Neck propagation in polycarbonate and its connection with the mechanism for dry craze growth

N. Verheulpen-Heymans
Physique des Matériaux de Synthèse, Université Libre de Bruxelles, 1050 Bruxelles, Belgium
(Received 3 August 1979)

An investigation of neck propagation in polycarbonate (PC) as a function of stress and temperature is presented. Neck propagation does not occur at a constant rate in this material: on the contrary, the propagation rate decreases continuously with time. A possible explanation for this behaviour is suggested. Also, a connection is sought between bulk neck propagation and craze growth rates.

INTRODUCTION

From our previous investigation on craze morphology during dry craze growth under creep in polycarbonate (PC)[1] it appeared that propagation of the walls of the craze towards the bulk occurred at a continuously decreasing rate. It was felt that drawing out of more material from the craze–bulk interface probably occurred by a mechanism similar to neck propagation in bulk specimens, as suggested by Lauterwasser and Kramer[2].

In this case, the experimentally observed decreasing rate for craze propagation was apparently in contradication with observations by Kramer[3] that in nylon-6,10 neck propagation occurred at a constant rate. This research was therefore undertaken in order to check the neck propagation behaviour of PC, and to investigate whether the kinetics of neck propagation were compatible with a propagation-controlled model for craze growth.

EXPERIMENTAL

Standard tensile specimens with flared ends and a gauge section 2 x 8 x 40 mm were cut from a 2 mm thick sheet of commercially available PC (Makrolon, Bayer). Light scratches were drawn every 2 mm along the gauge section to be used as bench marks. A neck was formed by straining the specimen in an Instron tensile machine at an extension rate of 0.02 cm min^{-1}. Necking generally occurred near one of the grips. The specimen was then loaded in creep and was photographed at intervals following a logarithmic time scale of ratio 2. The position of the end of the neck further from the grip was noted as a function of log (time). Tests were conducted at room temperature, at 40° and at 60°C. Prestraining was effected at the same temperature as subsequent testing.

One test piece with a square cross section 4 x 4 mm was tested at 45.1 MPa and at room temperature, to check whether there was any detectable effect of specimen shape on propagation rates.

RESULTS

Plots of neck position p against linear time showed no detectable delay time, and showed that neck propagation occurs at a continually decreasing rate. Typical plots of neck position as a function of log (time) are given in *Figure 1.*

It can be seen that these plots are linear after a time which depends on experimental conditions. This time, t^*, is defined by extrapolation of the linear portion of the plot back to the neck position before loading: t^* should be considered as a time constant for neck propagation rather than a delay time. The slope p_0 of the linear portion of the plot also depends on experimental conditions – it increases with increasing stress and temperature. The range of stresses covered by these experiments at each temperature is rather narrow, due to experimental difficulties. At high stresses it was found that propagation was so fast that p_0 could not be defined, and at low stresses the linear portion of the plot could not be reached, even after several weeks, leading to difficulties in determining t^*. For this reason the values of

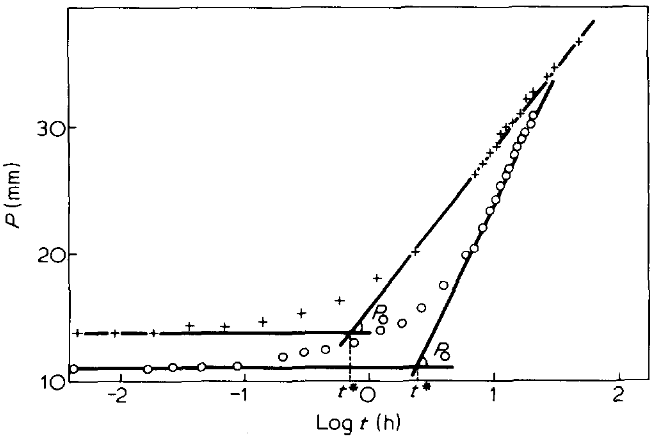

Figure 1 Variation of neck position p with time in PC. ○, 20°C, 47 MPa; +, 40°C, 40 MPa. Parameters p_0 and t^* are defined on the graph

