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Craze growth in annealed polycarbonate

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In a recent paper [5], it was shown that dry polycarbonate craze growth kinetics are compatible with a propagation mechanism based on the creep of craze material. Further confirmation of such a mechanism is found in the lack of variation of crazing kinetics with thermal pretreatment, as opposed to bulk yield stress which is known to vary significantly on annealing.

1. Introduction

Until recently, mechanisms for craze growth were generally based on conditions in the stress-concentration region at the craze tip [1–4]. However, a new mechanism has been presented, in which under stationary stress conditions, widthwise creep of material in the craze body entails lengthwise craze growth, independently of craze tip conditions [5]. It is the purpose of the present paper to give additional support to this mechanism by investigating the effect of thermal pretreatment on crazing kinetics.

There is substantial evidence that thermal pretreatments affect both the microstructure of amorphous polymers [6, 7] and their mechanical properties [7–13], in particular the yield stress [9–13]. As crazing can be thought of as a kind of localized yielding process, it is to be expected that the stress acting along the craze tip, where the transformation of undeformed to craze material takes place, must vary as a function of the bulk yield stress; thus, if craze growth depended on the craze tip conditions, any treatment modifying the yield stress would also entail a change in craze growth kinetics. On the other hand, craze stress, that is, stress acting along the craze body, would be largely unaffected if the bulk polymer microstructure were destroyed in the crazing process. Thus, an investigation into the effect of thermal pretreatment on craze growth kinetics can be expected to yield information on the craze propagation mechanism.

In this investigation, crazing kinetics were studied as a function of stress, in polycarbonate which had been submitted to two different thermal pretreatments.

2. Experimental

Two specimens with a variable cross-section and flared ends, as described previously [14] were cut from a commercially available 2 mm thick sheet of Makrolon (Bayer). The width of the gauge section varied linearly along the length from 1 to 2 cm. Groups of two light scratches 2 mm apart were spaced every centimetre along the gauge section to ensure recognition of the areas under observation. Specimen A was heated for 1 h at 160° C and air-cooled. Specimen B was heated for 45 h at 120° C and left to cool in the closed environmental chamber (the glass transition temperature of this polycarbonate is approximately 145° C). Specimens were then submitted to a constant load and photographed at intervals determined by a logarithmic time scale, using apparatus described in a previous paper [14]. At each stress level, lengths of a sample of eight non-interfering crazes were measured from the photographs and plotted as a function of log time. In areas where craze density was high, it was not possible to distinguish between crazes and no observations on these areas are given. Under low stress conditions, there were fewer than eight crazes in the field of view, which was about 10 mm^2.

The test temperature was 40° C. This temperature was chosen because it is far enough below the 80° C α' transition to avoid annealing effects during the test, and high enough above room temperature to allow stable temperature regulation.

