/2} \tag{4}$$

All the quantities introduced above are schematically represented in Fig. 1. It should be noted that the binomial distribution is non-uniform along the time axis. It is approximately symmetrical around its mean $\mathscr{P}(t)$ when $\mathscr{P}(t)$ is not too close either to zero or to unity and if N is fairly large; as $\mathscr{P}(t)$ approaches either zero or unity at the extremes of the time scale, the two bounds $\mathscr{P}(t) \gtrsim 0$ and $\mathscr{P}(t) \lesssim 1$ make the binomial distribution highly skewed.

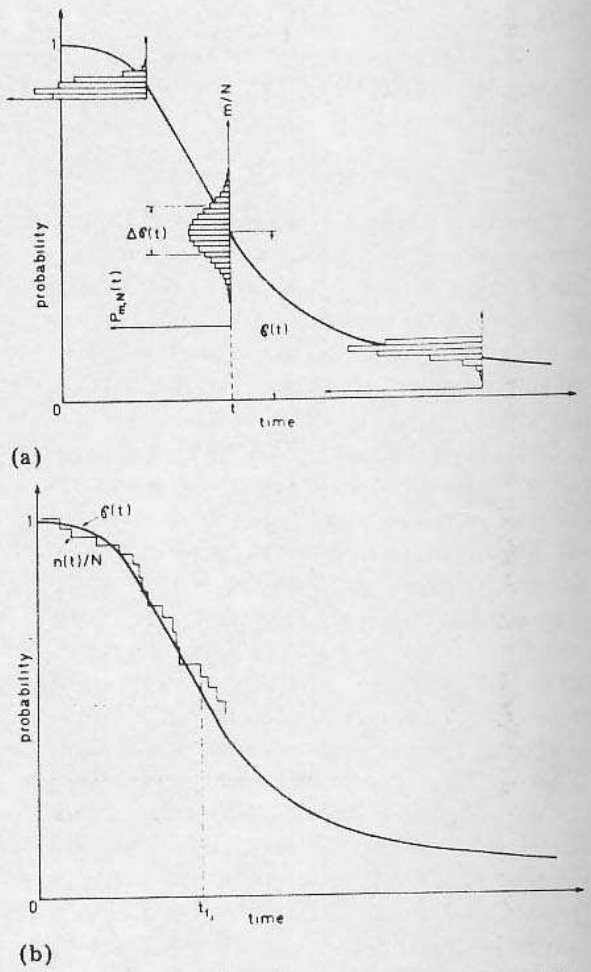

Fig. 1. (a) Probability $\mathscr{P}(t)$ *vs.* time t and time evolution of the probability $P_{m,N}(t)$; (b) probability $\mathscr{P}(t)$ and actual fraction $n(t)/N$ of unbroken specimens *vs.* time t. (All drawings are schematic.)

2.1. Sample size

The size of a statistical sample determines of course the precision with which any particular characteristic or property can be statistically estimated; the larger the sample size used, the more precise is the statistical estimate obtainable. In the planning of experiments the sample size has thus to be chosen, in general, as a compromise between the desired minimum variance estimation and the cost and trouble of testing a high number of specimens.

If the quantity that we are interested in is the probability function $\mathscr{P}(t)$, the precision of its statistical estimate can be measured by its standard deviation $\Delta\mathscr{P}(t)$ which is given by eqn. (4). This is a function of time which passes through a maximum as it ensues from the general properties of the function $\mathscr{P}(t)$ previously mentioned. While the position of this maximum on the time scale depends on the particular form of the function $\mathscr{P}(t)$, its extreme value $\Delta\mathscr{P}_{max}$ does not the derivation of $\Delta\mathscr{P}$ with respect to $\mathscr{P}$ in eqn. (4) gives

$$\Delta\mathscr{P}_{max} = (2N^{1/2})^{-1} \tag{5}$$

The maximum absolute error $\Delta\mathscr{P}_{max}$ in the experimental determination of the probability $\mathscr{P}(t)$ is thus dependent on the sample size N only. Equation (5) enables us to calculate the size of the statistical sample required to obtain the desired value of $\Delta\mathscr{P}_{max}$. For example, if the maximum tolerance on the estimate of $\mathscr{P}(t)$ is 0.05, *i.e.* if the probability $\mathscr{P}(t)$ is to be determined with a precision $\Delta\mathscr{P}(t)$ of less than or equal to 0.05 over the entire time scale, a sample of $N = 100$ specimens is needed. This condition is clearly conservative.

