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# Phenomenological study of a single craze propagating in several glassy polymers over a wide range of temperatures

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The single craze which appears at the crack tip in some amorphous polymers has been observed between − 100 and + 100° C in five different polymers. The results show that the single craze exists only between two temperatures: a certain critical temperature $T_c$ and the glass transition temperature. In the case of oriented block co-polymers the structure also affects the formation of the craze. Below the critical temperature $T_c$, a multiple craze appears ahead of the crack and the fracture toughness $K_c$ increases.

## 1. Introduction

The interferometric method has been used for several years to study the properties of crazes in transparent polymers. Kambour [1] and Ward *et. al.* [2–4] showed that the shape predicted by the Dugdale model is very close to the real shape of the craze in polymethylmethacrylate (PMMA) and polycarbonate (PC), while Döll *et al.* [5–8] investigated the relationship between the craze shape and the propagation velocity, the molecular weight and the temperature between 20 and 80° C, in both fatigue experiments and high velocity experiments. Gent [9] gave an interpretation of the behaviour of the craze in terms of variation of the glass transition temperature $T_g$. On the other hand, glassy polymers (as opposed to most metals) exhibit a particular property: they store up all or a part of their plastic deformation and when they are heated above $T_g$ they shrink and the plastic deformation is recoverable. This property is often used for investigating macroscopic plastic deformation in polymers. We used this technique combined with the interferometric method to investigate the relaxation properties of an unloaded single craze in PMMA at temperatures near $T_g$ [10]. This paper deals with the phenomenological behaviour of a single craze in several materials over a wide range of temperatures (− 100 to + 100° C) and is an attempt to relate this behaviour to the structure and the relaxation properties of the polymers. The dynamic effects (i.e. crack velocity, dynamic loading) are neglected. All the experiments were performed under constant load, and with very low crack propagation speeds (less than 10 $\mu$m sec$^{-1}$).

## 2. Experimental procedure

### 2.1. The materials

We used polymers with different structures, one of them anisotropic.

### *2.1.1. Triblock co-polymers*

This material was synthesized anionically at our laboratory [11]. The polymer consists of two phases: polyisoprene and polystyrene. Each macromolecule has three blocks: polystyrene, polyisoprene and polystyrene (SIS). The molecular weights of the three blocks are $M_n$ = (35 000, 23 000 and 35 000). The structure of the material is as follows: the two phases segregate into cylinders of polyisoprene in a matrix of polystyrene. The material can be almost perfectly oriented [12] with the cylinders of polyisoprene being parallel and located on a hexagonal structure. The glass transition temperature $T_g$ for polyisoprene is about − 60° C and + 100° C for polystyrene. The dimensions and perfection of the structure are well known [13, 14]. It should be noted that the material is highly anisotropic and that the size of the structural unit ($\simeq$ 30 nm) is very

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small compared with the size of a craze. Two kinds of samples were used: with the crack parallel to the cylinders (SIS ||) or perpendicular to them (SIS ⊥).

### 2.1.2. Polystyrene (PS)

This material has approximately the same molecular weight $M_n = 10^5$ as the co-polymer SIS and was also anionically synthesized. The samples were prepared by compression moulding above $T_g$.

### 2.1.3. Polyvinylchloride (PVC)

Extruded sheets from Dynamit Nobel, commercial reference TROVIDUR were used. Another type of PVC was also investigated by Döll *et al.* [8].

### 2.1.4. Polymethylmethacrylate (PMMA)

This was obtained as cast sheets from Altulor or Röhm and Haas with a molecular weight of several millions and it has been used by several authors. We used this material as a reference polymer for our experiments.

### 2.1.5. Polycarbonate (PC)

This was obtained in sheets from Bayer AG, commercial name Makrolon.

## 2.2. Experimental details

The samples we used were compact tension specimens (CTS) in the experimental apparatus shown in Fig. 1 [15]. The main features of such samples are that the crack grows in a straight line without side grooves and that only a small amount of material is required. We built a small tensile machine and adapted it with a HeNe laser in order to mount them on a Leitz microscope. This apparatus allows the measurement of: the applied load $P$, the crack velocity up to $10^{+2}$ $\mu$m sec$^{-1}$, the inference pattern of the craze, the crack length and the temperature between − 110 and + 140° C.

