

KINETICS OF STRESS-CRAZING AND FRACTURE PROCESSES IN  
MOULDED POLYSTYRENE AT DIFFERENT STRAIN RATES

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ABSTRACT

Initiation and growth of inhomogeneous deformation processes and fractures in injection moulded transparent polystyrene at different strain rates have been investigated by means of conventional and hf-cinematography. Under impact tensile load a maximum crack velocity of about 970 m/s was detected. Strain rate, sample deformation and craze concentration are strongly correlated. The formation of shear bands and macroscopic necking only can be observed at very low strain rates verified in creeping tests. Morphological studies led to the assumption that during craze propagation and necking processes the chain molecules in microregions possess the same mobility like thermal activated material above glass transition temperature.

KEYWORDS

Stress-crazing, shear bands, necking, molecular movement, morphology, fractography, hf-cinematography, crack velocity.

INTRODUCTION

Various authors investigated and described the fibrillar morphology of crazes in several amorphous polymers. So, for example, Spurr and Niegisch (1962) used the low temperature fracture technique; due to the existence of craze matter in the case of polystyrene, polymethyl methacrylate and polycarbonate the experimental evidence leads to the conclusion that stress induced crazes are not cracks in the usual sense of open void cleavages. The fibrous nature mostly was studied by means of ultramicrotomed sections and transmission electron microscopy (TEM); osmium-tetroxide (Matsuo, Nozaki and Jyo 1969) and iodine-sulphur eutectic (Kambour and Russell 1971) has been impregnated into crazes in polystyrene and rubber-modified polystyrene to act as a reinforcing agent during microtomy and as a contrast enhancer during electron transmission. Unfortunately all these preparation techniques are combined with mechanical treatment and produce a lot of artefacts; furthermore it was impossible to get knowledge of the prefibrillar states of craze morphology and the molecular movements in microregions.

## EXPERIMENTAL

The material used for the experiments was commercial bulk polystyrene with a molecular weight of  $M_n = 111\,000$ . In order to mould specimens with significant molecular orientation differences in the cross section a low injection temperature of  $200^\circ\text{C}$  and a mould cavity wall temperature of  $40^\circ\text{C}$  have been chosen.

The strain rate of the specimens subjected to constant, normal and impact tensile load at room temperature varied between  $10^{-7}$  and  $10^1 \text{ s}^{-1}$ . The kinetics of crazing and fracture cinematographically have been recorded.

The prefibrillar craze morphology could be identified by means of electron microscopy and one-step-replica method after oxygen ion etching. The selective etching process is based on different degradation rates of regions with locally differing densities and/or differing packing types of the chain molecules (Großkurth, 1977a).

## KINETICS AND MORPHOLOGY OF INHOMOGENEOUS DEFORMATION AREAS

Because of injection processing internal stress and molecular orientation distributions exist in the specimen cross section. These effect that tensile bars always craze internally. Low elongation speeds show a small craze concentration. Near the highly oriented surface the material remains still uncrazed. The brittle fracture takes place without recognizable warning. Higher strain rates cause a great number of crazes growing partially into the oriented region near the surface. The craze concentration reaches its maximum at a strain rate of about  $1 \text{ \%}/\text{min}$  (Fig. 1a).