0032–3861/80/010097–06$02.00

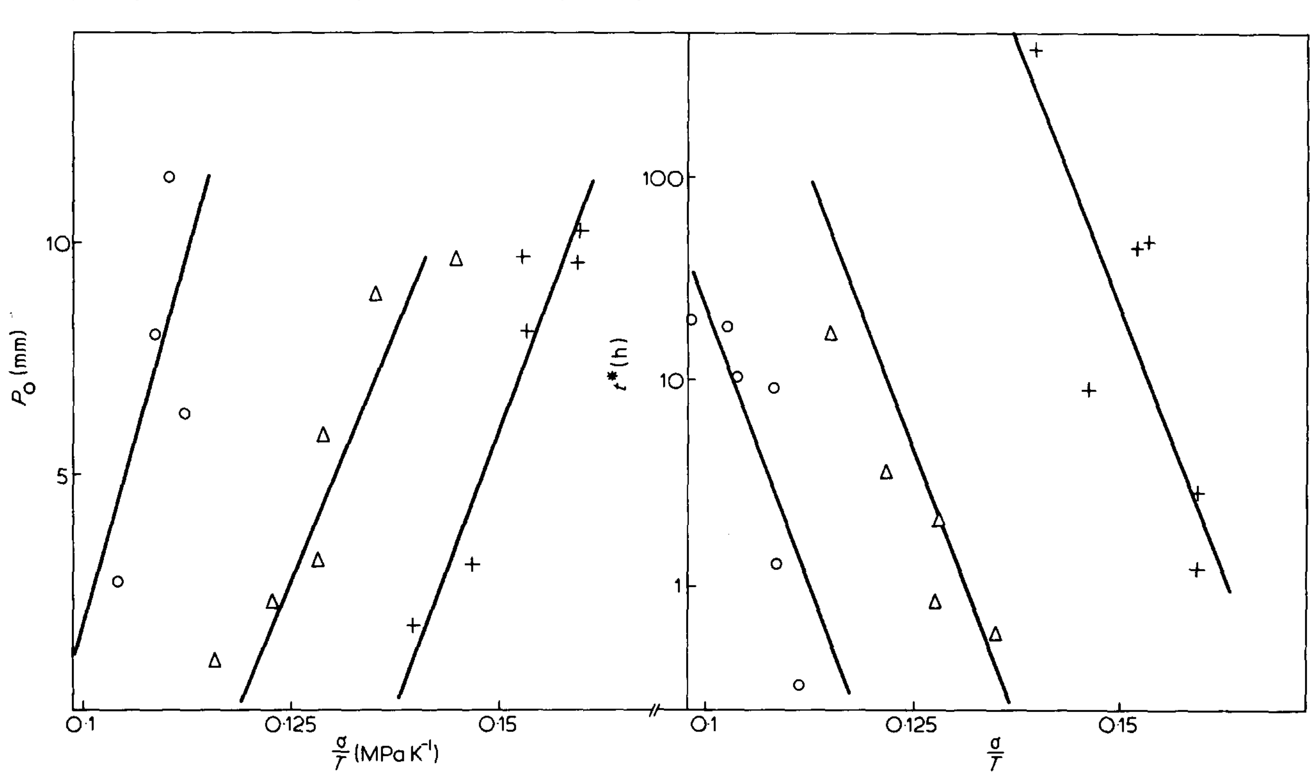

Figure 2 Variation with stress and temperature of parameters p_0 and t^* defined on *Figure 1.* +, 20°C; △, 40°C; ○, 60°C

t^* are probably somewhat underestimated for tests conducted at the lowest stress at each temperature.

Results for the square specimen fell well within experimental scatter corresponding to the flat specimens.

Figure 2 gives plots of log t^* and p_0 against σ/T; this representation is chosen to enable the following equation to be fitted to the data:

$$\frac{\sigma}{T} = A\left(\frac{Q}{RT} - \ln t^* + \ln 2C\right) \qquad (1)$$

where σ is the applied stress, defined using the initial section; T is absolute t^0; Q is the activation energy for neck propagation; and R is the universal gas constant.