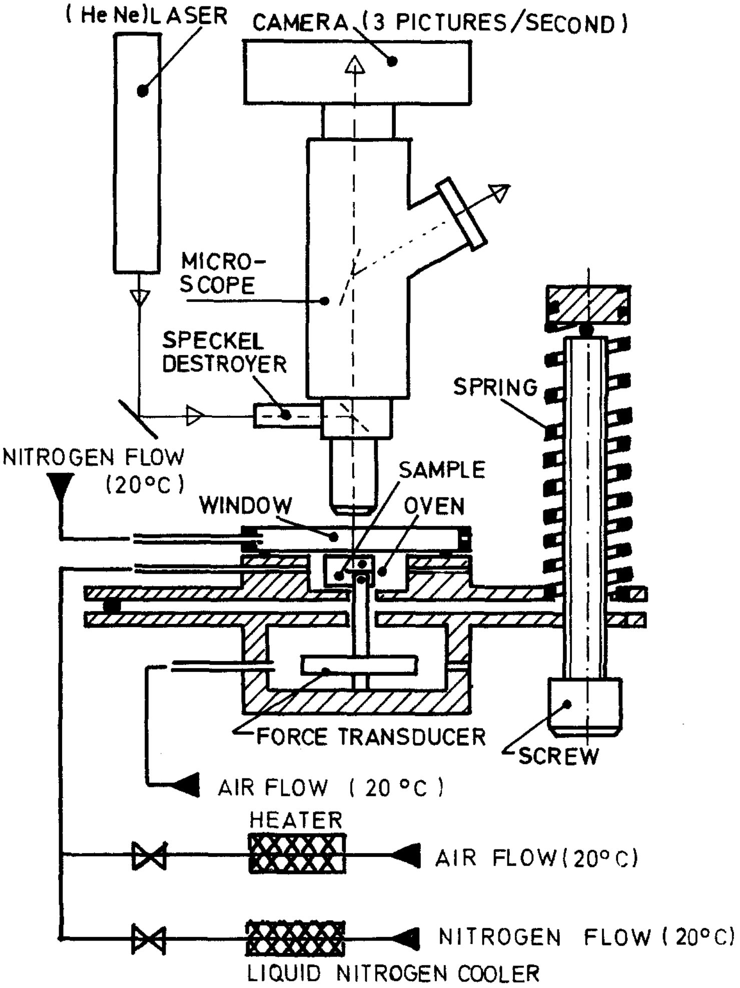


*Figure 1* Experimental set up. The different gas flows allow the temperature in the oven to be changed without temperature drift of the force transducer or moisture formation on the window. The spring keeps the force constant even when the whole mechanism relaxes slightly. The camera and the force transducer are connected to a recorder which gives the curve of force against time with small peaks each time a photograph is taken.

We had to solve the practical problems of moisture formation on the window of the oven at temperatures below the room temperature and temperature drift of the load measurement cell. For more details see Fig. 1. As yet the experimental limitations of the apparatus are in obtaining a sharp picture at the highest crack velocity and the load applied by a screw, that is, without a well defined stress or strain rate.

Young's modulus $E$ and the craze stress $\sigma_y$ of the bulk material around the crack tip may be calculated by means of the Dugdale model

$$E = \frac{K_1^2(1-\nu^2)}{\sigma_y\, 2v_r} \qquad (1)$$

$$\sigma_y = \left(\frac{\pi K_1^2}{8S}\right)^{1/2} \qquad (2)$$

where $S$ is the craze length, $2v_r$ the craze displacement, $\nu$ the Poisson ratio and $K_1$ the stress intensity factor at the crack tip (see for example [2] or [5]).

### 2.2.1. Experiments

The experimental procedure was as follows: The compact tension specimens were slowly stressed at a certain temperature $T$ until the crack started to grow with a velocity of a few micrometers per second. Then $K_1$ took the particular value $K_c$. $K_c$ is a function of the crack speed $\dot{a}$ and the temperature i.e. $K_c(T, \dot{a})$, therefore we measured $K_c$ at a velocity of about $10\,\mu\text{m}\,\text{sec}^{-1}$ in all experiments.