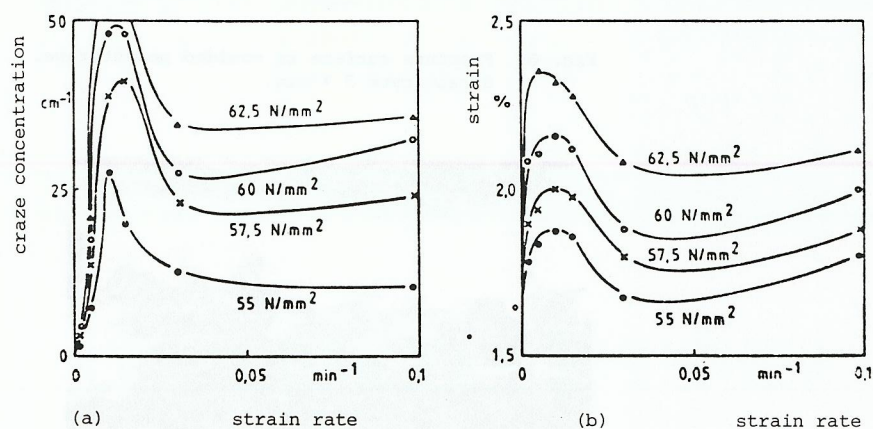


Fig. 1. Craze concentration (a) and strain (b) as a function of strain rate at respective constant tensile stress.

This value is in good agreement to the results given by Murray and Hull (1970); it is nearly independent of the actual tensile stress, but strongly correlated to the belonging strain (Fig. 1b). Therefore the greatest part of strain is based on the plastic deformation within the craze material.

As shown in Fig. 1b the deformability reduces with decreasing strain rate, if normal

stress induced deformation like crazing can be observed. At very low strain rates realized in creep tests besides crazing small shear initiated deformation takes place (Fig. 2a). Some further reduction of elongation speed effects a dramatic increase of molecular movement. Now after coarse shear band formation the amorphous polymeric material is necking and strained up to 50 % (Fig. 2b).

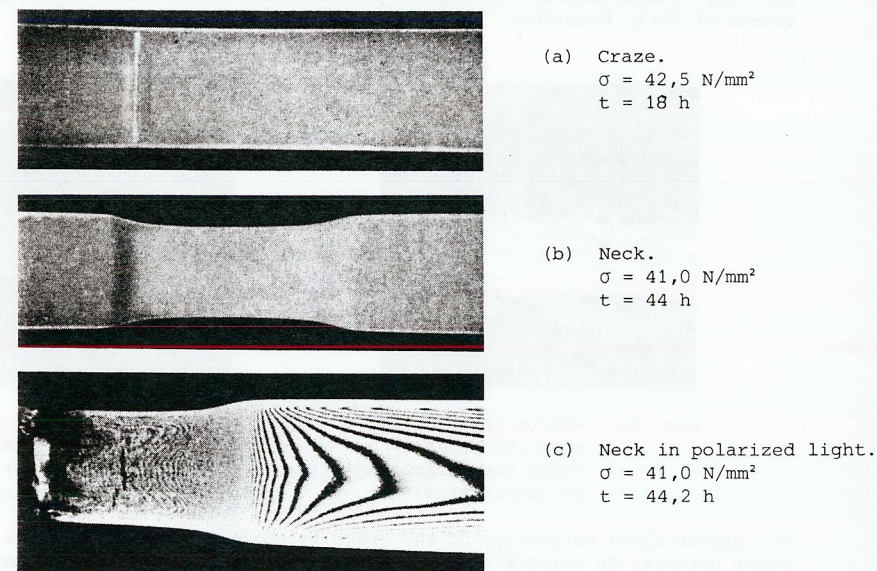


Fig. 2. Deformation processes in moulded polystyrene subjected to constant load.

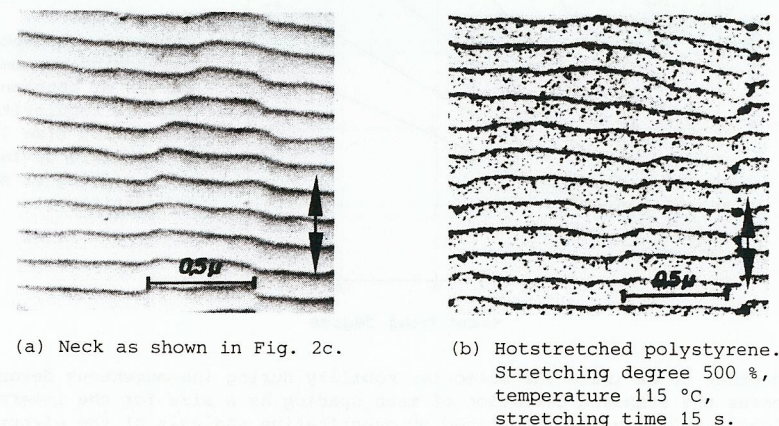


Fig. 3. Morphology of highly oriented polystyrene. Arrow marks the direction of deformation.

