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Some Molecular Aspects of Craze Formation

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Dedicated to C. C. Hsiao and J. A. Sauer on the occasion of the 30th anniversary of the publication of their paper: "On Crazing of Linear High Polymers"

Summary

The changes in molecular orientation occurring during craze initiation and growth are discussed. Craze initiation is considered as a stress-induced, rotational, collective reorganisation of stiff chain sections in volume elements having a particularly large compliance. An energy balance is established for the transformation of a partially oriented matrix into craze fibrils which relates the fibril diameter to fibrillation stress and surface energy parameters. The predicted dependence of fibril diameter on temperature and preorientation is confirmed by experiments on polycarbonate.

Introduction

In November 1950 Hsiao and Sauer published the first important paper dealing with the molecular mechanisms of craze initiation in glassy polymers, the possible microstructure of the formed crazes, and the role of sample preorientation. They stated:

- that the mechanism of crazing "is an actual mechanical separation of polymer chains or groups of chains oriented more or less at right angles to the direction of stressing",
- that crazing is accompanied "by orientation or crystallization of the material",
- and that "crazing will not occur if the material is fully oriented in the direction of stretching" (HSIAO and SAUER 1950).

In subsequent years more than a thousand publications on crazing have appeared reviewed e.g. by RABINOWITZ and BEARDMORE (1972), KAMBOUR (1973) and KAUSCH (1978). Those papers were mostly concerned with the effect of stress and environment on the initiation, morphology, propagation and breakdown of crazes. In recent years

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a number of observations as to the *molecular mechanisms* of craze initiation and propagation were made concerning especially the influence of molecular weight (FELLERS and KEE 1974, WEIDMANN and DOELL 1976), the presence of entanglements (KRAMER 1978), craze shape and stress distribution (LAUTERWASSER and KRAMER 1979), and the nature of plastic instabilities (ARGON and HANNOOSH 1977, ARGON and SALAMA 1977, PAKULA and FISCHER 1979).

In the following the two steps, *craze initiation* and *fibril growth*, will be discussed considering molecular orientation.

Molecular Mechanism of Craze Initiation

It is at present generally accepted that a solid amorphous polymer consists of interpenetrating random coils. Such a "statistical coil structure" is schematically shown in Fig. 1.

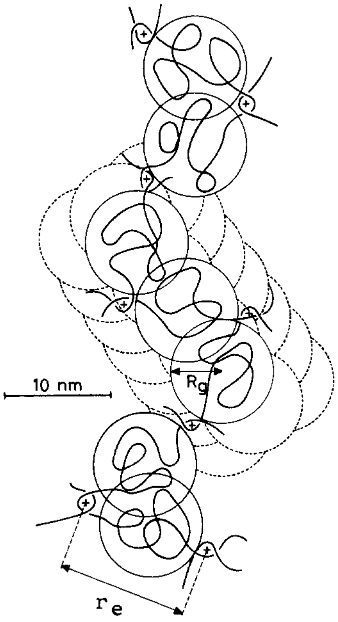

Fig. 1: Schematic representation of the "random coil structure" of an amorphous polymer (PMMA)
R_g: radius of gyration,
r_e: end-to-end distance of a segment M_c (= 30 000) between entanglement points (+)

The model represents the segments of molecular weight M_c between entanglement points (+) as spheres of radius R_g. It also recognizes the fact that no orientation correlation of segments occurs. It becomes evident that such a structure may in principle respond to large tensile stresses in two different ways: by shear displacement of neighboring segments with respect to each other or by collective rotational reorientation of chain sections. The exact size of the orienting sections is not known. One may say, however, that their mass M_r must be between M_c and several times M_o, the monomer molecular weight. If M_r were much larger than M_c

reorientation would not be very effective. If M_r were of the order of M_o one should be able to observe changes of e.g. birefringence with orientation several times larger than those actually observed (see below).

