Mechanical Properties of Crazes

investigated by Ultramicrohardness

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ABSTRACT

The ultramicroindentation hardness (down to penetration depth of $0.8\mu\text{m}$) of crack tip craze of several glassy polymers has been investigated. Hardness results were derived from the load-penetration depth curves. It is found that the hardness value of the craze fibrils is notably larger than the hardness of the bulk polymer. The elastic modulus of the craze was also calculated from the load-penetration depth curve. This value is larger than the elastic modulus of the bulk. Results also reveal that the craze length values examined by microindentation are in agreement with those of the craze shape investigated by interference optics and transmission electron microscopy.

§1. INTRODUCTION

Crazing is a widely occurring phenomenon in polymeric materials. Crazes are zones of highly plastically deformed and highly oriented polymer material and mainly consisting of fibrils along the direction of applied stress interconnected by cross tie fibrils. The structure of the crazes has been mostly investigated by transmission electron microscopy (Lauterwasser and Kramer 1979, Michler 1979, 1990) and both X-ray (Brown 1987) and electron diffraction (Yang and Kramer 1986). The shape of the crazes was examined by optical methods (Döll and Könczöl 1990, Döll, Könczöl and Bevan 1990). Various publications review the models of craze formation and the structure of craze zones in different polymers (Kambour 1973, Kramer 1983, Kramer and Berger 1990, Michler 1992).

In addition to these structural investigations, the craze fibril elongation ratio (Müller 1963, Kambour 1968, Kambour 1973) and the craze strength (Ishikawa et. al. 1996) were examined from the necking during elongation of the samples. In these studies the elongation of the fibrils was assumed to be equal to the elongation of the polymeric material in the necked region.

Microindentation hardness has been used to elucidate such phenomena as ageing (Ania et. al. 1989), thermally induced transitions (Baltá Calleja, Santa-Cruz, González Arche and Lopez Cabarcos 1992) and the plastic behaviour of polymer crystals and blends (Baltá Calleja, Santa-Cruz and Asano 1993, Santa-Cruz et. al. 1993). These studies have been carried out using the imaging method where the residual impression after indentation is used to characterize the permanent component of the hardness (Baltá Calleja 1994). Recent interest in hardness measurements of various polymers has been shown in the application of the compliance method where the force-displacement characteristic is measured (Ion et. al. 1990, Briscoe et. al. 1994). The advantage of this method lies in the possibility of measuring the relaxation of the

material upon unloading offering a mean to calculate the elastic modulus of the material (Doerner and Nix 1986, Pharr and Oliver 1992).

In the present investigation we report for the first time the measurement of microindentation experiments on crazes in the micron range. The length of the craze zones detected by microhardness is compared with the length of the crazes measured by interference optics. In addition the elastic moduli of the crazed material are calculated from the elastic recovery curves of indentations.

§2. EXPERIMENTAL

2.1. Materials

Commercially available samples of poly(styrene) (PS), poly(styrene-acrylonitril)-copolymers (SAN), poly(vinylchloride) (PVC) and poly(methylmethacrylate) (PMMA) were used. The molecular weight, polydispersity and mechanical properties of these materials are listed in Table 1.

The samples were miniaturized compact tensile (CT) samples ($10 \times 8 \times 4\text{mm}^3$) with a crack tip craze in front of a sharp notch as shown in Figure 1. The crazes were created during slow crack propagation under fatigue loading at room temperature.

2.2. Techniques

Microhardness was determined using a dynamic ultramicrohardness tester (Shimadzu DUH 202) with a Vickers square based pyramidal diamond indenter with an included angle between non-adjacent faces of the pyramid $\alpha = 136^\circ$. The experiments were performed at room temperature. During microindentation the force was applied up to a maximum load of 10mN at a constant loading rate of 1.4mN/s. The penetration depth was less than $1.5\mu\text{m}$ in all

experiments. In all cases the maximum load was applied for 6s (creep) and, then, the sample was unloaded at the same rate. Figure 2 shows schematically a typical loading-creep-unloading curve of a PS bulk specimen. The microhardness value (H) was calculated from the penetration depth and the applied load as

$$H=2P \cdot \sin(\alpha/2)/d^2 \quad (1)$$

where P is the force (in N) and the d the diagonal length of the projected indentation (in m).

