A STUDY ON THE CORRELATION OF POLYSTYRENE (PS) FILM CRAZE TO ITS FRACTURE BEHAVIOUR BY TEM

Lu Xici (吕锡慈) Fan Chenggau (范成高) Qian Ruzhen (钱汝正)
The University of Science and Technology of China

ABSTRACT

The microstructure, deformation and failure processes of PS film crazes were observed by TEM. It was discovered that the crossing of two crazes might affect their growing and the structure at cross point was stable. The entire craze fibrillar network and the large orientation of breaking fibrils were found. It was recognized that the process in which the craze fibrils failed or the microcrack was initiated was very similar to the "tearing cloth" model proposed by the same authours for explaining the slow crack propagation in PMMA and that the crack tip craze in PS film obeyed the Dugdale model in contour.

INTRODUCTION

It is well known that fracture of glassy polymers is correlated with crazes[1—6]. Although there are many papers discussing craze structure by electon microscopy[7—10], however, only a few papers concerned the failure of craze and the initiation of submicrocracks in craze. Since to prepare thin film craze is easier than to microtome bulk polymer previously crazed[10], in this paper the correlation of PS film craze structure to its fracture behaviours by transmission electron microscopy (TEM) is studied.

EXPERIMENTAL DETAILS

PS($\overline{M}_w$=3.14×10^5, $\overline{M}_w/\overline{M}_n$=1.77) was made in Gao Qiao Chemical Factory, Shanghai by suspension polymerization. A copper grid used for TEM was coated with 1% collodion and then dropped on it 5% polymer solution in toluene by weight. Excessive solution was absorbed by a small filter paper and then the dropsurface flattened. As the solvent evaporates, a film is formed. Under the action of multiaxial stress due to contraction of the film itself crazes are formed. Then the sample was observed in a Hitach HU-11 TEM.

EXPERIMENTAL RESULTS AND DISCUSSION

Fig.1 to Fig.8 are transmission electron micrographs of PS film crazes during their formations, growth, mature and failure.

Apart from the general craze thickening course, as discussed in many papers[1,7], we can see in Fig.1 that at the tapered craze tip the nearly circular voids arranged with fibrils alternatively as pearls in series, and we are mainly interested now in craze crossing, which is important for polymer fracture. Fig.3 and Fig.4 are examples where two close crazes with different directions crossed. Referring to Fig. 3, after crossing at point C, the thickening course of craze B changes. The thickness of the right side, where craze B forms an acute angle α with craze A is far smaller than the left side and at C the thickness of craze B changes abruptly. One can reasonably suggest that the appearance of a craze in a film might decrease the stress or release the strain energy stored in it to somewhat low level and thus retards the neighbouring crazes to grow or to crack. In Fig. 3 the acute angle is α, the decrease in stress due to craze A is asummed to be $\Delta\sigma$. Assuming the stress acting on craze B before crossing is σ_0, then after crossing it would reduce to $\sigma_0-\Delta\sigma\cos\alpha$ on the right side. However, the direction of stress component $\Delta\sigma\cos\alpha$ would never pass through the left side, the craze will continue to grow at the left side for a period of time until σ_0 relaxes to a low level due to growing itself. This is why the thickness of the craze changes abruptly at C_0.This idea could be confirmed by Fig.4, where two crazes crosses approximately at right angle. Because $\cos\alpha$ approaches to zero in this case, so they grow continuously as if they had not crossed. However, the thickening of the crazes at C was affected with each other. The fibrils in craze B deflect outwards to avoid the coming tip of craze A which is constrained by the thickening craze B and finally becomes a big angle "wedge" inserted into craze B. From the characteristic behavior of crazes crossing at C one can say that the stretching mechanism of thickening[2] for PS film craze could not be neglected. If this were not so, the fibrils would not deflect outwards.

It is also interested to note that the structure of craze B at C seems stable. There is no reason to expect that craze B would fail first at C. Because the crossing and bifurcation of crazes are very important in the study of polymer fracture[1,2], it seems necessary to study further about the structure and failure of crazes.

In matured PS craze the fibrils have developed to form a network, where the primary fibrils bind the bulk polymer and the fine fibrils connect the former (see Fig.5). Diameters are about 200—400Å for the former, and 50—100Å for the later. The former could split to form new voids, and in most case they occur near the boundary of the craze. The bulk polymer at the boundary constrain the fibrils near it to contract in transverse direction and thereby oblige them to split themselves to form small voids. This feature would be important in peeling fracture which always takes place at the craze/bulk polymer interface at the crack tip in PS and PMMA[1,5].

In the midst of matured PS craze there is a narrow brighter strip (see Fig.4), with width about a tenth part of the thickness of the craze. Kramer[9] has claimed that he observed it in PS air craze, about 75nm in width, and he called it as "mid-rib". We have not seen it in fresh crazes, however, after storing these samples in labortory for several days, it does appear. It is certain that the PS molecules in fibrils had relaxed during storing, but how this could correlate to the formation of the bright strip and how it affects the fracture of polymers is still not clear.

