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The disentanglement time of the craze fibrils in polymethylmethacrylate

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A breaking time has been defined for the fibrils in the craze at the tip of a steady-state moving crack. It has been shown that, for polymethylmethacrylate above the critical temperature of −20° C, the fibrils of the craze at the crack tip break due to a thermally activated process. The activation energy is equal to 23 kcal mol^{-1}, which corresponds fairly closely to the activation energy of the β relaxation. Then, the breaking time is probably a disentanglement time rather than a breaking time of chains, and this may be used to explain the time–temperature behaviour of the macroscopic fracture toughness.

1. Introduction

Many polymers develop crazes before or during breaking. The craze is a very small zone at the crack tip where the polymer is highly oriented. The polymeric material is drawn out of the bulk and forms fibrils interspersed by microscopic voids. One of the most important problems relating to crack propagation in polymers is the breakage of the fibrils of the craze. So, the study of polymer fracture is actually the study of the formation of the craze and the breakage of the fibrils of the craze.

The phenomenon of craze formation in brittle polymers is now quite well known. It has recently been shown that the fibrils grow by pulling fresh material out of the bulk rather than by increasing their draw ratio [1, 2]. The process seems to be thermally activated by the β relaxation [3]. The draw ratio of the fibrils is nearly constant over the whole craze volume. Nevertheless, it is slightly higher in the so-called "mid-rib" region and also at the craze end and tip [4, 5]. The draw ratio of the fibrils may be understood as some kind of natural draw ratio of the polymer. The molecules in the fibrils are highly oriented: the fibrils recover their original bulk structure when they are heated to even a mere 20 degrees below the glass transition temperature [6].

The problem of fibril breakage is much less well known, and it is not very easy to decide whether the fibrils break in the mid-rib region because of additional creep or some other mechanism: slippage and disentanglement, fibril rupture through breakage of chains etc [7]. The craze opening does not seem to be an efficient fracture criterion for the fibrils because it is related not to the extension ratio of the fibrils but to their length which is simply proportional to the amount of fresh material pulled out of the bulk. It has been shown that there are probably two mechanisms of breakage, depending on the temperature [8]. Above a certain critical temperature the craze breaks smoothly, probably in the mid-rib region, leaving two craze layers on each fracture surface. Below that temperature, the craze breaks in a very irregular way, forming many side crazes and leaving a fairly rough fracture surface.

2. Theory: the definition of the breaking time of the fibrils

In this paper another description of the craze fibril breakage will be developed, in order to associate an activation energy to the breakage phenomenon: the life-time τ of the craze fibril under a certain load or the time during which a fibril can carry a certain load before breakage. It is a convenient way of displaying the breakage properties of the craze fibrils and might be an intrinsic property of the fibrils. As will be seen later, this time could be interpreted as the disentanglement time of the macromolecules of the fibril: the disentanglement time of the fibrils.

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If a single planar crack in the plane strain state is propagated above the critical temperauture, a single craze exists at the crack tip with a well known shape [9] which can be observed by means of interferometry [10]. The crack–craze system may propagate in three ways, depending on the loading level and the craze size as shown in Fig. 1.

1. The case of craze growth (which seems to be thermally activated) has been studied by Döll *et al.* [11].

2. Experiments have been carried out for the case of crack growth without craze growth (the fibrils breakage) by using a very long craze (obtained by the craze growth technique) suddenly and strongly loaded. Photographs of the interference patterns were taken at a rate of 3 pictures per second. The craze being longer than the craze at the tip of a steady-state propagating crack, case (b) of Fig. 1 arises. As shown in Fig. 2, the craze tip remains immobile, whereas the crack tip propagates into the craze. These experiments clearly show that the fibril growth at the craze tip and the fibril breakage at the craze end are two independent mechanisms.