Indentations were performed on a straight line along the direction of crack propagation (Figure 1). The location of the indentation along the X-direction is referred with respect to the notch tip which is taken as the origin for the microhardness experiments. The diagonal of the indenter projections was oriented parallel to the crack/craze propagation direction (x-direction in Figure 1). The first indentations were placed into the cracked region. The tip of the indenter dips into the crack and the outer part of the indenter touches the bulk polymer. The following indentations were placed into the crazed zone. In this case the tip of the indenter pushes the craze fibrils while the outer part presses the undeformed polymer surrounding the craze. Finally the microhardness of the bulk polymer in front of the craze tip was also measured. The values of the bulk microhardness were derived from a mean of about 30 indentations.

The craze width at the area of indentation was measured by optical microscopy and scanning electron microscopy (SEM). Additionally the structure of the crazes was investigated by high voltage transmission electron microscopy (HVEM). Semithin sections of about 1µm were microtomed for HVEM observations. Structural inspection of the craze zone was done at the JEOL JEM1000 transmission electron microscope (HVEM). The fibrillated structure of a

craze zone in SAN is shown in Figure 2. The microstructure of this craze created in a CT-sample is similar to the structure investigated in situ strained semithin sections (Michler 1990).

2.3. Mechanical considerations

To derive the microhardness of the crazed region from the experimental indentation value a two-phase system was assumed. The experimental microhardness (H_{exp}) is assumed to be equal to the sum of the microhardnesses of the bulk polymer (H_{bulk}) and the craze (H_{craze}) weighted over their volume fractions at one indentation:

$$H_{exp} = (V_{bulk}H_{bulk} + V_{craze}H_{craze}) / V_{exp} \quad (2)$$

$$\text{with } V_{exp} = V_{bulk} + V_{craze} \quad (3)$$

where V_{exp} is the volume of the entire indentation, V_{bulk} is the volume fraction of the bulk polymer and V_{craze} is the volume fraction of the craze zone.

The fibrils within the craze occupy themselves only a certain portion of the craze volume, the fibril volume content v_f . To calculate the microhardness of the fibrils (H_{fibril}) the expression

$$H_{fibril} = v_f \cdot H_{craze} \quad (4)$$

was used.

The elastic modulus (E) was calculated directly from the experimental loading-creep-unloading curve (see Figure 3) according to the procedure of Doerner and Nix (1986).

A similar procedure as the one described above was used to calculate the elastic moduli of the craze fibrils (E_{fibril}). The elastic modulus calculated directly from the experimental data (E_{exp}) was estimated as the sum of the modulus of the bulk polymer (E_{bulk}) and the modulus of the craze weighted in their volume fractions. The fibril volume content in the craze was taken into account to calculate the modulus of the craze fibrils (E_{fibril}). The elastic modulus is then given by equation 5.

$$E_{\text{exp}} = (V_{\text{bulk}} E_{\text{bulk}} + V_{\text{craze}} E_{\text{fibril}} / v_f) / V_{\text{exp}} \quad (5)$$

The volume fraction of fibrils within the craze is fairly constant. Except near the craze tip a decrease of the fibril volume fraction was observed (Donald and Kramer 1982, Kramer 1983). Published data of the volume fraction values of the craze fibrils were taken for the calculation of the elastic modulus (Döll and Könczöl 1990, Kambour 1973, Kramer 1983).

For the investigation of the craze contours optical interference measurements were performed on crack-tip crazes in miniature compact specimens (CT, $4 \times 8 \times 10 \text{ mm}^3$). The principle of the interference optical arrangement and analysis, as well as the particular experimental set-up for interferometry during fracture mechanical tests, were described previously (Döll and Könczöl 1990, Döll, Könczöl and Becan 1990). Therefore only some fundamentals of the interferometric investigations should be recalled. The specimens are loaded in the test apparatus with simultaneous measurement of load and recording of the interference fringe patterns, generated by reflection of the monochromatic light on the craze/bulk interface. The craze refractive index is estimated by an iterative approach comparing the fringe patterns in the loaded and unloaded state. The interference fringe patterns are evaluated subsequently fitting the local craze displacements at the measured positions to a function as predicted by the

Dugdale model. This procedure includes the extrapolation of the measured data beyond the first light fringe to the craze tip enabling and estimation of the craze length.

