polymer communications

New type of crazes in oriented polycarbonate

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INTRODUCTION

The local transformation of glassy polymer matrix material into fibrillar structures, called crazing, is of basic importance for the mechanical properties of polymers. Crazing has been studied extensively in unoriented materials (see, for example refs 1–3). Orientation has a strong influence on craze initiation and growth[1–5]. Little attention has been given, however, to the effect of orientation on the craze microstructure. More information on this subject may lead not only to a better understanding of the mechanical properties of polymers in the oriented state but may also offer a deeper insight into the state of unoriented polymers.

EXPERIMENTAL

The measurements were performed on poly[2,2 propane bis(4-phenyl carbonate)] (PC), Makrolon 3200, produced by Bayer AG with a viscosity-average molecular weight $\bar{M}_v = 27000$ g mol^{-1}. The material was oriented by drawing at a temperature of 160°C with a strain rate of 200% min^{-1}. The degree of orientation was characterized by measuring the optical birefringence at a wavelength of 545 nm. Crazes were initiated by drawing these oriented samples to rupture parallel to the original draw direction at 119° and 129°C, respectively, with a strain rate of 0.28% min^{-1}. After drawing, the small-angle X-ray scattering (SAXS) of the crazed polycarbonate was measured with a Kratky camera using nickel filtered CuKα radiation. No desmearing procedure was applied to the scattering curves. Further experimental details are given elesewhere[6].

RESULTS AND DISCUSSION

Under the drawing conditions described above, numerous crazes which we shall call crazes (I) are initiated in unoriented PC well below the yield point. Observations with optical and scanning electron microscopes show that the majority of these crazes are well separated from each other. Frequently they start from inhomgeneities like surface scratches or defects. The fibrillar craze microstructure may be characterized by SAXS according to a method used by Paredes and Fischer[7]. This method is based on the fact that interfibrillar interferences give rise to a well-pronounced scattering maximum as can be seen from *Figure* 1. In this Figure and in the following SAXS is given as a function of the amount of the wavevector $s = (4\pi/\lambda) \sin(\theta/2)$ where λ is the savelength of radiation and θ the scattering angle. The fibril diameter d may be calculated from the position s_{max} of the scattering maximum provided that the correlation function of the fibril centres and the volume fraction c which the fibrils occupy within the craze are known. Assuming a liquid-type of order and a value $c = 0.45$ for unoriented PC, we obtain[7]:

$$d = \frac{4.90}{s_{max}} \qquad (1)$$

From this equation, fibril diameters of 27 and 36 nm are calculated for unoriented PC drawn at 119° and 129°C, respectively. These values are in agreement with those measured by Paredes and Fischer[7].

The same type of crazes with similar fibril diameters may easily be identified by SAXS in PC oriented up to a value $\Delta n \simeq 0.01$. In *Figure* 2 the position of the scattering maximum, rather than the fibril diameter, is given as a function of Δn. As far as oriented PC is concerned, equation (1) can only be regarded as an approximation since one has to assume that the volume fraction c will be a function of Δn.

If samples with $\Delta n \geqslant 0.01$ are drawn to rupture their SAXS behaviour is predominantly determined by a new type of fine crazes which we shall call crazes (II). These crazes are initiated well above the yield point just before rupture takes place and their initiation and growth is

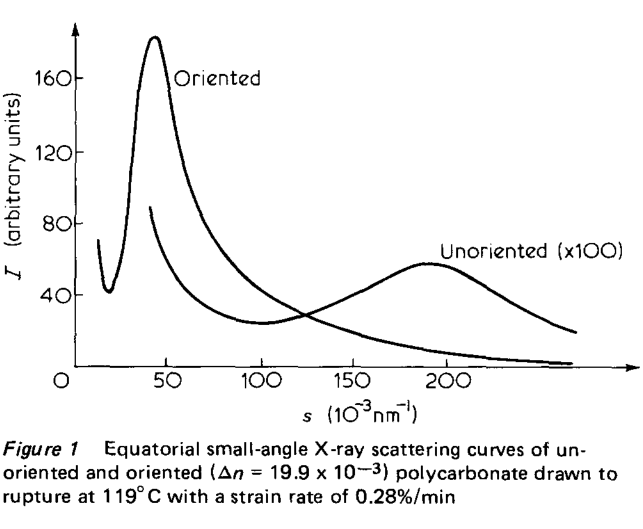

Figure 1 Equatorial small-angle X-ray scattering curves of unoriented and oriented (Δn = 19.9 x 10^{-3}) polycarbonate drawn to rupture at 119°C with a strain rate of 0.28%/min