3. The third case of Fig. 1 is the case of a steady-state propagating crack: the craze tip moves at the same velocity as the crack tip. The rate of fibril production is the same as the rate of fibril breakage. Then the breakage time of a fibril can be easily defined as the longest time a fibril can carry the stress σ_c at the craze boundary before breakage. Notice that the "oldest" part of a fibril growing by pulling fresh material from the bulk is the middle of the fibril (Fig. 3). If S is the craze length and $\mathrm{d}a/\mathrm{d}t$ the crack–craze velocity, the breaking time τ is:

$$\tau(\sigma_c) = S/(\mathrm{d}a/\mathrm{d}t) \tag{1}$$

for the part of the fibril drawn out of the bulk at the crack tip.

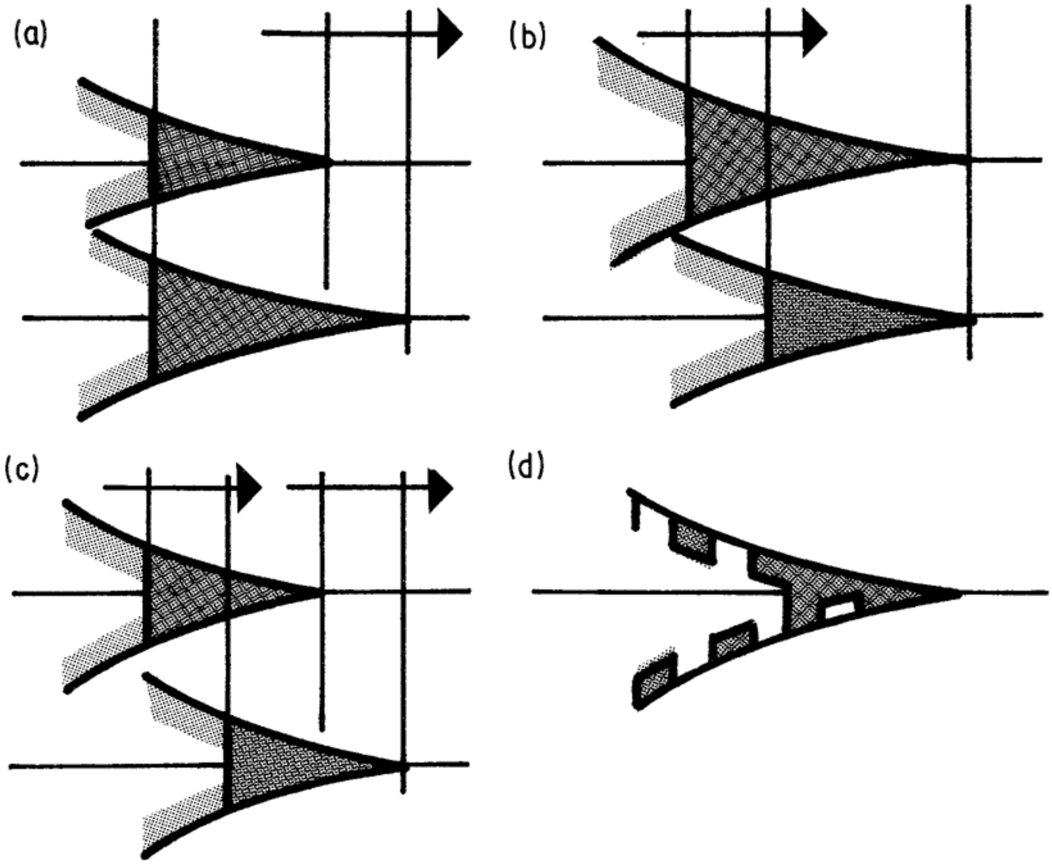

Figure 1 A, B and C show, at 2 successive moments, 3 types of evolution of a moving crack–craze system. (a) Static fatigue craze growth: new material flows into the craze. No crack growth. Generally a transient state. (b) No material flows into the craze but the craze fibrils break: the crack tip moves into the craze. Generally a transient state. (c) Steady-state propagation: craze growth and craze breakage occur at the same rate. (d) Random rupture of the craze: discontinuous phenomenon, not studied here.