§3. RESULTS AND DISCUSSION

3.1. Microhardness

Figure 4 shows the microhardness experimental data from various indentations on a PS specimen. The horizontal solid line represents the microhardness average value of the bulk polymer and the dotted lines represent the zone of scattering data. The experimental results show three distinct regions of behaviour: a) crack zone, b) craze region and c) bulk.

The H-values measured along the crack zone are lower than the microhardness of the bulk. In this case the indentations were made close to the notch tip. The indenter tip was placed into the crack and the outer part of the indenter pressed the bulk polymer. Assuming a two phase system consisting of the crack and the bulk material, a lower H-value than that of the bulk must be measured because the hardness of the cracked portion (H_{crack}) is equal to zero (equations 6 and 7).

$$H_{exp} = (V_{bulk}H_{bulk} + V_{crack}H_{crack}) / V_{exp} < H_{bulk} \quad (6)$$

$$\text{with } V_{exp} = V_{bulk} + V_{crack} \quad \text{and } H_{crack} = 0 \quad (7)$$

As we have seen in our samples the crack is followed by the craze. The microhardness increases rapidly in this region (see Figure 4). Table 1 shows the bulk microhardness values of the polymers investigated. In Table 2 the H-values of the craze fibrils are collected. The data of

Table 2 suggest that the mechanical properties of the craze fibrils are higher than those of the bulk polymer. This is consistent with the concept of highly oriented polymer chains within craze fibrils (Bin Ahmad and Ashby 1988). It is noteworthy that the microhardness of craze fibrils in amorphous polymers is of the same order of magnitude than the microhardness of fibrils of semicrystalline poly(ethelene terephtalate) (Krumova et. al. submitted). It is also to be noted that the craze strength, as a parameter capable to characterize craze stability, is comparable to the hardness of fibrils in amorphous polymers (Ishikawa et. al. 1996).

If we consider the PMMA, SAN and PS samples then it is seen that the ratios $H_{\text{fibril}}/H_{\text{bulk}}$ decrease with decreasing microhardness of the bulk polymer (see Table 2). This is so because of the existing correlation between the mechanical properties of each polymer and those of the crazes. A similar parallel behaviour between the microhardness values of the bulk and the craze fibrils was not observed for PVC. The reason for this discrepancy might be due to the presence of additives (polymerization initiators, stabilizers, ...).

The craze length derived from microhardness indentations was compared with the length detected by interference optics. An enlarged section of Figure 4 is shown in Figure 5a. The contour of the same craze measured by optical interferometry is depicted in Figure 6b. It is seen that the craze length derived from the microhardness experiments is slightly smaller than the interferometrically detected length. This is due to the lower resolution of the microhardness measurements close to the craze tip.

Another interesting finding should be pointed out: The experimental microhardness values of indentations in the area near the craze tip are smaller than the bulk microhardness (see Figure 6). From electron microscopy it is known that the craze fibrils are broken in the vicinity the sample surface (Ensslen et. al. in prep.). Our explanation for these low microhardness values is that near to the craze tip the indenter does not touch the craze fibrils because of the

small indentation depth. Therefore the superposition of normal and lateral forces at the indenter tip can give smaller experimental microhardness values. Nevertheless the microhardness measurement is shown to be successful in detection of very short crazes. Figure 6 illustrates the location of a craze shorter than $30\mu\text{m}$. Figure 7 shows the contour of the same craze detected by interference optics.

3.2. Elastic modulus

The elastic moduli were calculated following the method of Doerner and Nix (1986). Bulk and craze moduli were separated by applying a parallel model as shown in equation 5. Craze fibril moduli (Table 2) as well as bulk moduli for the various polymers (Table 1) were derived. Results show that the craze fibrils modulus is, at least, twice than the value of the bulk. A proportionality between the elastic modulus of the bulk and of the craze fibrils is not obvious. This may be due to the lower accuracy in the calculation of this parameter.