This plastic deformation yields high molecular orientations within the neck as evidenced by means of polarized light observations (Fig. 2c). In addition, the morphology of the neck obtained by ion etching and replica method in the TEM is rather similar to the superstructure of identical, but hotstretched polystyrene (Fig. 3). It consists of parallel lines ordered perpendicular to the deformation direction. Previous morphological studies indicate that the line boundaries possess higher density than the intermediate material (Großkurth, 1972; Kämpf and Orth, 1975). Therefore inhomogeneous deformation processes in microregions were suggested as the reason of their formation.

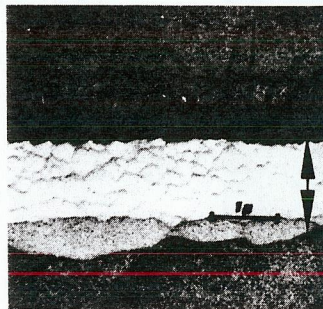


Fig. 4a. Prefibrillar craze morphology. Arrow marks the direction of deformation.

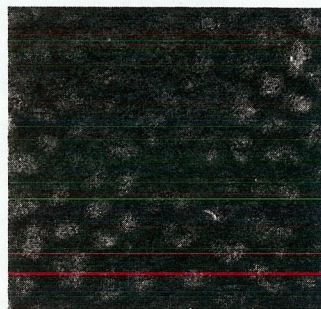


Fig. 4b. Hotstretched polystyrene. Stretching degree 50 %, temperature 115 °C, stretching time 15 s.

The prefibrillar morphology of the craze is shown in Fig. 4a. It consists of a globular network. An orientation of the globules in the transverse direction is indicated. With respect to the different micrograph magnification in Fig. 4b the structure of the hotstretched material drawn up to 50 % is nearly identical.

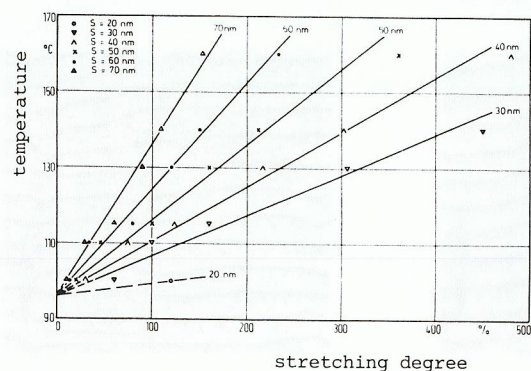


Fig. 5. Connection between the stretching parameters and curves of constant morphological regularity. Stretching time 15 s. S: standard deviation from mean spacing of structure boundaries.

In order to estimate the molecular mobility during inhomogeneous deformation processes the standard deviation of mean spacing as a size for the inverse morphological regularity was determined by quantitative analysis of the electron micrographs (Großkurth, 1977b). In Fig. 5 curves of constant structure regularity are plotted against the chosen stretching conditions. It is clearly visible that all the curves start at the glass transition temperature. Obviously heating above glass

transition is necessary for morphological changes of the observed type. Using these connections the temperature analogue chain mobility for necking and crazing can be determined by the same quantitative micrograph analysis. Resulting values of 98 °C for the shear induced necking and 117 °C for crazing have been found. With remarkable agreement Opfermann (1978) predicted for constant loaded polymethyl methacrylate according to the particle model proposed by Menges (1973) a local adiabatic heating of more than 100 °C.