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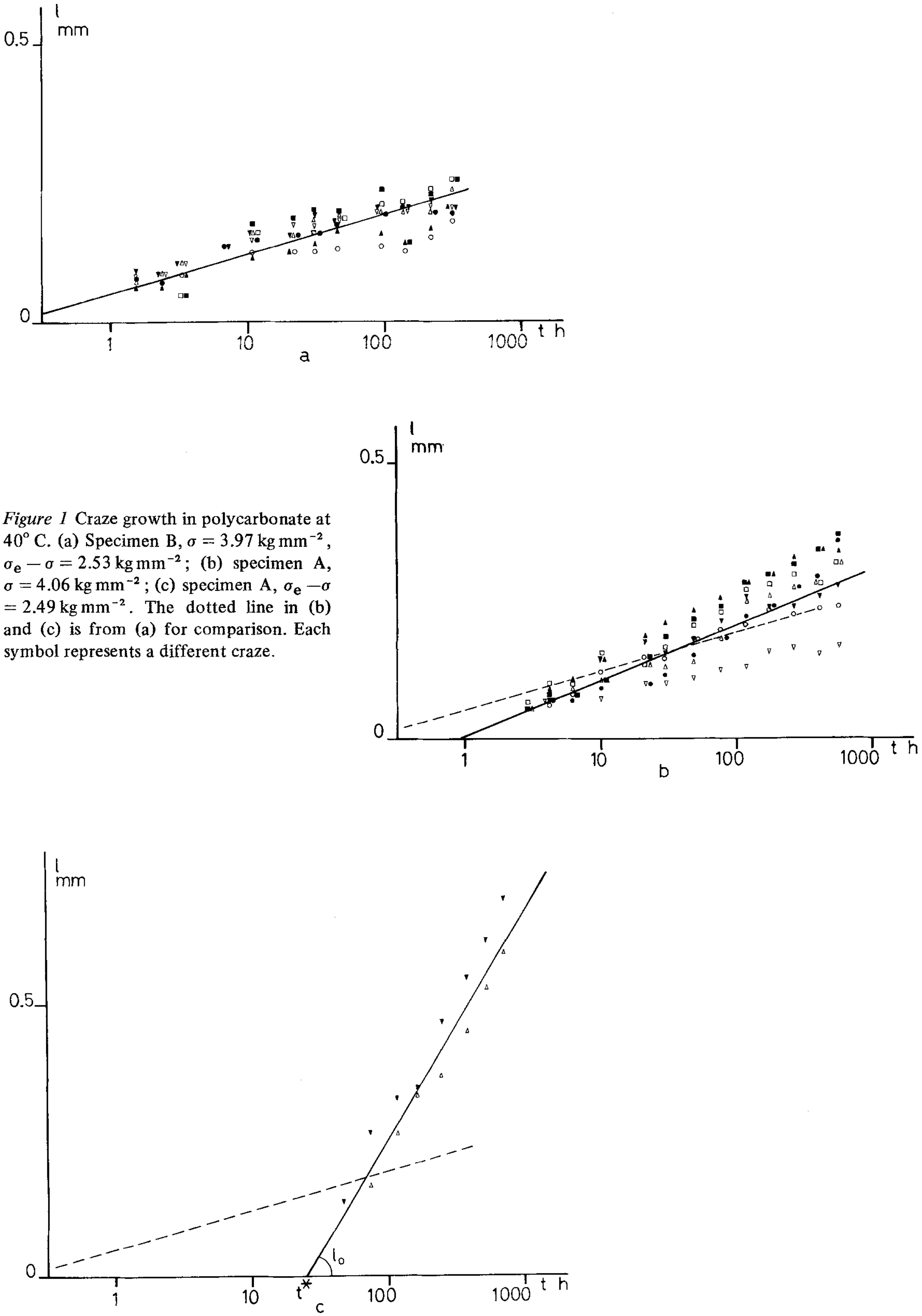


Figure 1 Craze growth in polycarbonate at 40° C. (a) Specimen B, $\sigma = 3.97\ \text{kg mm}^{-2}$, $\sigma_e - \sigma = 2.53\ \text{kg mm}^{-2}$; (b) specimen A, $\sigma = 4.06\ \text{kg mm}^{-2}$; (c) specimen A, $\sigma_e - \sigma = 2.49\ \text{kg mm}^{-2}$. The dotted line in (b) and (c) is from (a) for comparison. Each symbol represents a different craze.