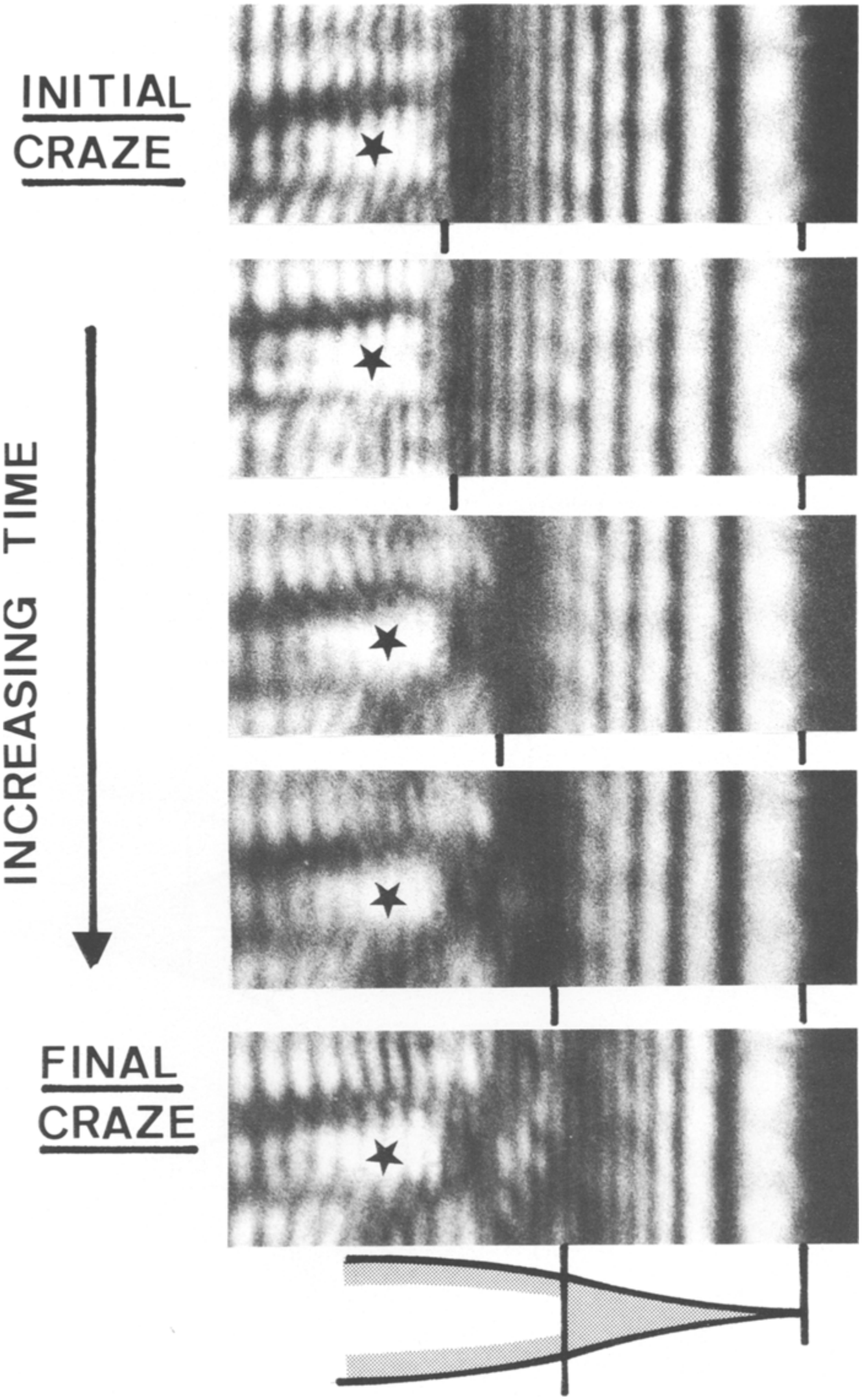

Figure 2 The interference pattern at successive times of a long craze suddenly and strongly loaded: the craze tip remains immobile whereas the crack tip moves into the craze. The fibrils break until the craze length is sufficient for steady-state propagation. The stars show a defect on the fracture surface that proves the craze tip does not move.