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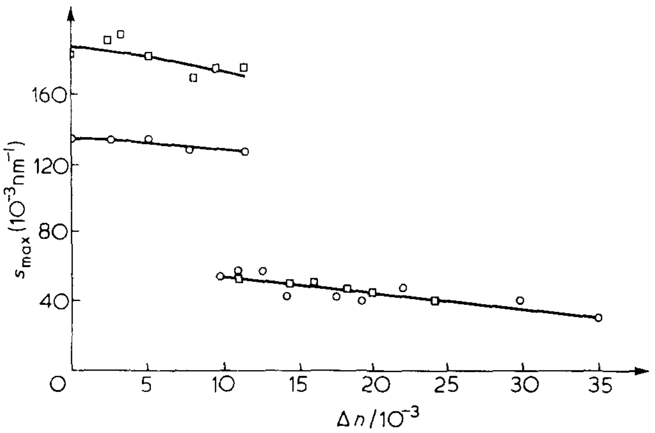

Figure 2 Position of the small-angle X-ray scattering maximum (s_{max}) of polycarbonate as a function of preorientation given by the optical birefringence Δn. Samples have been drawn to rupture at 119°C (□) and 129°C (○), respectively, with a strain rate of 0.28%/min

accompanied by a flattening out of the engineering stress–strain curve. The pronounced shift of the scattering maximum towards smaller scattering angles (*Figures* 1 and 2) shows that the fibril diameter is considerably larger than the diameter measured for normal craze fibrils. It is thus possible to observe the fibrillar craze structure by scanning electron microscopy as shown in *Figure* 3. The cylindrical shape of the fibrils is clearly visible. A distinctive midrib, such as discussed for crazes (I) by Lauterwasser and Kramer[8], may be seen.

The crazes of the type found in oriented PC completely cover the material giving rise to an increase of SAXS by two orders of magnitude (*Figure* 1). In addition, the optical properties of the sample change considerably. Irradiation by white light causes those samples drawn at 119°C to appear blue in the direction of backward scattering whereas the samples drawn at 129°C show what is usually called stress whitening. The blue colour may be explained by the fact that the SAXS maximum falls into an s-range accessible to wide-angle light scattering. On the other hand, the while colour may be attributed to the intensive light scattering ability of the crazes themselves which, produced at the higher draw temperature of 129°C are more numerous and have critical dimensions for light scattering. Our results show that, at least in the case of PC, stress whitening may be attributed to the new craze phenomenon reported here.

Examination of a zone close to the fracture surface of the specimens with $\Delta n \leqslant 0.01$ revealed that sufficiently high stresses had been built up during the fracture process to initiate the same type of crazing as in more highly oriented PC. By slightly changing the experimental conditions used in these investigations, crazes II may even completely cover unoriented samples.

It should be mentioned that crazing and, as a consequence the pronounced SAXS maximum is no longer observed in highly oriented samples. A detailed analysis of the scattering behaviour will be given in a future publication[6].

DISCUSSION

The meniscus instability mechanism which has been proposed by Argon and Salama[9] for the advance of the craze tip accounts in a satisfactory manner for the regular fibril structure observed in both types of crazes described here. It may be shown[7,9] that the fibrillation stress σ_{fib} is one of the basic parameters which determine the fibril diameter d, in that d increases with decreasing σ_{fib}. The temperature dependence of σ_{fib} accounts for the different fibril diameters found at 110° and 129°C, respectively, for the crazes (I) (*Figure* 2).

To explain the different initiation conditions for crazes (I) and crazes (II), we assume that two different molecular processes are involved in the formation of each type of craze. The phenomenon of initiation of conventional crazes (I) is the stress-induced collective break-up of a matrix region due to the rotational reorganization of chain segments subjected to local bending moments. This process essentially takes place under the constraint of stable entanglements. Crazes (II) form under considerably higher stresses where the stretching of chain sequences between entanglement points has already led to a large amount of strain hardening. We must, therefore, assume that the resolution of entanglement points or chain scission play an important role in the initiation of crazes (II). It is evident that the mechansim starting at high elongation of the samples and leading to the formation of thicker fibrils in case of crazes II relates to an instability different from the plastic instability considered thus far[3,9]. The fact that a transition of the deformational mode can occur in highly stressed polymers has been demonstrated convincingly by Pakula and Fischer[10] for poly(ethylene terephthalate), isotactic polypropylene and polyamide-6.

In unoriented PC or PC with a small degree of orientation cracks under the given experimental conditions will initiate and propagate from crazes (I) before the material has reached the conditions for craze (II) initiation. It is only in proximity to the advancing crack tip that sufficiently high stresses are built up which lead to formation of crazes (II). In view of the rather general mechanism of craze (II) initiation it may be expected that this type of craze can also be found in other polymers