We observed two cases:

(1) When a single craze existed at the crack tip, the latter was propagated over a distance greater than the craze length.

(2) As we shall see later, when a multiple craze appeared ahead of the crack, $K_c$ depended on the crack length. Therefore, the crack was propagated just a few micrometers in order to avoid further miltiple craze formation.

Thus we obtained $K_c$ versus temperature curves as shown in Fig. 2. These curves reflect some particular properties of the materials:

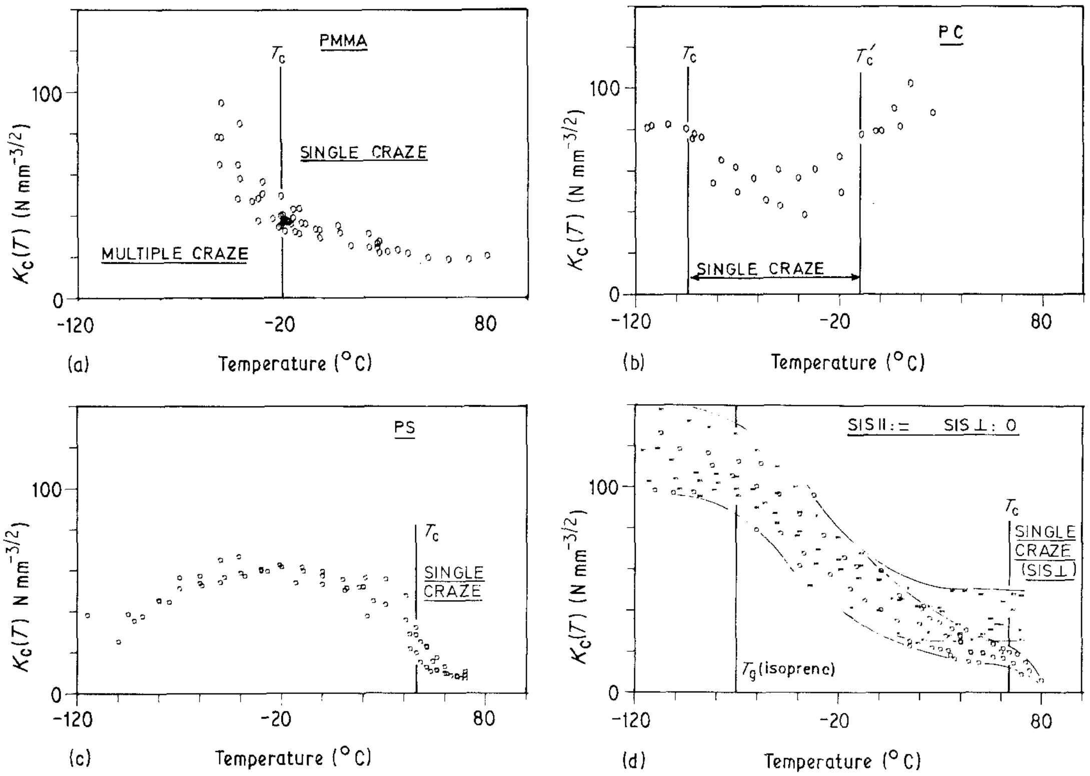


*Figure 2* The $K_c(T)$ curves for PMMA, PS, PC, SIS $\parallel$ and SIS $\perp$. Notice the drop at -- 50° C for SIS $\parallel$ and SIS $\perp$ (d) due to the glass transition of the polyisoprene. Also notice the drop at − 20° C for PMMA (a), − 90° C for PC (b), 45° C for PS (c) and 65° C for SIS $\perp$ (d), below which multiple crazes appear at the crack tip. There is another critical temperature for PC at 10° C, above which single craze does not exist, but this transition is not as sharp as the transition at − 90° C.