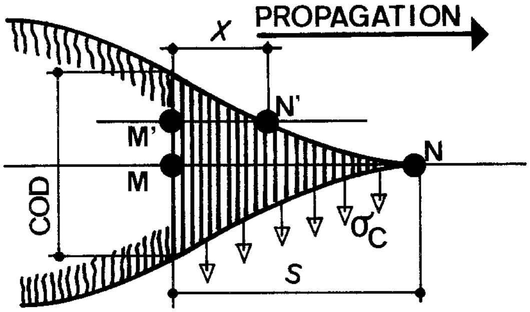

Figure 3 The age of the molecules in the craze fibrils produced by pulling fresh material out of the bulk and propagating at a constant velocity $\mathrm{d}a/\mathrm{d}t$: the molecule M′ enters the craze at point N′ and carries the load σ during a time lapse $\tau = X/(\mathrm{d}a/\mathrm{d}t)$. The "oldest" part of the fibril is the middle, where $X = S$.

3. Experimental procedure and results

In order to measure τ, a single crack–craze system was propagated in a compact tension specimen using an apparatus similar to that described in [12] and having a heating chamber as described in [8]. The propagation velocity was constant and obtained by static loading at temperatures of −10, 20 and 60° C in polymethylmethacrylate (PMMA). The velocity was varied between 10^{-5} and $0.1\,\mathrm{mm\,sec^{-1}}$. Photographs of the interference pattern of the craze were taken and the load on the sample measured. The experimental results obtained are the fracture toughness K_{1c}, the craze length S and the craze width COD as a function of crack speed and temperature. These curves are shown in Fig. 4. By means of the Dugdale model the stress at the craze boundary can be estimated as:

$$\sigma_c = \left(\frac{\pi}{8S}\right)^{1/2} K_{1c}. \qquad (2)$$

By means of Equation 1, τ is calculated as a function of σ_c. Fig. 5 shows the obtained breaking time as a function of the stress σ_c at the craze boundary. There are 3 curves for the 3 temperatures −10, 20 and 60° C. The breaking time is always between 0.1 and 1000 sec, due to the crack–craze propagation speed, which can only be selected between 10^{-5} and $0.1\,\mathrm{mm\,sec^{-1}}$. Despite some scatter of the experimental points, it can be clearly seen that the 3 curves may be superimposed by a simple horizontal shift along the time axis, as shown in Fig. 6. The master curve on that figure shows the breaking time as a function of the stress over 8 decades of time. The left end of the plot (0.001 sec) corresponds to a crack velocity of about $30\,\mathrm{mm\,sec^{-1}}$, (too fast to follow under the microscope) and the right end (10^5 sec) to $3 \times 10^{-7}\,\mathrm{mm\,sec^{-1}}$, which is a very low speed difficult to achieve practically. None of the other curves (K_{1c}, S, COD) can be shifted like τ to obtain a master curve. Therefore τ, which is a property obtained by combining K_{1c} and S, is probably more significant than K_{1c} or S alone.

The experiments must be very carefully conducted to keep the final scatter at an acceptable level. The values of K_1, in particular, are very sensitive to twisted crack planes or imperfect crazes over the whole sample thickness. The physical or chemical ageing of PMMA seems to play an important role in the shape of the craze. Much care has been taken to measure reproducible values of K_{1c} and craze shape. Very old PMMA sheets (5 years old) gave no reproducible values and irregular crazes, whereas moderately old sheets (1 year old) gave good results. The sheets must not be too fresh, because the physical ageing may be visible.