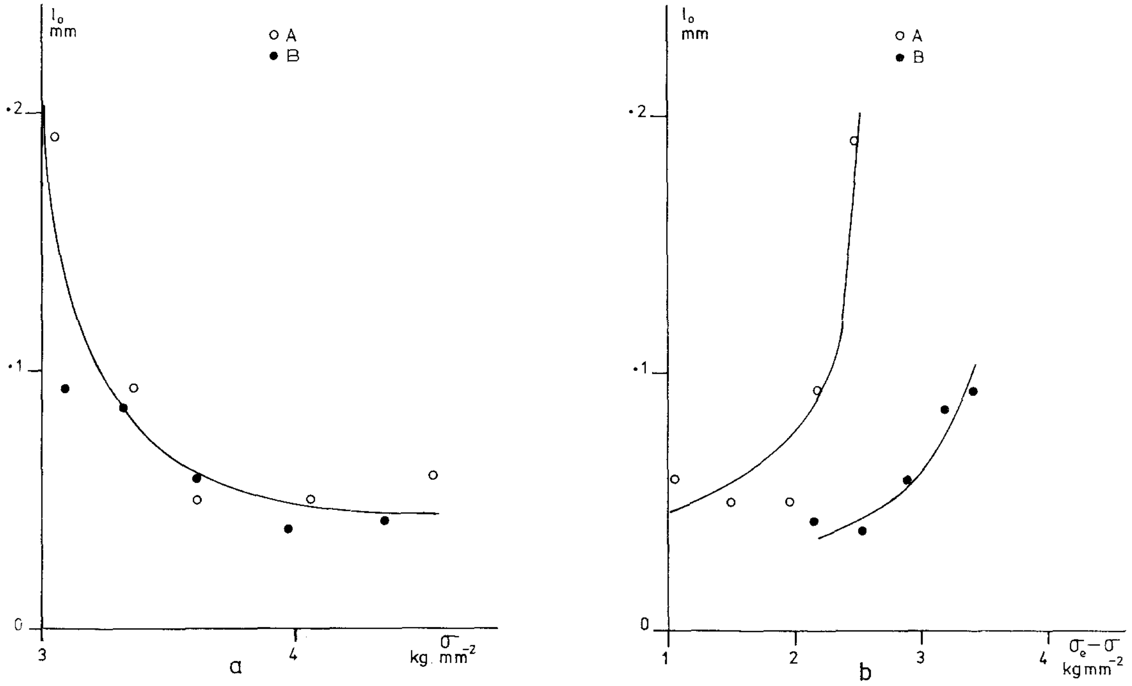


Figure 2 (a) Dependence of slope l_0 for craze growth on applied stress in PC. (b) As (a) plotted against the difference between yield stress and applied stress, $\sigma_e - \sigma$.

3. Results

Plots of craze lengths against log time are given in Fig. 1. These may be approximated by a straight line, of slope l_0 and abscissa intercept log t^*. Values of l_0 and t^* for specimens A and B are plotted against applied stress σ in Figs. 2a and 3a and against $\sigma_e - \sigma$ in Figs. 2b and 3b, where σ_e is the yield stress at 40° C at a reference deformation rate of 4 10^{-5} sec^{-1}, and takes the values 5.55 $\text{kg}\,\text{mm}^{-2}$ for specimens submitted to pretreatment A, and 6.50 $\text{kg}\,\text{mm}^{-2}$ after pretreatment B. It can be seen that correlation between specimens is good in Figs. 2a and 3a, but non-existent in Figs. 2b and 3b.

Fig. 4 is a plot of craze density (number of crazes per unit area) against applied stress. Although the densities for specimen A are systematically lower than those of specimen B, the difference is not large compared with the experimental scatter, and further investigation would be needed to establish whether this discrepancy is due to the thermal pretreatment. The density at the highest stress investigated on specimen A was substantially lower than at an equivalent stress after pretreatment B. This could be attributed to competition between crazing and homogeneous creep, which was far more rapid in specimen A than in specimen B. The same effect might be responsible for larger values of t^* in specimen A at high stresses than are expected from extrapolation of low-stress data (Fig. 3).

4. Discussion

It appears from the above that the dependence of crazing kinetics on thermal pretreatment is insignificant compared with yield-stress variations. Thus, crazing stress is not proportional to yield stress, in contrast to the interpretation by Haward *et al.* of observations on polystyrene [15].

The implications of the results from this work, concerning the mechanism for craze growth will now be discussed. First, it should be noted that if there existed a unique relationship between average stress and average strain-rate along the craze tip, it would be possible to calculate the craze propagation rate using this relationship and taking account of the stress field around the craze, which can be determined from craze geometry. In this case, any change in yield stress, that is, any modification of the above-mentioned relationship, would necessarily affect craze growth kinetics. That this is not so can be seen in the following manner. The applied stress σ_a, craze body stress σ_c and craze tip stress σ_e are related to