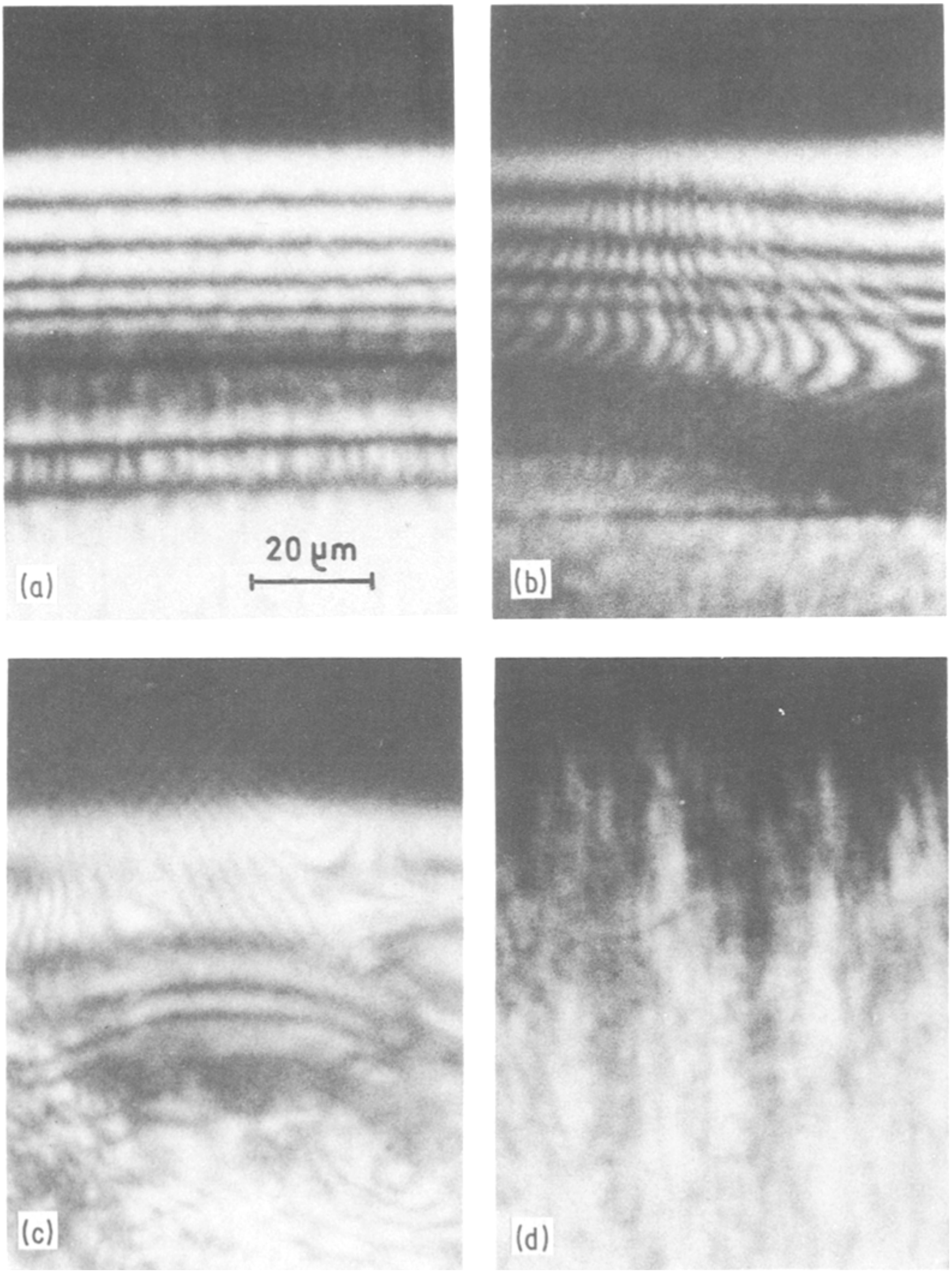


*Figure 3* (a), (b) and (c) the inference pattern obtained for PMMA in the region of $T_c$ at 3 temperatures: (a) −19, (b) −20 and (c) −21° C. The phenomenon remains the same but the temperature changes for PS, PVC, SIS ⊥ and PC (d) the inference pattern for SIS ∥ at all temperatures.