4. Discussion and molecular interpretation

4.1. Relation between breaking time and fracture toughness

The macroscopic fracture toughness K_{1c} can be easily calculated as a function of τ and the craze stress σ_c by means of the Dugdale model.

$$S = \pi K_{1c}^2/8\sigma_C^2. \qquad (3)$$

Combining Equations 1 and 3:

$$K_{1c}^2 = 8\tau\sigma_c^2\pi^{-1}(\mathrm{d}a/\mathrm{d}t) \qquad (4)$$

Now the fracture toughness K_{1c} is written as a combination of two other material properties: τ and σ_c. τ has been defined above, and σ_c, as defined by Dugdale, is the stress required to transform bulk material into craze material and is the stress at the craze boundary for an equilibrium craze. It has also been shown that σ_c has almost the same value as the macroscopic yield stress [13]. The advantage of writing K_{1c} as a function of τ and σ_c is that these properties may be more easily interpreted in molecular terms. τ and σ_c being time and temperature dependent K_{1c} is too. The calculations are based on the Dugdale model, which is a rather rough model of the craze. Nevertheless the use of a more refined model would not change the overall result and the breaking time would remain the same. Only the numerical value of the stress applied at the fibrils would be slightly different. Anyhow, the true stress on the fibrils is

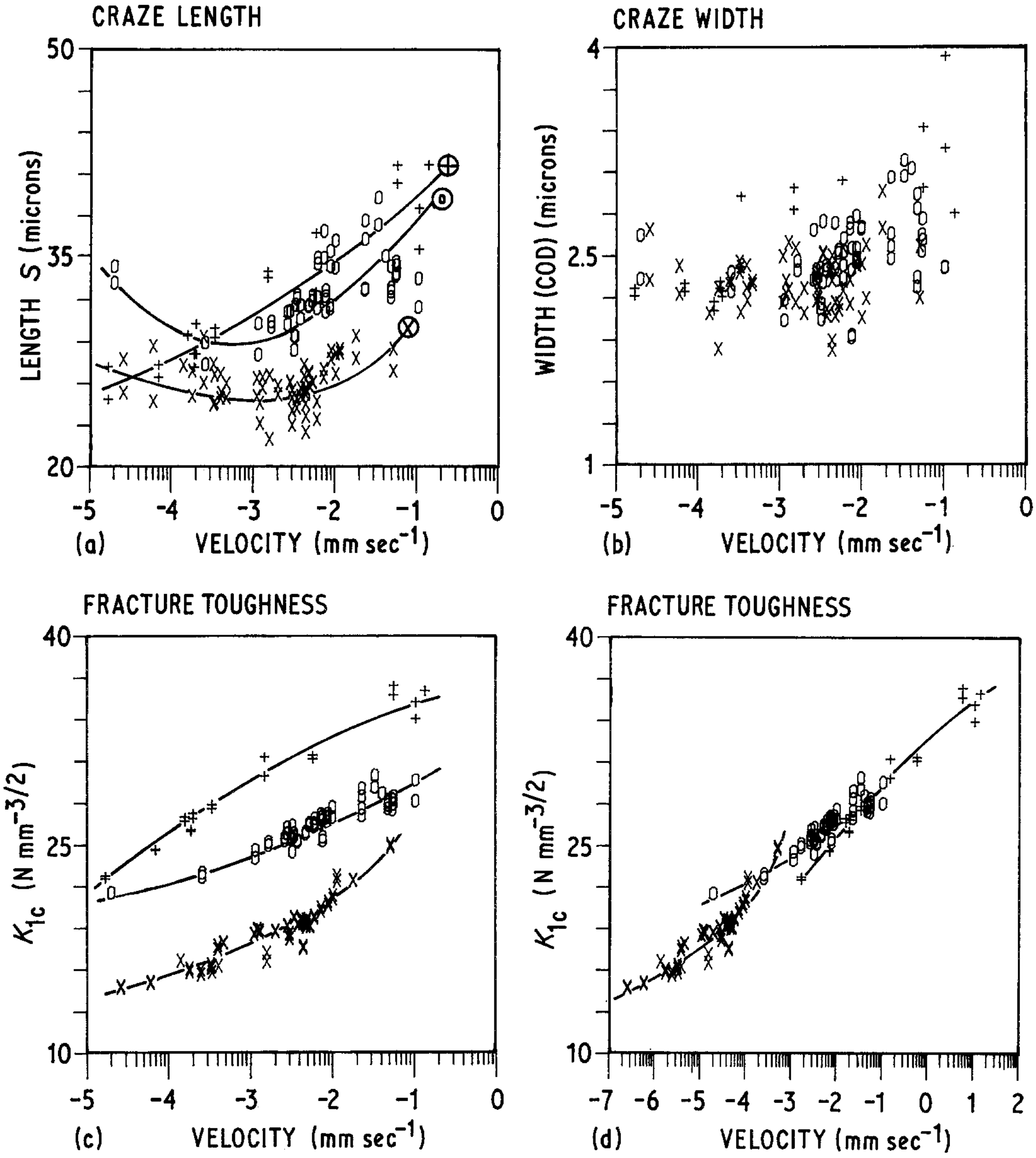

Figure 4 3 types of experimental values recorded as a function of the propagation velocity at 3 temperatures. Notice that K_{1c} for the 3 temperatures may more or less be drawn on a master curve by a horizontal shift (Fig. 4d), whereas S and COD may not. +: — 10° C, 0: 20° C and ×: 60° C.

much greater than σ_c, because there is at least 50% void between the fibrils and on Figs. 5 and 6 the stress scale should be multiplied by at least a factor 2.