2.2. Form of the distribution function $\mathscr{P}(t)$

Whenever we can write an expression for the function $\mathscr{P}(t)$, *i.e.* whenever a parametric mathematical model can be assumed or proposed, a best-fit analysis of the data can be performed*. The primary product of such an analysis is of course the estimated values of the parameters of the distribution. As a by-product of the best-fit analysis, an estimate of the error $\Delta\mathscr{P}(t)$ can also be obtained via eqn. (4). This then makes it possible to test the goodness of the fit and so to judge quantitatively the validity of the trial function examined.

As a test of the best fit, it is often convenient to use the χ^2 test, as χ is a direct measure of the deviations of the experimental data from the fitting curve; in our notation,

$$\chi^2 = \sum_{j=1}^{N} \left| \frac{1 - n(t_{f_j})}{N - \mathscr{P}(t_{f_j})} \right|^2 \Big/ \{\Delta\mathscr{P}(t_{f_j})\}^2 \tag{6}$$

in which t_{f_j} is the set of measured values of the time to fracture and $n(t_{f_j})$ is the actual number of specimens surviving in the experiment at the instant $t = t_{f_j}$. According to its definition, the smaller the value of χ, the better is the fit.

3. TEST APPARATUS AND PROCEDURE

A satisfactory statistical characterization of creep fracture is not a trivial task, as it calls for testing a large number of specimens over long time intervals for each set of test conditions (deformation mode, stress level, temperature and environment). In designing our apparatus we set the following target: (i) a large number of testing stations within a single compact instrument; (ii) automatic recording of the breaking events; (iii) retention of the failed specimen; (iv) temperature control above room temperature; (v) reasonably practical, simple and economical manufacture.

3.1. Apparatus

The instrument that we have set up can contain and simultaneously test up to 104 specimens in a cabinet 100 cm × 70 cm × 80 cm in size. The test stations are distributed over two planes (Fig. 2(a)), and on each plane they are arranged in a centre-faced pattern (Fig. 2(b)), so as to minimize the encumbrance of the loading weights. Figure 2(c) shows the three-point bend fixture used in this study, but other variants of specimen shape and loading configuration could easily be accommodated. When a specimen breaks, its load falls and hits a stopper that operates a lever switch. This activates an impulse generator, which monitors the event; its output signals are recorded on a constant-speed chart recorder (Fig. 2(d)).

*This practice can be criticized on the grounds of the complexity of the mechanisms underlying the fatigue phenomena; the observable lifetime is an integral result of this (ref. 6, p. 222).

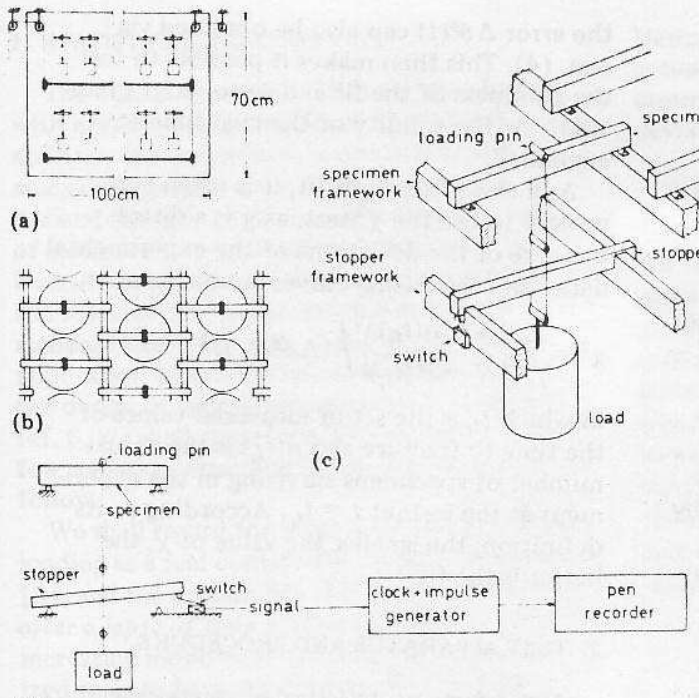

Fig. 2. Automatic recording apparatus for the measurement of times to fracture in creep: (a) arrangement of test stations in the thermostatically controlled cabinet, showing the two-floor hoist for lifting the loads (front view); (b) centre-faced load pattern (top view); (c) three-point bend fixture; (d) layout of the testing instrument and ancillary equipment.

To prevent any transmission of shocks or vibrations to the surviving specimens, the two frameworks supporting the specimens and the stoppers are independent and rest on suitable dampers.

Temperature control in the cabinet is to within ±1 °C; this is provided by a regulated electrical heater and forced ventilation.