The dependence of the elastic modulus of craze fibrils of PMMA, SAN and PS on the entanglement density (ν_e) is shown in Figure 8. It is known that the increasing density of entanglement in a polymer induces an increase of the bulk elastic modulus (Aharoni 1989, Elias 1993). In accordance with this concept, the results of Figure 8 show that the modulus of the craze fibrils also increases with entanglement density. Most interesting is, however, the finding that the elastic modulus of the craze fibrils is proportional to the critical stress required to create the crazes (crazing stress, σ_c) (Figure 9). This finding is, in turn, in agreement with the known proportionality between crazing stress and the molecular entanglement weight (Wu 1990). A remaining question is the dependence of both the craze fibril microhardness and the fibril elastic modulus on the loading history. This will be discussed in a subsequent paper.

§4. CONCLUSIONS

- a) Small craze zones in glassy polymers can be detected by means of the ultramicrohardness indentation technique. The microhardness values for all investigated samples can be divided into three regions: 1) the cracked region, 2) the crazed zone and 3) the bulk material.
- b) The microhardness and elastic modulus values of the crazed material are notably larger than those of the bulk polymer. This is due to the orientation of the polymer chains within the craze fibrils. These results underline the role of crazes as precursors of cracks providing resistance against crack propagation within the polymer.
- c) It is shown that the elastic modulus of craze fibrils (PMMA, SAN, PS) is proportional to both the crazing stress and the entanglement density.
- d) It is pointed out the possibility to estimate craze length from microhardness indentations though the measurement is less accurate than carried out by other techniques.

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CAPTIONS TO FIGURES

- Fig. 1: Schematic view of the compact tensile sample illustrating the position of: the notch (0), the crack (1) and the craze region (2); indentations were placed along the x straight line
- Fig. 2: Transmission electron micrograph of the fibrillar craze structure in SAN
- Fig. 3: Scheme of a typical load-penetration depth-curve
- Fig. 4: Microhardness values measured along the crack propagation direction in PS. Cracked, crazed and bulk zones are shown.
- Fig. 5: a) Variation of the experimental microhardness in the crazed zone of Fig. 4.
b) Craze opening ($2v$) vs. length (l) of the same craze shown in Figure 5a measured by interference optics
- Fig. 6: Microhardness values measured along the craze propagation direction in PMMA.
- Fig. 7: Craze opening ($2v$) vs. length (l) of a craze in PMMA measured by interference optics
- Fig. 8: Elastic modulus of the craze fibrils vs. the entanglement density
- Fig. 9: Elastic modulus of the craze fibrils vs. the crazing stress

Table 1

Polymer	M_w [kg/mol]	M_w/M_n	H_{bulk} [MPa]	E_{bulk} [GPa]
PMMA	2200	2.5	182±2	4.8±0.2
SAN	249	2.3	178±2	4.7±0.2
PS	476	4.2	164±3	4.3±0.1
PVC	181	1.7	145±2	4.2±0.2

Molecular weight, polydispersity and mechanical properties of the bulk polymers investigated

Table 2

Polymer	$H_{\text{craze fibril}}$ [MPa]	$H_{\text{fibril}}/H_{\text{bulk}}$	$E_{\text{craze fibril}}$ [GPa]	$E_{\text{fibril}}/E_{\text{bulk}}$
PMMA	537±16	3.0	13.4±1.1	2.8
SAN	510±20	2.9	12.2±1.4	2.6
PS	414±33	2.4	11.2±1.6	2.6
PVC	698±82	4.8	11.4±1.5	2.7

Microhardness and elastic moduli of the craze fibrils and the ratio of these values to the bulk properties of different polymers

Figure 1. Schematic view of the compact tensile sample illustrating the following positions: 0, the notch region; 1, the crack region; 2, the craze region; 3, indenter. Indentations were placed along the x straight line.

Figure 2. Scheme of a typical load-penetration depth curve.

Fig 3

Figure 4. Microhardness values measured along the crack propagation direction in PS. Cracked, crazed and bulk zones are shown.

Figure 5. (a) Variation in the experimental microhardness in the crazed zone of figure 4. (b) Craze opening 2ν against length l of the same craze shown in measured (ia) by interference optics.

Figure 6. Microhardness values measured along the craze propagation direction in PMMA.

Figure 7. Craze opening 2ν against length l of a craze in PMMA measured by interference optics.

Figure 8. Elastic modulus of the craze fibrils against the entanglement density.

Figure 9. Elastic modulus of the craze fibrils against the crazing stress.