*2.2.1.1. For PMMA, PS, PC and SIS* ⊥. The $K_c(T)$ curve drops at a certain temperature. Below this temperature, instead of a single craze, a multiple craze appears ahead of the crack.

*2.2.1.2. For SIS* ∥ *and SIS* ⊥. The $K_c(T)$ curve drops at −50° C. This temperature is near the glass transition temperature of the polyisoprene.

*2.2.1.3. For SIS* ∥. No single craze appears at the crack tip whatever the temperature. Moreover, the value of $K_c$ here depends on the crack length

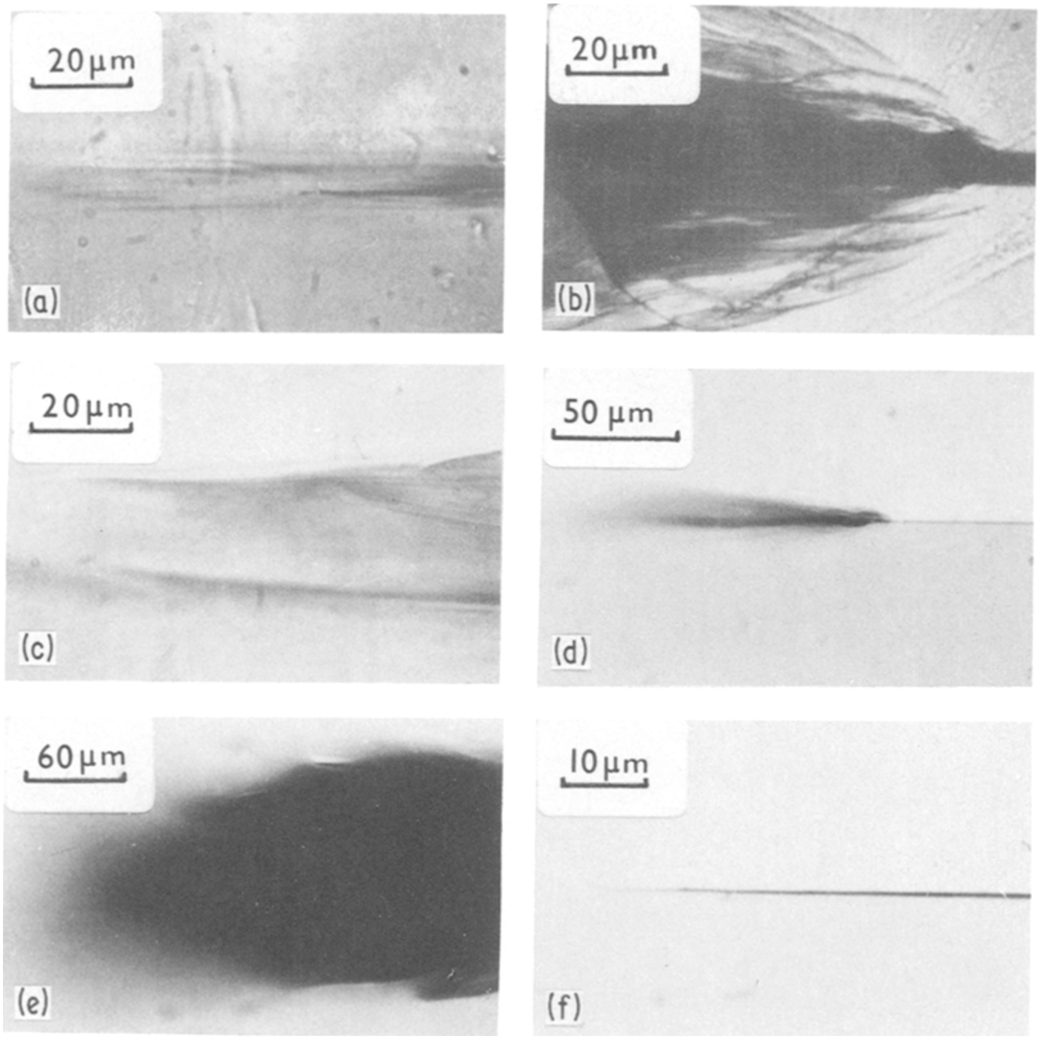


*Figure 4* (a) to (e) Side view of the crack propagated below $T_c$ for different polymers. (a) PMMA, (b) PS, (c) SIS $\perp$, (d) PVC, (e) PC and (f) side view of the crack propagated above $T_c$. The picture is the same for all polymers.

and is not a material constant. These results, summarized above, will be discussed and enlarged upon by means of photographs of the craze (Figs 3 to 6).