4.2. The activation energy of the fibrils breakage

The master curve on Fig. 6 shows that the breaking time of the fibrils is thermally activated. In Fig. 7, two Arrhenius plots for PMMA obtained by means of mechanical loss peak measurements and the breaking time measurements are shown. The mechanical loss peak is the known β peak. Many authors have already associated the β loss peak with the macroscopic fracture properties [14]. Here, it is shown that the breakage of the microscopic craze fibril itself is controlled by a β process in the experimental conditions used. This process being a creep phenomenon, it is inferred that the craze fibrils break by chain slippage or disentanglement of the physical network rather than by chain breakage. Therefore the term of disentanglement time has been used. This type of fibril breakage has several consequences:

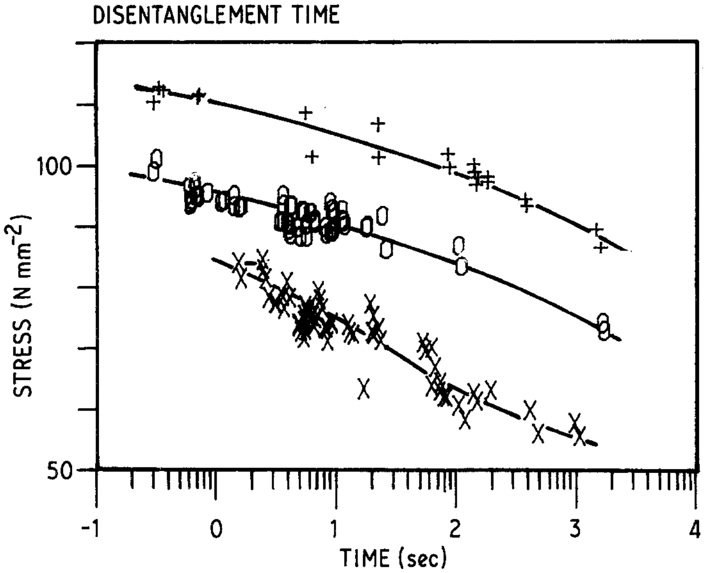

Figure 5 The breaking time or disentanglement time of the fibrils of the craze calculated from K_{1c}, S and da/dt by means of the Dugdale model of the craze. (Same symbols as in Fig. 4).

1. As shown in Fig. 3, since the oldest part of the fibrils (therefore the first to break) is the middle, the craze should break in the mid-rib region. This is actually observed in some experimental cases.

2. If the β process is frozen in (at low temperature), the fracture mechanism of the fibrils must change: this explains the results previously obtained [8]: it has been shown that the crack tip configuration changes from a single craze type, leaving a smooth fracture surface, to a multiple craze leaving a rough surface when the temperature drops below T_β. Then the fibrils no longer break by continuous disentanglement in the mid-rib and the fracture occurs anywhere in the craze (case (d) of Fig. 1).