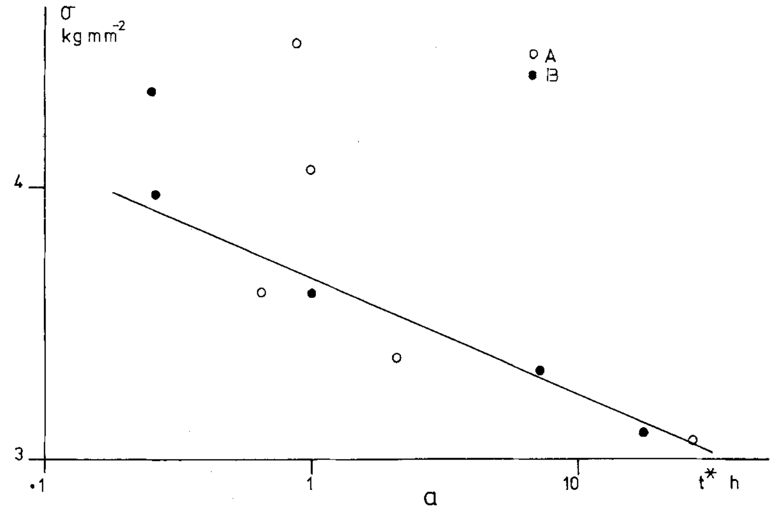
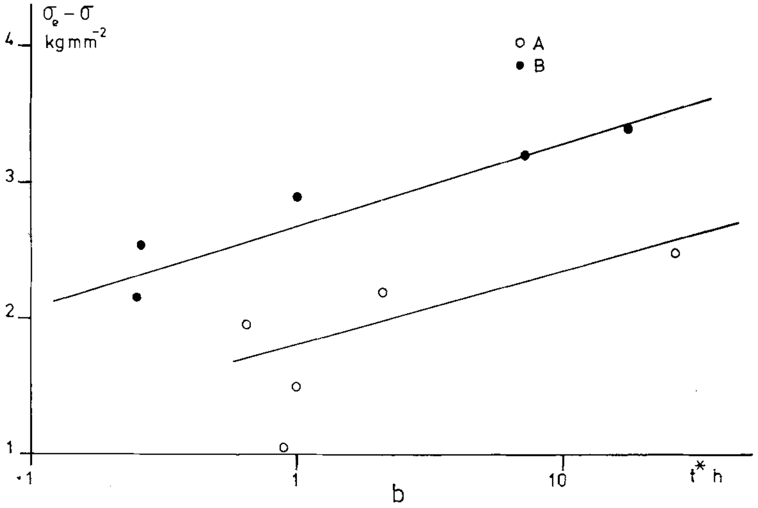
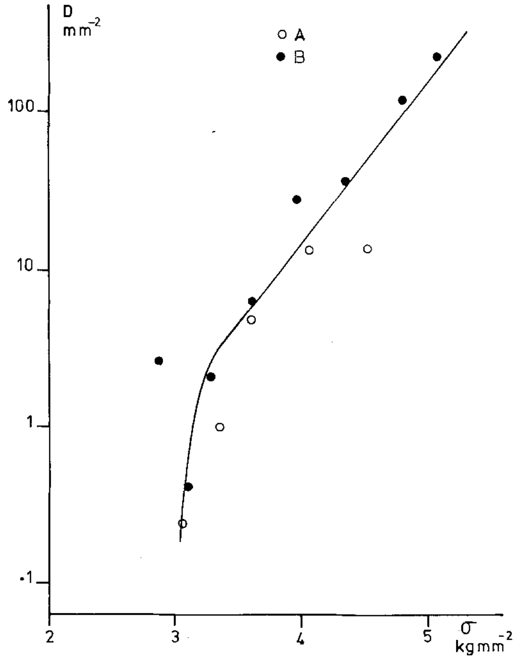


Figure 3 (a) Dependence of time constant for craze growth t^* on applied stress σ in PC. (b) As (a), plotted against $\sigma_e - \sigma$.





craze geometry by the following condition for stress to be bounded at the leading edge of the craze:

$$\frac{\sigma_a - \sigma_c}{\sigma_e - \sigma_c} = \frac{\arccos\left(1 - \frac{2r}{l}\right)}{\pi/2}$$

where the craze of total length l has tips of length r. This condition, however, gives only the average stress σ_e, and not the exact distribution of stress. Also, for a craze as opposed to a crack, the tip length is not uniquely defined, and if for any reason it becomes shorter, the stress rises to fulfil the above condition. Since strain-rate at yield of glassy polymers is an exponential function of stress, a slight deviation of the local stress from the

Figure 4 Increase in craze density with applied stress.

average value must entail a very large variation of strain-rate; thus the average strain-rate is a function not only of the average stress in the craze tips, but also of the exact stress distribution there. In this case, transformation of bulk material to craze material can take place as rapidly as needed, and cannot, therefore, be the process limiting craze growth kinetics.