It was reported[12—14] that the streching ratio λ of craze is about 3 to 4. Especially when λ exceeds 2.5, the fibrils begin strain hardening and it might break at some weak point in the network. In Fig.6 some fine fibrils have broken, the residuum of which likes a "protruding tumour" in a fibrillar "trunk". Because the fine fibrils must bear both transverse and longitudinal load during craze thickening, they would rupture first and result in combination of nearby voids to form larger one (V in Fig.6), in stress redistribution among fibers and finally in breading of fibrils to form submicrocracks (a,b, c,d in Fig.7). At b in Fig. 7 most of the fibrils have broken and only one left and only two left at c. Submicrocracks in Fig.7 may grow or combine with each other to form microcrack (see Fig.8). The boundary surfaces seperate further after the fibrils break and become lip-like. In Fig. 8, its length and width are about 5 and 1.5 μm respectively. Indeed, it is very small and the naked eyes are unable to resolve it. However it is a real crack and it could grow further to form macrocrack and finally results in material failure.

CONCLUSIONS

From the above discussion we could get the following conclusions about PS craze correlated with its fracture:

(1) A crack was initiated in PS film due to craze failure.

(2) The crossing of crazes might retard their growth and stabilize the material by releasing strain energy.

(3) In our experiment the primary fibrils in PS craze break at their middle (Fig.8), and this fact confirms the "tearing cloth"model for crack tip craze fracture of PMMA at subcritical crack speed[4].

(4) PS molecules in fibrils are situated in high orientation and retain certain degree of orientation after breaking. The length of broken and unbroken fibrils are clearly shown in Fig.7 and Fig.8. We have observed on TEM screen that the electron beam has no sooner heated the broken fibrils than their ends begin to retract, resulting in darkened broken ends. This behavior is very similar to the contraction of hair as its end is fired.

(5) The tip of microcrack developed in craze is a cone, its radius of curvature is about several microns (see Fig.2). The somewhat blunt tip would result in limited stress near the crack tip.

(6) It is proved directly be TEM that crack tip craze in Fig. 2 obeys the Dugdale model in its contour and that there is a inflection point in crack-craze/ bulk polymer interface which has been observed by optical interference method[12,15]

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Fig. 1 to Fig. 8 are transmission electron micrographs of PS film crazes in different stages in experiments:

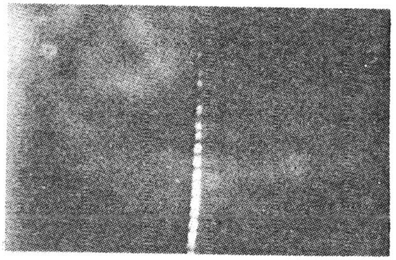

Fig.1 Craze tip region,×30000.

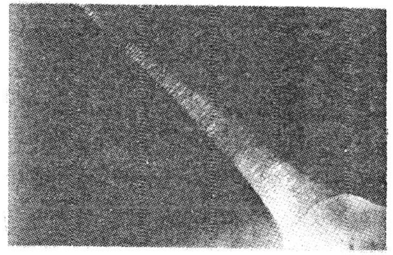

Fig.2 Crack-tip craze, ×10000.

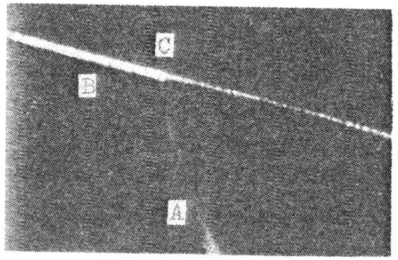

Fig.3 Craze crossing, ×30000.

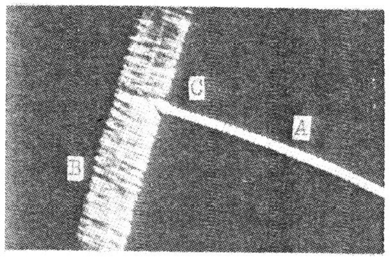

Fig.4 Craze crossing, ×30000.

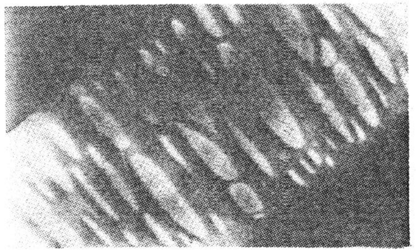

Fig.5 Matured craze, ×46000.

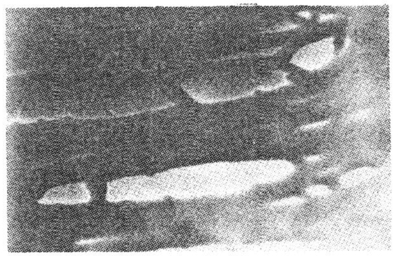

Fig.6 Craze failure, ×46000.

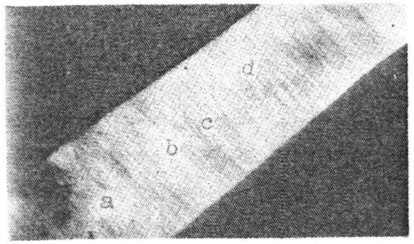

Fig.7 Submicrocrack in craze, ×16500.

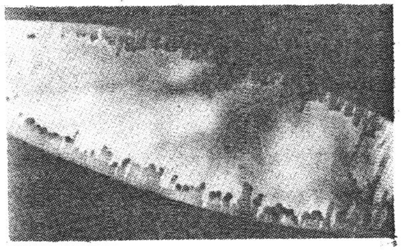

Fig.8 Microcrack in craze, ×18000.