

Infrared Spectroscopic Study of the Atomic Mechanism of the Growth of Crack in Polymers

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In the last few years considerable advances were made in the study of the atomic mechanism of fracture and crack growth in polymers. It was concluded that the crack propagates due to accumulation of stressed chemical bond scission at its tip caused by thermal fluctuations.

The measured local stresses in the crack tip vicinity in amorphous-crystalline polymers proved to be an order of magnitude less than the strength of chemical bonds (1). Such stresses cannot break a chemical bond. In this work an attempt is made to understand these contradictions.

Experimental

The experiments were carried out on oriented polyethylene, polypropylene and polyethylterephthalate films. To form the crack the specimen was cut. To measure the stresses and scission concentrations at different distances from the tip the specimens were placed into the infrared microscope. A small infrared beam was transmitted at different distances from the crack tip and the infrared spectra were recorded using the spectrophotometer. The methods for determination of stresses and scissions are described in detail elsewhere (2-4).

Results of Measurements

Fig.1 presents the dependence of local stresses averaged over the beam area upon the distance from the crack tip. The local stresses in the tip vicinity

exceed the external load by approximately an order of magnitude and falls smoothly as the distance from the tip increases.

However their value at the tip is one order of magnitude less than the strength of polymeric molecules and they cannot break the chemical bond.

Our measurements have shown that local stresses are distributed over interatomic bonds nonuniformly. The example of such distribution for polypropylene is shown in Fig. 2. The stress on the majority of bonds is approximately equal to the local stress. At the same time there is a small quantity of bonds the stress on which reaches about 1000 kg/mm^2 . Strongly overstressed bonds were also observed in the other investigated polymers. The existence of strongly overstressed bonds, the loads on which reach $1000 - 2000 \text{ kg/mm}^2$, is characteristic of not only materials with cracks. Such bonds were also observed in stressed polymer films without macroscopic defects (5). Their number increases with the imperfection of the molecular structure of the polymer. This enables us to connect the existence of overstressed bonds with the heterogeneities of polymer structure and the presence of the atomic concentrators of stresses.

Overstressed chemical bonds have a reduced activation energy of scissions and they, therefore, must rupture first of all as compared to the less stressed ones. As indeed, in our work the increase in the concentration of the end groups of molecules formed at scission of chemical bonds near the crack tip was observed. As an example the results of measurements for polypropylene are shown in Fig. 3. The concentration of scissions is seen to diminish only slightly as the distance from the crack tip increases and scissions are observed not only in the tip vicinity but also at considerable distances from it.

Fig. 4 shows the distribution of the load over bonds at different distances from the crack tip. One can see that the maximum stress on bonds increases up to some distance (~100 microns) after which it remains constant. From the same distance approximately the appearance of new end molecular groups is observed. Thus, the stress on bonds has reached such a value that they rupture during the time of infrared spectrum recording. At further approach to the tip the quantity of the overstressed bonds grows. This results in the increase of the number of scissions. The change in the number of scissions while approaching the crack tip is, therefore, due to the increase of the maximum stress on bonds and of the quantity of strongly stressed bonds.

We determined the concentration of scissions in thin surface layer of the crack, about 1-2 microns thick, using the method of attenuated total internal reflection. The total number of new end molecular groups on the surface was found to be approximately $0.5 \cdot 10^{22} \text{ cm}^{-3}$. This value is of the same order as the total number of chemical bonds in a polymer in cm^3 . Thus, the crack surface consists practically of the ends of polymer molecules.

Discussion of Results

The data obtained in this work permit to offer the following atomic mechanism of crack growth in polymers. The crack creates ahead of itself the region of local stresses. The local stresses are distributed among separate bonds very nonuniformly due to imperfection of the atomic structure of the polymer. The stress on a small number of bonds reaches such values that thermal motion break them during the experiment. Finally the surface of the macrocrack consisting almost entirely of the ruptured bonds is formed.

References

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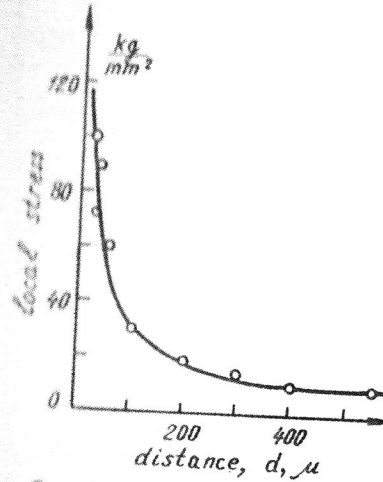


Fig.1 Local stresses at different distances from the crack tip

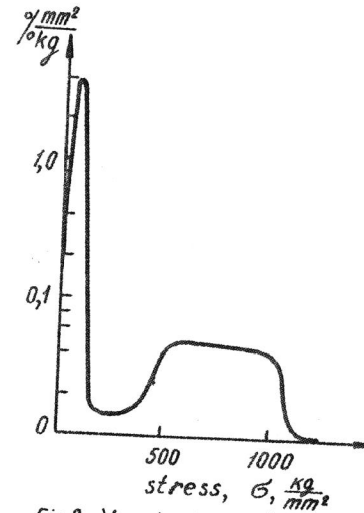


Fig.2 Load distribution among bonds at 20 micron distance from the crack tip

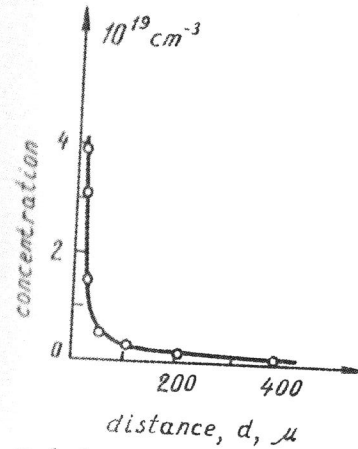


Fig.3 Scission concentration change as a function of distance

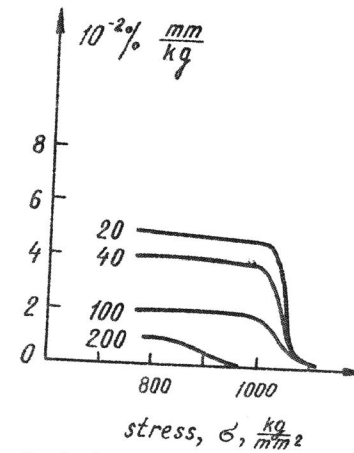


Fig.4 Load distribution among bonds at different distance from the crack tip

VI-333