#### FRACTURE PROCESSES

Fig. 6 shows the typical surface of fractures in moulded polystyrene. The mirror region was identified by Murray and Hull (1969) as the crack initiation and slow growth area where the crack propagates along the center of the craze formed by coalescence of voids. This very smooth area is surrounded by a multiplanar cleavage

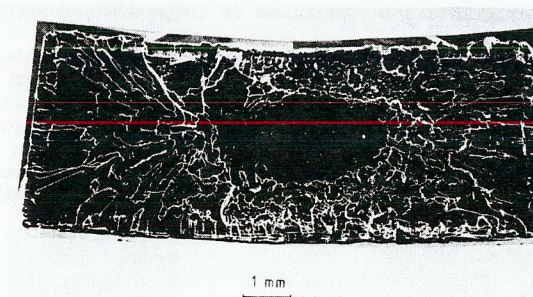


Fig. 6. Fracture surface in moulded polystyrene. Strain rate 5 %/min.

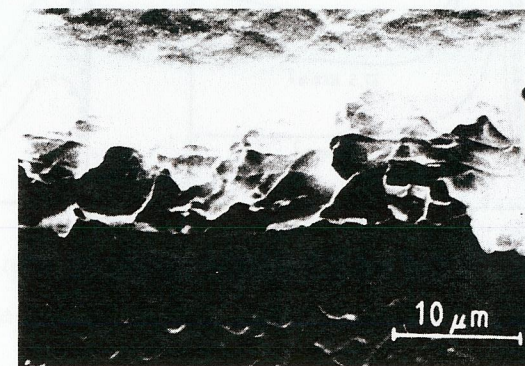
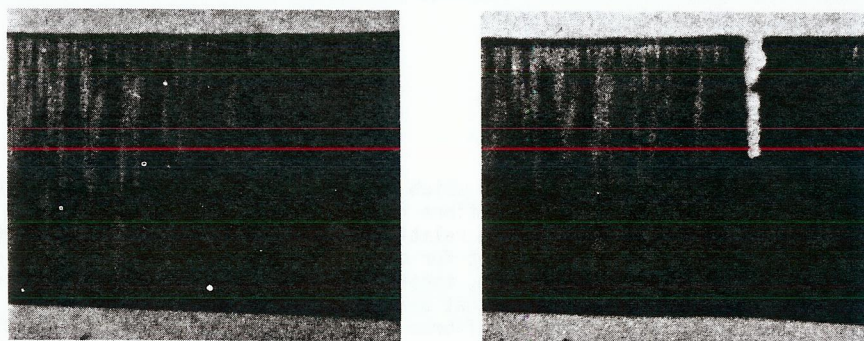


Fig. 7. Fracture morphology of the multiplanar cleavage region. Detail from Fig. 6.

region. It characterizes the fast crack area and contains crack branches as well as shear fractures with more directional texture between the normal stress induced planes. Some authors supposed that here the crack tends to propagate along the

interface between the craze and the bulk material, jumping from one craze-matrix interface to another. However, the globular structure in the fracture planes (Fig. 7) with a mesh size of some  $\mu\text{m}$  represents exactly the morphology of moulded uncrazed polystyrene (Großkurth, 1978).

The rough area near the highly oriented sample surface represents the greatest velocity of the running crack. According to measurements at those single frames shot by the high speed rotation mirror camera with a frequency of  $10^6$  frames per second the maximum crack velocity obtained in an impact tensile test reaches approximately 970 m/s (Großkurth, 1979). Some moments before cracking the specimen is filled with a lot of internal crazes (Fig. 8a). Their concentration arises enormously in the near of the expected crack. Therefore here no transparency can be observed any more. Ahead of the crack tip an area of strongly deformed material is recognizable (Fig. 8b.)



(a) Crack initiated deformation.

(b) Running crack.

Fig. 8. Development of the crack in moulded polystyrene subjected to impact tensile load. Hf-cinematographical frames.

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