Equation (1) is adapted from the equation derived by Bauwens[4] to describe the yield behaviour of polymers, based on the Eyring theory of the rate processes. Taking the value of A found previously for the upper yield point of PC[5], $A = 4.08 \times 10^{-3}$ MPa K^{-1}, it is found that $Q = 70$ kcal mol^{-1} between 20° and 40°C, and 50 kcal mol^{-1} between 40° and 60°C. The straight lines drawn in *Figure 2a* correspond to the best fit to the experimental data, taking the above value of A. In view of the experimental scatter, the fit obtained can be considered satisfactory, especially since the highest values of t^* are probably somewhat underestimated, as pointed out above.

DISCUSSION

Neck propagation

The absence of delay times can be attributed to the time needed to transfer specimens from the Instron machine to the strain frame for creep. This is equivalent to an erasing treatment at zero stress; as shown by Kramer[3] erasing times are much shorter than the corresponding stress aging times, and it is therefore probable that any stress aging that might have occurred during sample preparation would be erased before the sample was subsequently loaded.

The values of 70 and 50 kcal/mol^{-1} found here for the activation energy for neck propagation are somewhat lower than those found for the upper yield stress for this material (81 kcal mol^{-1}, ref 5) but are close to the value found for the lower yield stress in tensile tests (65 kcal mol^{-1}, ref 6). A smaller value of the activation energy for the lower yield point is to be expected, since it is known that the magnitude of the yield drop decreases with temperature[6].

One somewhat unexpected finding is that neck propagation occurs at a decreasing rate. This is apparently in contradiction with previous observations by Kramer[3]. However, Kramer's experiments were conducted on nylon-6,10, which is partly crystalline and which might not be expected to present the same behaviour as polycarbonate. Also, in Kramer's work neck propagation was only followed for a few minutes, and it can be problematic to distinguish between linear and logarithmic propagation after such short times.

A tentative explanation for the decreasing rates observed here is that stress aging occurs not only in the neck but also in the undeformed part of the specimen, causing increased resistance to flow. This is apparent from the fact that at the lowest stress at each temperature, after a short initial period of neck propagation, further propagation is arrested. Also, it was found that propagation occurred at a higher velocity in quenched specimens, but that in a quenched specimen stress-aged for three days at a stress below the yield point prior to necking, velocities dropped considerably. This is an indication that two competing mechanisms influence neck propagation, one being plastic deformation leading to strain softening, and the other stress aging which leads to hardening[3,7,8].

Correlation between neck propagation and craze growth

It was shown previously[1], first, that craze thickening

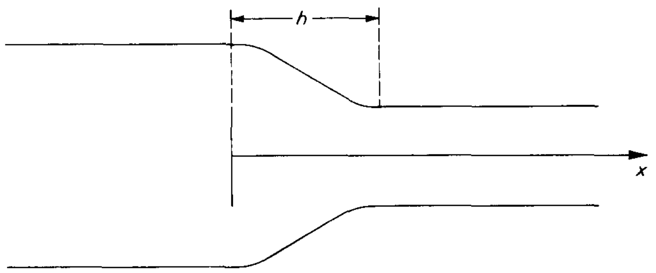

Figure 3 Definition of reduced coordinates used in transforming neck propagation rates to fibril propagation rates

during growth occurs by drawing in fresh material continuously from the bulk, and second, that for crazes that can be considered as being embedded in an infinite matrix, growth in length is proportional to growth in thickness. It was therefore thought that the craze growth rate in length was determined by the rate at which craze fibrils propagate towards the matrix, and the purpose of this work was to investigate how well this hypothesis accounts for various aspects of craze growth kinetics.