## 3. Results and discussion

### 3.1. Single craze versus multiple craze

Fig. 3 shows the evolution of a single craze when propagated at decreasing temperatures. Below the critical temperature, $T_c$, multiple crazing appears at the crack tip in PMMA, PC, PS, SIS and PVC. The values of $T_c$ at which multiple crazing appears are given in Table I (see also Fig. 7).

The $\beta$ relaxation has often been associated in other studies with the fracture processes of polymers. If we estimate the time lapse, $\tau$, during which a molecule is subjected to the stresses and strains in the craze (from the tip of the craze to the end of the craze where the molecule breaks) to be

$$\tau = \frac{S}{\dot{a}} \tag{3}$$

where $S$ is the craze length, $\dot{a}$ is the crack speed, $S \simeq 20$ to 200 $\mu$m and $\dot{a} \simeq 1$ to 10 $\mu$m sec$^{-1}$; then, $\tau \simeq 2$ to 200 sec, which is in the range of frequency where $T_\beta = T_c$ for PMMA, PS and PC. It does not seem realistic to look for any more precise correlation between the $\beta$ frequency and the crack speed, because the $\beta$ frequency is based on a stress–strain measurement at very low stresses and strains, whereas at the crack tip, the craze

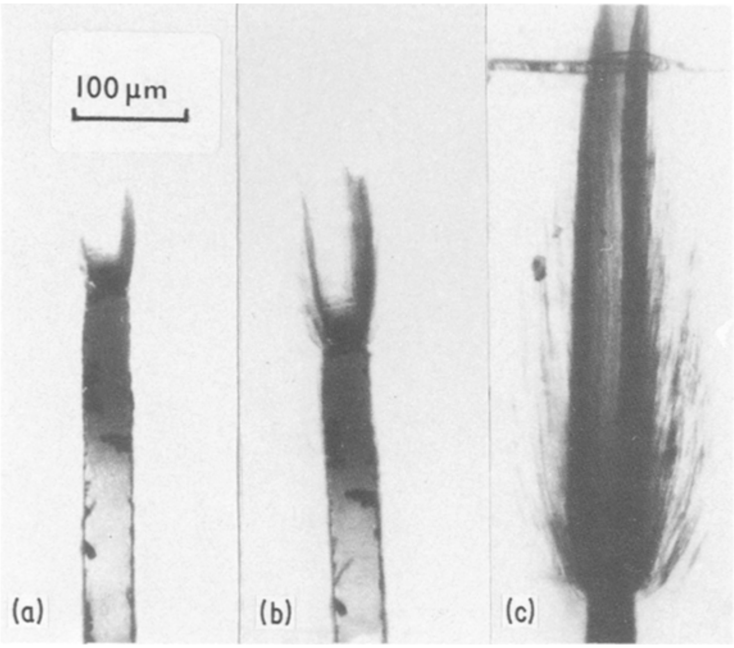
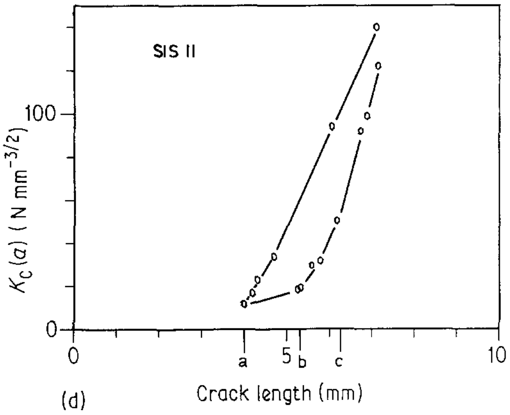


*Figure 5* (a) to (c) are side views of the crack in SIS || propagated at 20° C, (d) shows the relationship between crack length and $K_c(a)$. $K_c$ is not a material property in this case because it depends on crack length.



involves very high stresses and strains. On the other hand, the interface between the bulk material and the craze is very thin. Then, when the crack and the craze propagate, the strain rate during the transformation of the bulk into the craze is very high. The transition $T_c$ is very sharp except for PVC: this material was anisotropic (extruded sheet) and even after anealing two different patterns of crazing behaviour and two different temperatures $T_c$ were obtained parallel and perpendicular to the direction of extrusion.