The collective rotational mechanism evidently depends on the tensile compliance of the reorienting volume element. It is thus favored by the presence of a large number of sections oriented perpendicular to the direction of tensile stress. Since the orientation distribution of sections in a small volume element shows a considerable scatter throughout the total matrix it must be assumed that in any sample there are volume elements of widely different "strength". The weakest of these elements will be activated under stress in the neighborhood of defects or impurities. The common observation that crazes are initiated as isolated events and preferentially on surfaces can be taken as an indication that craze initiation depends more on the rotational reorientation mechanism than on the much less fluctuating shear mechanism.

The step of craze initiation locally transforms the solid glassy matrix into an assembly of partially oriented chains interconnected by entanglements. It seems to be reasonable to assume that this assembly shows at first no fibrillar structure and that fibrils form while the craze grows, for instance according to the meniscus instability mechanism (ARGON and SALAMA 1977). In looking at a well developped PS craze one recognizes a fibrillar structure as close as 100 nm from the craze tip (BEAHAN, BEVIS et al. 1971). LAUTERWASSER and KRAMER (1979) observed that the fibrils in a crazed PS film reach a certain equilibrium thickness (of about 15 nm) once the craze thickness surpasses the width (of about 75 nm) of the so-called midrib, which occurred in their specimens at some 15 µm from the craze tip. The relation between fibril diameter, orientational strain and fibrillation stress under equilibrium will be discussed in the following.

Craze Fibril Formation

Under most experimental conditions a craze thickens by drawing uncrazed matrix material from the boundaries into the fibrils. This amounts to the transformation of a rectangular matrix element of volume $F_o\ L\lambda_o$ into a fibril element of volume $d^2\pi\ L\lambda/4$ (see Fig. 2 for notation). If volume is conserved during the transformation, a mechanical work of

$$A = \sigma\ d^2\ \lambda\ (\lambda L - \lambda L_o)\ /\ 4\lambda_o \qquad (1)$$

is done by the stress σ acting on the surface F_o of the volume element. The work is used for material separation (γ_1) and the surface work parameter (γ_2) of the four faces of the matrix element, for the increase in surface (surface work parameter γ_3) during the stretching of the element and to overcome the stress σ_4 caused by internal friction during the extensional elongation of the element:

$$A = 4\lambda_o L \sqrt{F_o}\,(\gamma_1+\gamma_2) + (\lambda-\lambda_o)\,L\,(d\pi\gamma_3+F_o\sigma_4). \qquad (2)$$

From Equ. 1 and 2 one obtains after rearrangement

$$(\sigma-\sigma_4)\,d = \frac{8(\gamma_1+\gamma_2)}{(\lambda/\lambda_o-1)}\left(\frac{\lambda_o}{\pi\lambda}\right)^{\frac{1}{2}} + \frac{4\lambda_o\gamma_3}{\lambda} = f\,(\gamma,\ \lambda/\lambda_o). \qquad (3)$$

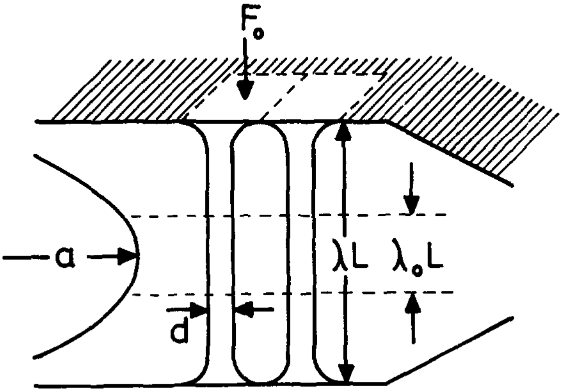

Fig. 2: Fibril formation during craze growth; $\lambda_o L$ width of primordial layer of bulk matrix material which fibrillates; λL, d length and diameter of fibril; section of craze surface corresponding to one fibril

Taking the experimental data of KRAMER (1978): $\sigma = 30$ MPa, $d = 15$ nm, $\lambda/\lambda_o = 3.5$, the surface work parameter γ_3 as about equal to the known value of unoriented polystyrene: $\gamma_3 = 0.040\ \mathrm{Jm}^{-2}$, and neglecting σ_4 one calculates $(\gamma_1+\gamma_2)$ to $0.42\ \mathrm{Jm}^{-2}$, i.e. to about 10.5 times the value of the pure surface work parameter. This value corresponds very well to the energy of separation measured by ROBERTSON (1976) for short PS molecules ($M_w \simeq 10'000$).