It is first necessary to transpose neck velocity measurements effected on bulk specimens to equivalent propagation rates for craze fibrils. This is done quite simply in the following manner. Consider a necked specimen as shown in *Figure 3*. The origin of the x-axis is taken at the edge of the undeformed material, and the length of the shoulder where transformation from undeformed to necked material takes place is h. To a first approximation, the following equation holds between local strain-rate $\dot{\epsilon}(x)$ and global neck propagation rate $\dot{p}$:

$$\dot{\epsilon}(x) = \dot{p}\frac{\mathrm{d}\epsilon}{\mathrm{d}x} \tag{2}$$

$\dot{\epsilon}$ is a function only of the local stress $\sigma(x)$ and is therefore independent of dimensions for solids where a condition of geometrical similarity holds. In this case,

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}x} = f\left(\frac{x}{h}\right)\frac{\epsilon(h) - \epsilon(0)}{h} \tag{3}$$

where $f(x/h)$ is a dimensionless function of x/h, and is therefore independent of the dimensions of the test-piece; $\epsilon(h)$ and $\epsilon(0)$ are strains in the neck and in the bulk, respectively, and are also taken to be independent of absolute dimensions. Introducing (3) into (2)

$$\dot{p} = \frac{\dot{\epsilon}(x)}{f\left(\frac{x}{h}\right)} \cdot \frac{h}{\epsilon(h) - \epsilon(0)} \tag{4}$$

If propagation occurs with no change in shape of the neck, $\dot{p}$ is the same for all x and therefore $\dot{\epsilon}(x)/f(x/h)$ is a constant. Therefore $\dot{p}$ is proportional to h. However, for solids between which a condition of geometrical similarity holds, any dimension can be chosen to characterize the solid, and the square root of the cross-section was chosen as being more readily measurable than the length of the neck. The corresponding dimension for the fibril is taken to be the fibril diameter a. Strictly speaking, a factor $(\pi/4)^{1/2} = 0.89$ should be introduced but considering the uncertainty both in propagation rates and in fibril diameters this is not considered here.

In a previous investigation[1], it was shown that during dry craze growth in PC, the relative displacement of the craze faces, 2δ, remained in a constant ratio to the craze length l, this ratio being on average 0.78×10^{-3}. This value must be divided by the craze strain ϵ, since propagation of one end of the neck or fibril a distance p into the matrix corresponds to a relative displacement of the undeformed material equal to $2\epsilon p$. Also, a test-piece,of undeformed cross-section S has a neck of cross-section $S/1 + \epsilon$ if yielding is assumed to occur with no change in density. Finally, equation (4) can be rewritten as:

$$\left[\frac{p}{(S)^{1/2}}\right]_n = \frac{1}{(1+\epsilon)^{1/2}\epsilon}\left(\frac{\delta}{a}\right)_c = \frac{1}{(1+\epsilon)^{1/2}\epsilon}\left(\frac{\delta}{l}\right)\left(\frac{\dot{l}}{a}\right)_c \tag{4a}$$

and the fibril diameter is:

$$a = \frac{\delta\dot{l}(S)^{1/2}}{l\epsilon^{3/2}\dot{p}} \tag{5}$$

Since variation both of craze length l and neck position p is linear on a log$t$ basis:

$$l = l_0\log\frac{t}{t^*} \quad \text{and} \quad p = p_0\log\frac{t}{t_i} \tag{6}$$

and

$$\dot{l} = \frac{l_0}{t}\ln(10) \quad \text{and} \quad \dot{p} = \frac{p_0}{t}\ln(10) \tag{6a}$$

Therefore in equation (5) craze and neck velocities can be replaced by l_0 and p_0, whether t^* is equal to t_i or not. Equation (5) then becomes:

$$a = \frac{\delta l_0(S)^{1/2}}{l(1+\epsilon)^{1/2}\epsilon p_0} \tag{7}$$

To be valid, the comparison should be made between a craze submitted to a craze stress σ_c and a neck propagation specimen submitted to the same engineering stress σ_c. It was found previously[1] that at room temperature the difference between the craze stress and the average stress on the specimen was $\sigma_a - \sigma_c = 3.8$ MPa. For example, at room temperature in a sample having a cross-section of 16 mm^2 submitted to a stress of 45 MPa, p_0 was found to be 20 mm/decade. At the corresponding stress $\sigma_a = 48.8$ MPa, the constant for craze growth l_0 was on average 0.23 mm/decade[9]. The strain in a craze under stress was found from previous investigations to be 1.4 on average[1]. This value is comparable with the lowest values observed in a crack tip polystyrene craze by Doyle and Wagner, who observed values as high as 6 just prior to breakdown[10]. From equation (7), the craze diameter is then estimated as $a = 0.83$ Å. This value corresponds very closely to observed craze filament diameters, which vary from 100 to 300 Å in PS[11–17] and are approximately 200 Å in PPO[18] and 100 Å in PC[19]. Much larger filaments have been observed but only in the case of solvent crazing[20] or of plasticization by a reinforcing impregnant for microtomy[21]. Small filaments, 30–60 Å, have also been observed, but these have been shown to be a con-

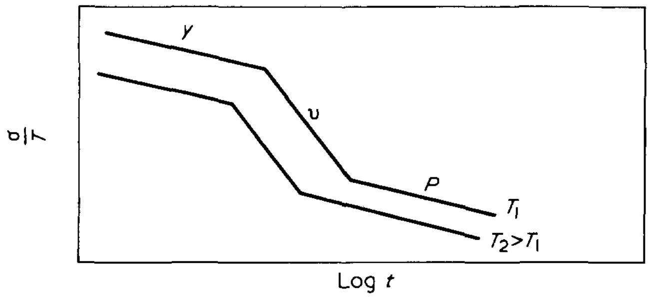

Figure 4 Transition from yielding (*y*) to voiding-controlled crazing (*v*) to propagation-controlled crazing (*p*) (schematic)

Table 1 Average parameters for crazing in polycarbonate (23)

T (°C)	*A* (MPa K^{-1})	*Q* (cal mol^{-1})	2*C* (s)
20	0.0114	23	2.2×10^{-8}
40	0.0052	22	2.1×10^{-8}
60	0.0081	57	2.1×10^{-8}
80	0.0060	46	1.1×10^{-27}
100	0.0053		1.5×10^{-27}

Upper yield point: $A = 0.0041$ MPa K^{-1}; $Q = 81$ kcal mol^{-1} (ref 5)
Lower yield point: $A = 0.0041$ MPa K^{-1}; $Q = 81$ kcal mol^{-1} (ref 6)

sequence of the breakdown of larger filaments[13,14].

To summarize the discussion so far, the hypothesis that the craze growth rate is controlled by propagation of plastic deformation towards the matrix appears to be confirmed, first by the similarity of the time dependence of both propagation rates, and secondly by the close correspondence between filament diameters as observed in the electron microscope and as estimated from the model.

There are, however, one or two points of disagreement between the two mechanisms. Firstly, the stress and temperature dependence of the time constant t_1 for neck propagation is entirely different from that for craze growth t^*: the former has a lower stress dependence and a higher activation energy. Secondly, the craze growth rate constant is practically independent of stresss at high stresses, and rises at low stresses, whereas the rate constant for neck propagation p_0 increases with stress. This would imply a rather large variation of a, the filament diameter, as can be seen from equation (7) and seems highly unlikely, since all observations found in the literature indicate the same order of magnitude of filament diameters.

The cause of this discrepancy probably lies in the difference in morphology between a macroscopic sample, and filamentary craze material in which there are numerous small voids interspersed between the filaments (in order for plastic deformation to propagate towards the matrix some void formation has to occur). The craze growth rate must then be determined by the slower of the following two processes: neck propagation or void formation. The possibility that more than one mechanism might be necessary for craze propagation, only one of which controls the growth rate, was also suggested by Kramer[22].

A transition from propagation-controlled growth to void formation-controlled growth is then expected as shown schematically in *Figure 4*. Such a transition was not previously recognized, but several discrepancies in our previous work on the effects of stress and temperature on craze growth[23], which were attributed to experimental scatter owing to the statistical nature of crazing, can in fact be explained by this kind of transition. These discrepancies are discussed below.