The $K_c(T)$ curve drops at the same temperature $T_c$ where the single craze appears. This leads to the conclusion that certain molecular motions are free above $T_c$, which may correspond to $T_\beta$. Another support for this conclusion is given by Struik [18], who noticed that the position of the $\beta$ peak on the temperature scale is relevant for ductility. He compiled, for several materials, a table of the temperature $T_b$ at which the creep compliance at 10 sec is $0.9 \times 10^{-9}$ m$^2$ N$^{-1}$. These temperatures correspond more or less to our $T_c$ temperature if we take into account that a 10% change in the value $0.9 \times 10^{-9}$ m$^2$ N$^{-1}$ changes $T_b$ by between 20 and 50° C.

Below $T_c$ there are multiple crazes at the crack tip. Fig. 4 gives a side view for the different

TABLE I

| | Values of $T_c$ | | | | |
|---|---|---|---|---|---|
| | PMMA at<br>$-20 \pm 2°$ C | PS at<br>$+45 \pm 2°$ C | SIS at<br>$+65 \pm 2°$ C | PVC at<br>7 or 30° (see text) | PC<br>$-95 \pm 2°$ C |
| Frequency (Hz) of the $\beta$ relaxation for $T_\beta = T_c$ (see Fig. 7) | $2 \times 10^{-2}$ [17] | $1.5 \times 10^{0}$ [16] | Composite material | $3 \times 10^{4}$ or $10^{6}$ [17] | $2 \times 10^{0}$ [17] |
| $T_b$ (°C) (see text) | + 30 | + 35 | – | + 5 | – 90 |

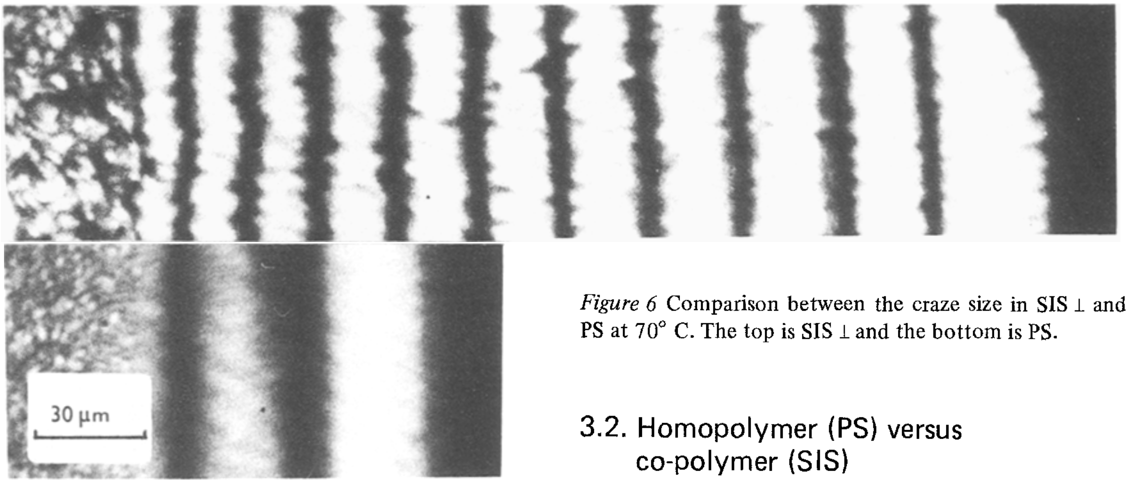


*Figure 6* Comparison between the craze size in SIS ⊥ and PS at 70° C. The top is SIS ⊥ and the bottom is PS.

materials. This explains the slope of the $K_c(T)$ curves below $T_c$: multiple craze formation requires more energy than single craze formation.