In view of these considerations, a model was sought in which the governing process is creep of the craze material itself: this causes the craze to thicken, even if no extra material is drawn into the craze, and stress equilibrium can only be maintained if lengthwise growth occurs simultaneously. This model was given in detail in a previous paper [5] and only results will be given here. The law for craze growth, derived from this model, is

$$l = l_0 \ln \frac{t - t_i + t^*}{t^*}$$

where $l_0 = (eAT)/(E\Delta)$, t^* is a time constant for craze growth, defined by

$$t^* = \frac{2\,CAT}{E} \exp\left(\frac{Q}{RT} - \frac{\sigma}{sAT}\right).$$

t_i is craze initiation time; e is craze thickness prior to craze formation; E, Q, A and C are constants related to rheological properties of craze material: Δ is the constant ratio of the relative displacement of the craze–matrix interfaces to craze length; σ is applied stress; T is absolute temperature; R is the universal gas constant and s is a constant slightly larger than unity. It was shown previously [14] that experimental results on dry craze growth in polycarbonate are described well by this model.

The above mechanism is further confirmed by present results on effect of thermal pretreatments on craze growth: if growth were influenced by the craze tip regions, it would be expected that parameters defining growth would vary as a function of both applied stress and yield stress. That this is not the case is clear from Figs. 2b and 3b. Thus, craze growth kinetics depend only on applied stress and vary only negligibly or not at all with thermal pretreatment. This, in turn, is an indication that rheological characteristics of craze material are themselves independent of thermal pretreatment.

5. Implications concerning ductile-brittle transition in polycarbonate

It has frequently been observed that annealing polycarbonate below its glass transition temperature causes its impact strength or energy-to-fracture to drop [8–10, 13]. Both Allen *et al.* [8] and Legrand [10] suggested that this transition occurs because annealing below T_g causes the yield stress to rise but leaves the fracture or crazing stress unaffected; however, the effect of annealing on crazing stress was not investigated. Kambour *et al.* [16] also observed that in three-point bending tests on Izod bars of polycarbonate, brittle failure occurs below −15° C and that the variation of the brittle failure stress as a function of temperature parallels that of the craze initiation stress. The present work offers fresh confirmation of such a mechanism for the ductile-to-brittle transition, since the time for a craze to reach a critical size under given stress and temperature conditions would not depend on thermal pretreatment. Annealing below T_g does not enhance crazing, but allows larger loads to be applied to the specimen, and it is under these larger loads that dense crazing characteristic of annealed specimens can be observed.

6. Conclusions

Thermal pretreatments, which are known strongly to affect certain mechanical properties, such as modulus, yield stress and damping, appear from the results of this work to have little or no effect on craze growth kinetics in polycarbonate. This confirms a craze growth mechanism depending primarily on the properties of the craze material itself.

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References

1. A. N. GENT, *J. Mater. Sci.* 5 (1970) 925.
2. *Idem, J. Macromol. Sci. Phys.* **B 8** (1973) 597.
3. G. P. MARSHALL, L. E. CULVER and J. G. WILLIAMS, *Proc. Roy. Soc. Lond.* **A 319** (1970) 165.
4. G. P. MARSHALL and J. G. WILLIAMS, *J. Appl. Polymer Sci.* 17 (1973) 987.
5. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, *J. Mater. Sci.* 11 (1976) 7.

6. W. FRANK, H. GODDAR and H. A. STUART, *J. Polymer. Sci. B* 5 (1967) 711.
7. K. NEKI and P. H. GEIL, *J. Macromol. Sci. Phys.* B 8 (1973) 295.
8. G. ALLEN, D. C. W. MORLEY and T. WILLIAMS, *J. Mater. Sci.* 8 (1973) 1449.
9. J. H. GOLDEN, B. L. HAMMANT and E. A. HAZELL, *J. Appl. Polymer. Sci.* **11** (1967) 1571.
10. D. G. LEGRAND, *ibid* **13** (1969) 2129.
11. T. E. BRADY and G. S. Y. YEH, *J. Appl. Phys.* **42** (1971) 4622.
12. R. E. ROBERTSON and C. W. JOYNSON, *J. Appl. Polymer. Sci.* **16** (1972) 733.
13. G. A. ADAM, A. CROSS and R. N. HAWARD, *J. Mater. Sci.* **10** (1975) 1582.
14. N. VERHEULPEN-HEYMANS and J. C. BAUWENS, *J. Mater. Sci.* **11** (1976) 1.
15. R. N. HAWARD, B. M. MURPHY and E. F. T. WHITE, *J. Polymer. Sci. A-2* 9 (1971) 801.
16. R. P. KAMBOUR, D. FAULKNER, E. E. KAMPF, S. MILLER, G. E. NIZNIK and A. R. SHULTZ, Am. Chem. Soc. Advances in Chemistry series, Symposium Volume "Toughness and Brittleness of Plastics" 1975 (to be published).

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