In *Table 1*, which is taken from ref 23, values of A, Q and $2C$ are given for crazing in PC from a least-squares analysis of experimental data following equation (1). The parameters for yielding in PC, from ref 4 for the upper yield stress, and from this work for the lower yield stress, are also given. The parameters for craze growth are completely different from those for yielding below 60°C, but become quite similar at higher temperatures. (It should be pointed out that as the value obtained for $2C$ is highly dependent on A and Q, the discrepancy between the various values of $2C$ above 60°C is not considered to be of any great significance.) Consequently, there is positive evidence for a transition in the rate-controlling step of the mechanism for craze growth, at approximately 60°C. A transition at this temperature could also possibly account for the considerable data scatter at 60°C.

The results obtained previously were therefore reanalysed, discarding all crazes having $l_0 > 250$ μm, and also discarding crazes terminated by deformation bands which were found to lead to larger values of t^* than would be expected from extrapolation of data obtained at lower stresses[24]. The results of this analysis are given in *Table 2*, from which it is apparent that the slope A of the relationship between σ/T and t^* is independent of temperature within experimental error. (The higher value obtained for $T = 100$°C is not considered significant since the range of stresses within which no deformation bands were observed and l_0 was smaller than 250 μm was in fact too narrow for statistical analysis to be of any value.) The range of values of Q is somewhat narrower when the results are analysed in this manner; nevertheless, the rise in Q at high temperatures is still present and is far too large to be attributed to experimental scatter.

If it is supposed that craze development in this region is controlled by voiding, this rise in activation energy towards that relevant to neck propagation can be taken as an indication that the stress at which voiding occurs is itself dependent on the yield stress. Indeed, as pointed out by Andrews and Bevan[25], expansion of a void of radius r in an elastic–plastic solid occurs at a hydrostatic tension:

$$p = \frac{2\gamma}{r} + \frac{2\sigma_e}{3}\left[1 + \ln\left(\frac{E}{3(1-\nu)\sigma_e}\right)\right] \qquad (8)$$

In Andrews and Bevan's work on solvent crazing, the surface tension γ was relatively low and r was relatively large (500 Å), so that the hydrostatic tension needed for void expansion depended mainly on the yield stress. In the present work, which concerns dry crazing, typical void sizes at room temperature are of order 100 Å[19] or perhaps even smaller, making the surface energy contribution much larger. However, void sizes are probably larger in crazes grown at higher temperatures; in fact, a coarse grainy tex-

Table 2 Parameters for voiding-controlled crazing in polycarbonate

T (°C)	*A* (MPa K^{-1})	*Q* (kcal mol^{-1})	2*C* (s)
20	0.0094	27	4×10^{-16}
40	0.0102	27	2×10^{-15}
60	0.0081	43	9×10^{-14}
80	0.0085	41	5×10^{-23}
100	0.0115		4×10^{-22}

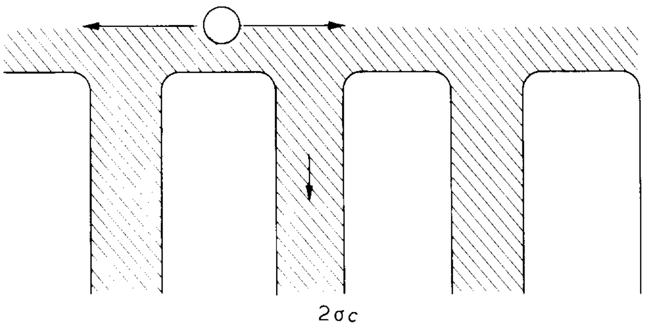

Figure 5 Inhomogeneous stress distribution near embedded fibrils (schematic)

ture typically 500 Å in size, reaching 1000 Å or more along the midrib has been observed on replicas of polycarbonate crazes grown at 100°C (*Figure 7*, ref 23), whereas no such texture was observed in crazes grown at room temperature. The surface energy contribution is thus expected to become smaller as the temperature rises, making the craze growth rate more and more dependent on the lower yield stress parameters.