The structure of the impulse generator monitor makes it possible to calibrate each signal. Each rupture event and time can thus be related to the corresponding individual specimen. This enables us to examine each fractured specimen after completion of the test and to relate its appearance to the corresponding time to fracture. There are two aims in doing this. Firstly, spurious ruptures such as those due to holes or other macroscopic defects in the specimen may be recognized by subsequent optical examination and, consequently, the corresponding data points can be censored. Secondly, the appearance of the fracture surfaces can provide valuable supplementary information on the type of fracture and modes of crack propagation. For example, the proportion of oblique fracture surface area to flat fracture surface area on each specimen could be measured and whether it bears any relationship to the dynamics of the creep fracture phenomenon as characterized by the observed time to fracture could be investigated.

3.2. *Procedure*

The loading operation is very simple, although it requires some accuracy. First the weights are placed precisely in their positions on the plates of the hoist. This is held at a height such that the loading pins are slightly above their in-service position. Next each specimen is inserted between the loading pin and supports and is set in place with the notched centre-line exactly midway between the supports and square to their axes by means of a special tool.

The thermostatically controlled cabinet is then closed and, when thermal equilibrium is reached, the test can be started. The hoist is gently lowered (from outside by pulleys) until the weights hang freely. At this instant the clock and the impulse generator monitoring unit are activated.

4. EXAMPLE AND COMMENTS

As an example of the statistical characterization of creep fracture in polymers with data obtained in a single experiment by means of the apparatus just described, we shall report here the results of a test carried out on a sample of poly(methyl methacrylate) (PMMA). In this experiment the number of specimens loaded simultaneously was 97.

4.1. *Material and preparation of specimens*

The material used in this experiment was commercial Vedril 9D, a heat-resistant grade PMMA manufactured by Montedison SpA and characterized by a tensile strength of 75 MPa [7], a heat distortion temperature (1.85 MPa) of 105 °C [8] and a Vicat softening point (0.1 kPa) of 120 °C [9]. The polymer which was supplied in the form of pellets was compression moulded at 190 °C under a pressure of 5 MPa into plates 12.7 mm thick, from which 127 mm × 12.7 mm × 6.5 mm bars were cut. A flat sharp notch was produced in the narrower edge of each bar by means of an automatic cutting machine equipped with a razor blade. The notch tip radius was not measurable.

The specimens were not subjected to any particular thermal treatment prior to testing; they were stored at 22 °C and 50% relative humidity for a few days.

4.2. *Test conditions*

The single-edge-notched specimens were tested in flexure (three-point bending) and loaded to a nominal applied stress of 0.713 MPa, giving an initial stress intensity factor K_{Ii} of 0.171 MPa $m^{1/2}$. The stress intensity factor K_I is defined as $K_I = \sigma Y a^{1/2}$ where σ is the nominal applied stress, Y a geometrical factor and a the crack length. The subscript I refers to the crack-opening mode of failure. The value of Y for three-point bending is given by a fourth-degree polynomial [10]. For the chosen conditions (span $S = 100$ mm; specimen depth $W = 12.7$ mm; notch length $a_i = 7.00$ mm), $Y = 2.875$.

The measurement was made in air at 90 °C.

4.3. *Results and statistical analysis*

The distribution of measured lifetimes is plotted in Fig. 3 (full circles) as the fraction $n(t_{f_j})/N$ of specimens surviving at each time

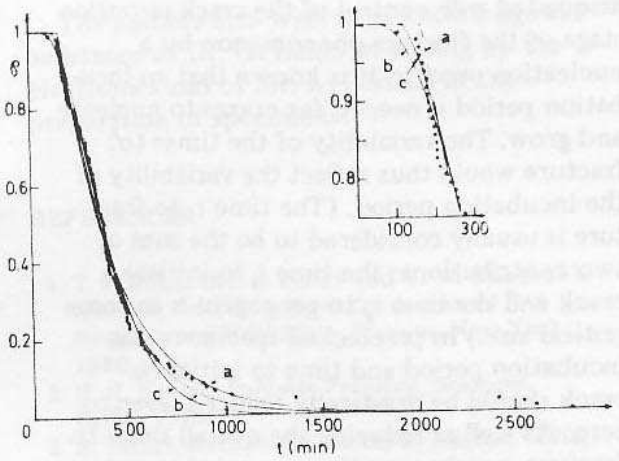

Fig. 3. Cumulative distribution of the measured times to fracture (●) and the fitting curves of the functions (curves a, function (a); curves b, function (b); curves c, function (c)) given in Table 1 (see text). The inset shows an enlargement of the initial part of the distribution.