For SIS || there is no single craze. This may be explained by the structure of the material: it is known [13] that this co-polymer is brittle when the crack propagates perpendicular to the cylindrical structure (SIS ⊥) and rather ductile when the crack propagates parallel to the structure (SIS ||). Then the crack in the case of SIS || tends to bifurcate in order to follow the easiest path requiring the least energy (SIS ⊥) and so a multiple craze appears at the crack tip. Fig. 5 shows the development of the crack tip in SIS || during crack propagation: the crack itself does not propagate, but the "tree" formed by the crazes grows in volume and the $K_c$ curve becomes dependent on the crack i.e. craze length. Then $K_c$ is no longer a material property. This also explains the fact that the scatter of the curve $K_c(T)$ is greater for SIS || than for SIS ⊥.

## 3.2. Homopolymer (PS) versus co-polymer (SIS)

Another influence of the structure of the polymer on the craze may be emphasized by the comparison of the craze size in PS and SIS ⊥ (Fig. 6). The single craze in SIS ⊥ is about twice as large as in PS. At 70° C, $K_c$ is about the same for PS and SIS ⊥. Thus, Equations 1 and 2 show that $E$ and $\sigma_y$ are lower in SIS ⊥ than in PS: the polyisoprene cylinders in the SIS co-polymer act as a plasticizer (from the crazing point of view) without increasing the $K_c$ value at high temperatures, whereas at low temperatures (below −40° C) they cause a drastic increase in the $K_c$ value for both SIS || and SIS ⊥. This effect is well known for rubber reinforced polystyrene. At 70° C the numerical values computed by means of Equations 1 and 2 are:

$$\mathrm{PS}: E \simeq 2500,\ \sigma_y \simeq 28\ \mathrm{N\,mm^{-2}}$$

$$\mathrm{SIS}: E \simeq 1200,\ \sigma_y \simeq 14\ \mathrm{N\,mm^{-2}}.$$

Thus, the structure of the SIS block co-polymer has two different effects: an anisotropic effect at high temperatures (single craze/multiple craze)

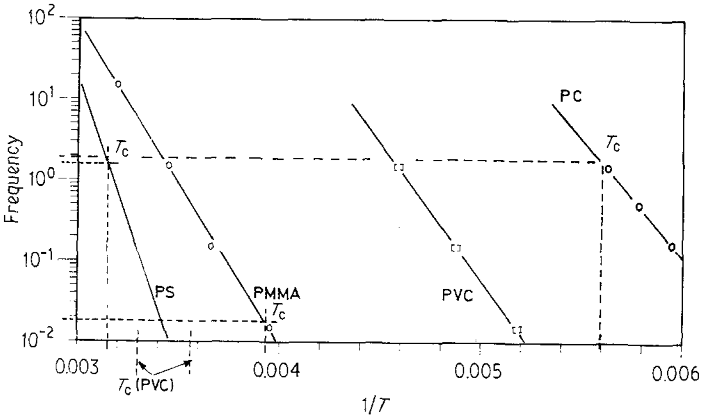


*Figure 7* Variations in the β temperature with the frequency for some polymers. The curves for PMMA, PC and PVC were measured by means of a Rheometrics mechanical spectrometer [17]. For the curve for PS see [16].

and an isotropic effect at low temperatures; increasing the value of $K_c(T)$ without regard to the orientation (SIS $\|$ or SIS $\perp$).

## 4. Conclusion

The experiments reported here show that, when there is no structural effect on the craze formation, a single craze appears ahead of the crack tip only above the critical temperature $T_c$. Simultaneously the value of $K_c(T)$ drops at $T_c$. Above $T_c$, a uniaxial structure may prevent the formation of a single craze when the fracture mechanisms are different in the two principal directions of the structure. It seems that $T_c$ may be related to the $\beta$ relaxation temperature of the polymer. But the latter is very time-dependent and it is intended to perform further experiments under cyclic loading in order to make clear whether $T_c$ follows the same time–temperature law as $T_\beta$ or not.

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