It was found that the range of stresses within which the craze growth rate was considered to be controlled by voiding became narrower with rising temperature; this is normal since the yield drop, i.e. the difference between upper and lower yield stress, decreases with rising temperature. This is illustrated schematically in *Figure 4*.

It might be proposed that voiding cannot occur in the vicinity of the craze body, since the hydrostatic tension is lower there than the average hydrostatic tension at which no voiding is observed. In fact, using a two-dimensional analysis with the x-axis parallel to the craze and the y-axis parallel to the applied stress σ_a, it was found that:

$$\sigma_y = \sigma_c$$

$$\sigma_x = -(\sigma_a - \sigma_c)$$

in the vicinity of the craze body[26]. However, in this analysis it was presumed that stress was transmitted homogeneously from the craze to the matrix, which is certainly not a valid approximation at the scale of the craze fibrils; in fact for a craze having a void content of 50% each fibril must transmit an average stress equal to $2\sigma_c$ parallel to the y-axis, and none parallel to the x-axis. Since σ_c is not a great deal lower than the average stress, the local stress is in fact much higher than the average stress, enabling void formation even in the vicinity of the craze body. This is shown schematically in *Figure 5*.

Another phenomenon which had so far remained unexplained is the variation of l_0 with experimental conditions: l_0 correlates reasonably well with t^*, and is approximately constant at low values of t^* rising at higher values of t^*. Also, the dependence of l_0 on t^* is virtually independent of temperature for low values of t^*, but is strongly temperature dependent at high values of t^*, the transition occurring at lower t^* the higher the temperature (*Figure 6*). This also confirms that the voiding mechanism operative at high stresses has a low activation energy.

CONCLUSIONS

A mechanism for craze growth has been proposed whereby growth is controlled both by formation of voids along the craze matrix interface and by propagation similar to macroscopic neck propagation, the rate-controlling step being that which occurs at the higher stress. This mechanism is compatible with experimental evidence, in particular with a transition which occurs in the stress dependence of the parameters determining the craze growth rate, and with the variation with temperature of the range of stresses within which 'voiding-controlled growth' occurs. It has been qualitatively shown that voiding is possible in this region because of the inhomogeneous stress field due to the filamentary nature of craze matter, and also that, since the voiding stress depends on the yield stress, similar growth kinetics are expected for propagation-controlled growth as for voiding-controlled growth.