3. The macroscopic fracture property K_{1c} being controlled by two microscopic properties (Equation 4) following a β process, it is obvious that the macroscopic properties exhibit a time–temperature behaviour connected with the β peak.

4. It may be difficult to understand how a secondary relaxation can be responsible for a full disentanglement of the macromolecular coils: this can be explained by the fact that the molecular movements in the craze fibrils are probably much

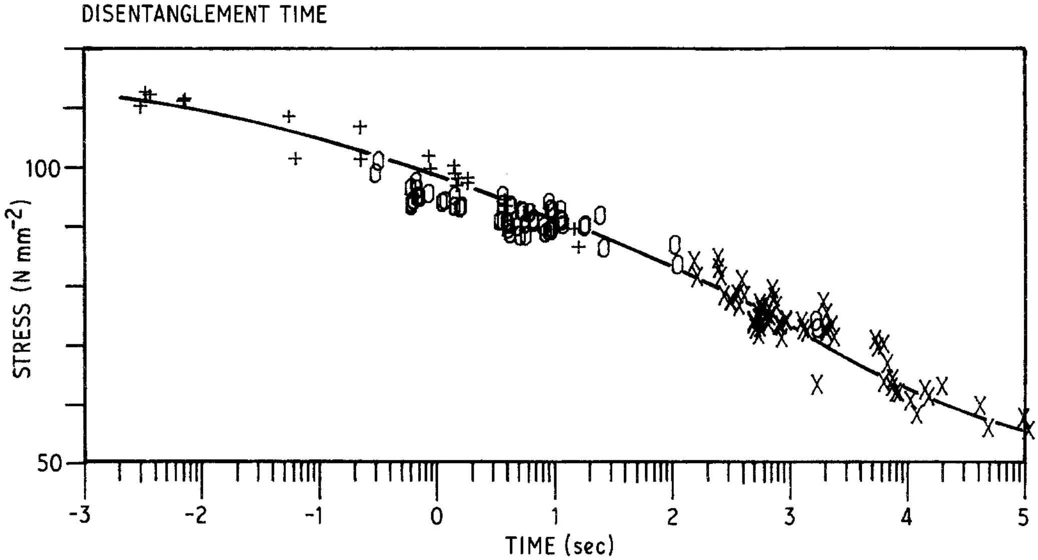

Figure 6 The master curve of the breaking time (Fig. 5) τ. Notice that τ can be drawn on a master curve much more easily than K_{1c}. (Same symbols as in Fig. 4).

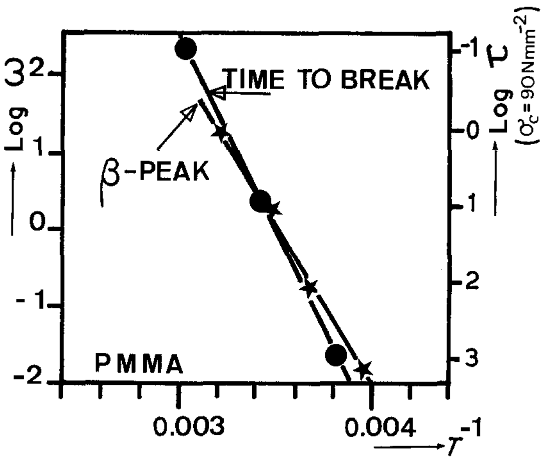

Figure 7 The arrhenius plot for PMMA of the β relaxation peak and of the breaking time τ. Activation energy: α peak: 80 kcal mol^{-1}, β peak: 20 kcal mol^{-1}, and τ breaking time: 23 kcal mol^{-1}.

freer than in the bulk material because the fibril diameter is of the same order of magnitude as the coil diameter [15], giving a high surface/volume ratio and hence leaving much more free volume. This has already been shown by the fact that the fibrils shrink at temperatures as low as $T_g - 30°$C [6].

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