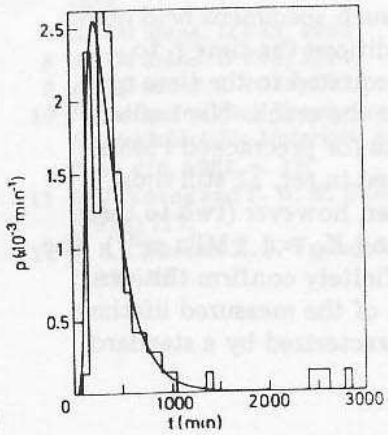

Fig. 4. Density distribution of measured times to fracture (histogram) and density function corresponding to the fitted log-normal distribution (full curve).

t_{f_j} at which a specimen j broke. In Fig. 4 the same data are replotted in the form of a histogram as $\Delta n(t)/(N\,\Delta t)$ where $\Delta n(t)$ is the number of specimens broken at times between t and $t + \Delta t$ and Δt is a constant suitable time interval. In other words it could be said that Figs. 3 and 4 show the *experimental* cumulative distribution $\mathscr{P}(t)$ and density function $p(t)$ respectively.

It is worth noting the width of the distribution of these experimental data. It has often been assumed that a considerable scatter in the times to fracture for glassy polymers is

associated with control of the crack *initiation* stage of the fracture phenomenon by a nucleation process. It is known that an incubation period is needed for crazes to nucleate and grow. The variability of the times to fracture would thus reflect the variability of the incubation period. (The time t_f to fracture is usually considered to be the sum of two contributions: the time t_i to initiate a crack and the time t_p to propagate it to some critical size.) In precracked specimens the incubation period and time to initiate a crack should be drastically reduced, even to zero. As well as reducing the overall times to fracture, notches are thus expected to reduce the scatter in the times to fracture (ref. 3, p. 142). In fact, from a comparative study on the time-dependent fracture of PMMA carried out on both notched and unnotched specimens, Young and coworkers [11, 12] concluded that in notched PMMA specimens the fracture stress is controlled principally by *propagation*. For such specimens held under creep loading conditions the time t_f to fracture was thus equated to the time t_p taken to propagate the crack. The limited time-to-failure data for precracked PMMA specimens presented in ref. 11 still show a considerable scatter, however (two to three decades at 20 °C and $K_{Ii} \approx 1.1\,\mathrm{MPa\,m^{1/2}}$). The present results definitely confirm this variability. The width of the measured lifetime distribution is characterized by a standard deviation of 483 min around a mean lifetime of 501 min. The dispersion is expected to increase even further with decreasing temperature and increasing stress intensity factor. A consideration of these facts clearly raises the question of the statistical significance of single-point testing. Even an indication of the average time to fracture alone would, in practice, provide a little information. The need for a thorough probabilistic characterization is evident.

Some estimated distributions obtained by fitting some trial functions to the experimental points are also shown in Figs. 3 and 4 (full curves). Three mathematical models were examined: (a) an exponential distribution, with a constant decay rate beyond a threshold time (one parameter with a threshold); (b) a log-normal distribution (two parameters with no threshold); (c) a three-parameter Weibull distribution (two parameters with a threshold). The analytical expressions for (a)–(c) are given in Table 1, together with the best-fit estimates of their parameters. (It should be noted that the parameters have the same meanings in the different functions: τ_0 represents a threshold or minimum lifetime (the "fail-safe" time), τ is a characteristic lifetime in the distribution and β is a shape parameter.)

The best-fit analysis was performed by a least-squares procedure based on a χ^2 parabolic extrapolation and by weighting the data

TABLE 1

Fitted probability distribution functions and best-fit estimates

Distribution function	*Analytical expression*		τ_0 (min)	τ (min)	β	χ^2
(a) Exponential with threshold	$\mathscr{P}(t) = 1$	for $t \leq \tau_0$	168	286	—	132
	$\mathscr{P}(t) = \exp\left\{\frac{-(t-\tau_0)}{\tau}\right\}$	for $t > \tau_0$				
(b) log-normal	$\mathscr{P}(t) = \frac{1}{\beta\pi^{1/2}} \int_t^\infty \frac{1}{t'} \exp\left[-\left\{\frac{1}{\beta}\ln\left(\frac{t'}{\tau}\right)\right\}^2\right] dt'$		—	368	0.75	64
(c) Three-parameter Weibull	$\mathscr{P}(t) = 1$	for $t \leq \tau_0$	113	447	1.56	514
	$\mathscr{P}(t) = \exp\left\{-\left(\frac{t-\tau_0}{\tau-\tau_0}\right)^\beta\right\}$	for $t > \tau_0$				

with a constant absolute error. As a test of the goodness of the three best fits, in Table 1, last column, we show the corresponding χ^2 values computed according to eqn. (6). The complete expression (6) was used here, including a varying error $\Delta\mathscr{P}(t)$; it was possible to determine this *a posteriori* as a deviation with respect to the value of the best-fitted function $\mathscr{P}(t)$ via eqn. (5). To avoid singularities, eight out of the 97 experimental points (at the two tails of the distribution) had to be excluded in this last analysis. According to the χ^2 test the log-normal distribution model turns out to give the best statistical fit of the set of data presented here merely as an example.

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