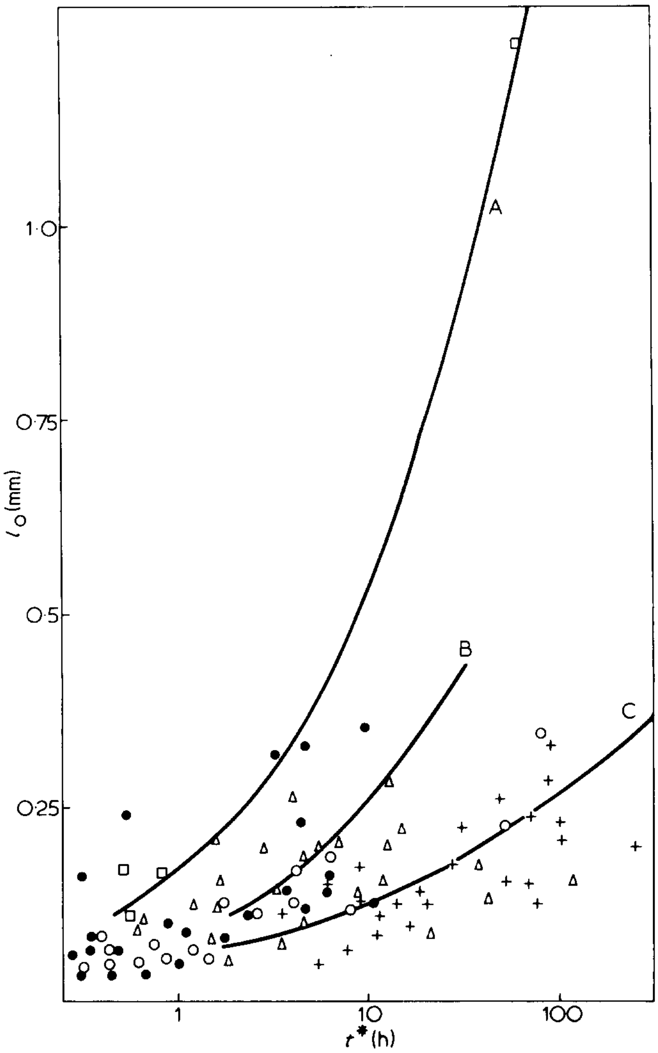

Figure 6 Variation of l_0 with t^*. +, 20°C; ○, 40°C; △, 60°C; ●, 80°C; □, 100°C. A, T = 100°C; B, T = 80°C; C, $T \leq 60$°C

ACKNOWLEDGEMENTS

Thanks are due to Professor J. -C. Bauwens and to Mme C. Bauwens-Crowet for helpful discussions during the course of this work.

REFERENCES

1 Verheulpen-Heymans, N. *Polymer* 1979, **20**, 356
2 Lauterwasser, B. D. and Kramer, E. J. MSC report 3076, Cornell University, 1978
3 Kramer, E. J. *J. Appl. Phys.* 1970, **41**, 4327

4 Bauwens-Crowet, C., Bauwens, J. C. and Homès, G. *J. Polym. Sci. (A-2)* 1969, 7, 735
5 Bauwens-Crowet, C. and Bauwens, J. C. *J. Mater. Sci.* in press
6 Bauwens-Crowet, C. personal communication
7 Myers, F. A., Cama, F. C. and Sternstein, S. S. *Ann. NY Acad. Sci.* 1976, **279**, 94
8 Struik, L. C. E. personal communication
9 Verheulpen-Heymans, N. *Thèse de doctorat,* Université Libre de Bruxelles, 1976
10 Doyle, M. J. and Wagner, J. G. *Adv. Chem. Ser.* No. 154. 'Toughness and brittleness of Plastics' (Eds. R. D. Deanin and A. M. Crugnola) American Chemical Society (1976)
11 Legrand, D. G., Kambour, R. P. and Haaf, W. R. *J. Polym. Sci. (A-2)* 1972, **10**, 1565
12 Beahan, P., Bevis, M. and Hull, D. *Phil. Mag.* 1971, **24**, 1267
13 Beahan, P., Bevis, M. and Hull, D. *J. Mater. Sci.* 1972, **8**, 162
14 Beahan, P., Bevis, M. and Hull, D. *Proc. Roy. Soc. London (A)* 1975, **343**, 525
15 Wellinghoff, S. and Baer, E. *J. Macromol. Sci. (B)* 1975, **11**, 367
16 Lainchbury, D. L. G. and Bevis, M. *J. Mater. Sci.* 1976, **11**, 2222
17 Lainchbury, D. L. G. and Bevis, M. *J. Mater. Sci.* 1976, **11**, 2235
18 Kambour, R. P. and Holik, A. S. *J. Polym. Sci. (A-2)* 1969, **7**, 1393
19 Beahan, P., Bevis, M. and Hull, D. *Polymer* 1973, **14**, 96
20 Thomas, E. L. and Israel, S. J. *J. Mater. Sci.* 1975, **10**, 1603
21 Kambour, R. P. and Russell, R. R. *Polymer* 1971, **12**, 237
22 Kramer, E. J. MSc report 3051, Cornell University, 1978
23 Verheulpen-Heymans, N. and Bauwens, J. C. *J. Mater. Sci.* 1976, **11**, 1
24 Verheulpen-Heymans, N. *J. Mater. Sci.* 1976, **11**, 1003
25 Andrews, E. H. and Bevan, L. *Polymer* 1972, **13**, 337
26 Verheulpen-Heymans, N. and Bauwens, J. C. *J. Mater. Sci.* 1976, **11**, 7