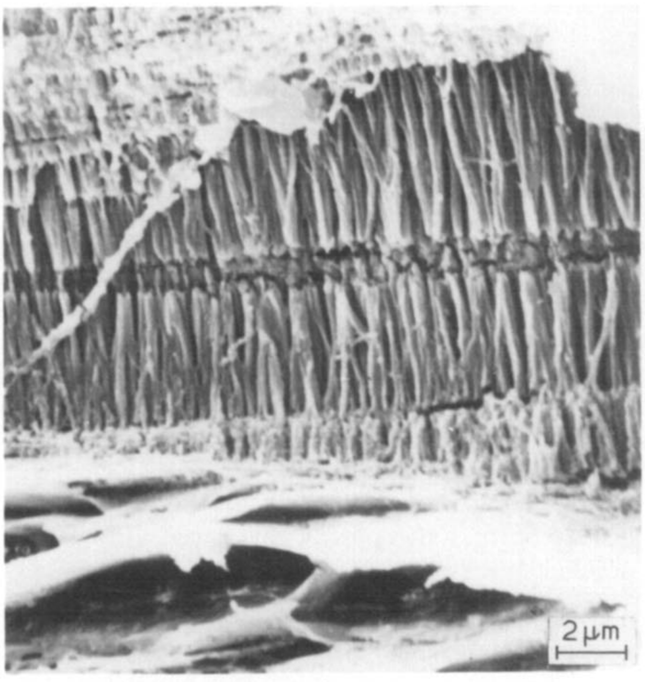

Figure 3 Scanning electron micrograph of the fibrillar craze structure taken from oriented (Δn = 19.9 x 10^{-3}) polycarbonate drawn to rupture at 129°C with a strain rate of 0.28%/min

under suitable experimental conditions. Some observations[11–13] have been reported in the literature which might be interpreted on this basis.

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Correlation of impact strength and rubber phase volume fraction in impact polystyrene

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A recent paper[1] considered the effect of rubber phase volume fraction (*RPVF*) on the mechanical properties of impact polystyrene. The authors found, among other things, that the notched Izod impact strength increased with increasing RPVF.

Although they do not discuss this relation quantitatively, their data are plotted in *Figure* 1; the impact strength at 0% *RPVF* has been added, and is taken as the 0.25 ft lb/in. found in most tables for general purpose polystyrene. The data are linear and fit the equation:

$$(\text{Impact strength } \pm 0.045)\ \text{ft lb/in.} = (2.17 \pm 0.14) \times RPVF + 0.23\ \text{ft lb/in.} \qquad (1)$$

As expected, the intercept is near 0.25 ft lb/in. Statistical analyses by *T*-test and correlation coefficient indicate significances to greater than the 99.95th percentile. This volume effect is surprising, since impact strength in such cases was thought to be due to the ability of the rubber phase surface to limit the extent of experimentally seen[2] voids and crazes.

Table 2 of the paper indicates that the rubber phase damping peak areas of the samples are in the ratio 1:2:3, while their *RPVF* and impact strength ratios are both 1:1.4:2. Thus, while qualitatively correlating well with both *RPVF* and impact strength, the peak areas quantitatively correlate poorly.

It was recently pointed out[3] that impact strength and dissipation factor are linearly related when both are evaluated under the same conditions. The main reason for this, as indicated earlier[3], is the absence of plastic deformations at the high strain rates of impact.

While impact strength has an equivalent frequency in the kHz range, dynamic mechanical properties are evaluated at much lower frequencies. Using the extrapoaltion scheme discussed in ref 3, an impact at ~2 kHz/20°C is equivalent to one at 1–10 Hz/10°C. Such dissipation factor values correlated well with impact strength for a wide variety of materials[3].

In the present case, log decrement values ($= \pi \times$ dissipation factor) were taken directly from the figures of the paper at 10°C, in addition to a value of 0.01 for 0% *RPVF*[4]. They are plotted in *Figure* 2, which fits the equation:

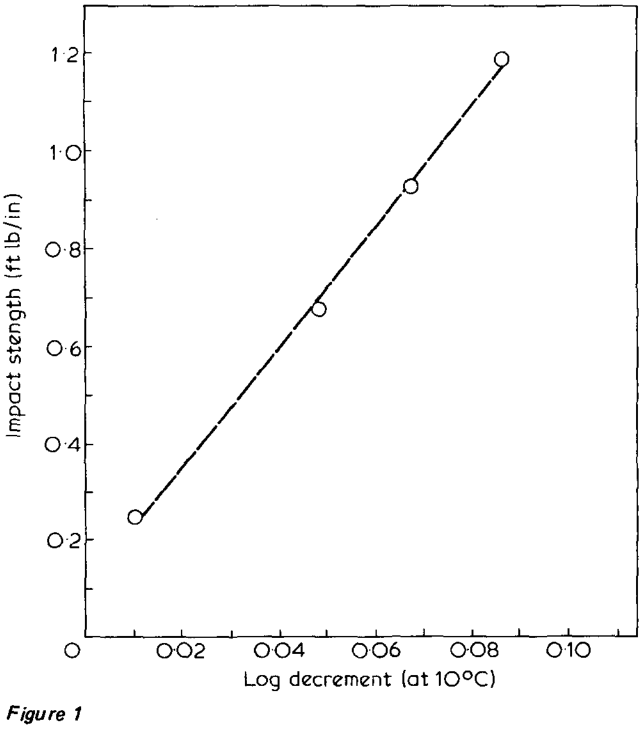

Figure 1

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