If $f(\gamma, \lambda/\lambda_o)$ can be considered as a slowly varying function of temperature then d should increase if $(\sigma-\sigma_4)$ decreases. On the other hand if $f(\gamma, \lambda/\lambda_o)$ can be increased as for instance by sample preorientation then d should also increase. In the following some results obtained by the authors (DETTENMAIER and KAUSCH 1980a) for preoriented polycarbonate will be discussed.

Effect of Preorientation and Temperature on Fibril Dimensions

In their recent publication DETTENMAIER and KAUSCH (1980a) reported on the formation of craze fibrils in bisphenol-A polycarbonate.

Characterizing the state of preorientation by the birefringence Δn and the fibril diameter d by the position s_{max} of the maximum of small angle X-ray scattering they obtained the data shown in Fig. 3.

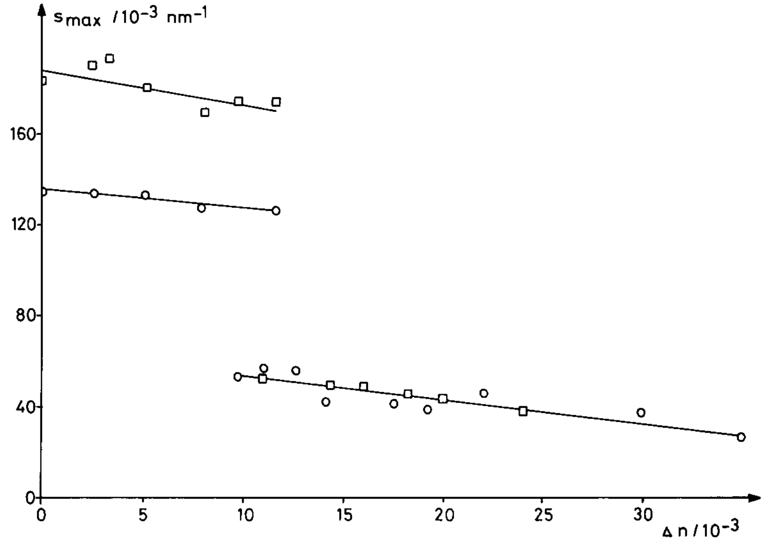

Fig. 3: Position of the small-angle X-ray scattering maximum (s_{max}) of polycarbonate as a function of preorientation given by the optical birefringence Δn. Samples have been drawn to rupture at 119 °C (□) and 129 °C (○) respectively with a strain rate of 0.28 %/min (Dettenmaier and Kausch)

Since s_{max} is inversely related to d (PAREDES and FISCHER 1979) it follows that d increases with increased preorientation and with increasing temperature. The data are thus compatible with the conclusion drawn from the energy balance discussed in the previous section. The notable change in fibril diameter at a preorientation $\Delta n > 10 \cdot 10^{-3}$ will be discussed in the following paper (DETTENMAIER and KAUSCH 1980b).

Conclusions

The role of sample preorientation discussed by HSIAO and SAUER (1950) has been reassessed in the light of the random coil structure of amorphous polymers. Arguments have been derived for the craze initiation through rotation of chain sections and for the relation between matrix orientation and craze fibril dimensions. In view of the several uncertainties still concerning the relation between λ and Δn, the dependence of γ_3 on λ and T, and the influence of σ_4 no further quantitative evaluation of Eq. 3 is attempted at this point. The morphological aspects of what must be considered as a new craze phenomenon will be discussed, however, in the following paper (DETTENMAIER and KAUSCH 1980b).

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