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Specific Features of the Mass Transfer of the Liquid Component in Poly(ethylene terephthalate) Crazing in Poly(ethylene oxide) Solutions

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Crazing of polymers in liquid adsorptive media is plastic deformation of a special type, which is accompanied by the development of nanoporosity in the polymer [1]. This property of crazing was repeatedly used for creating polymer-matrix nanocomposites of new types, including polymer–polymer nanocomposites [2]. In particular, it turned out that the crazing of a polymer (polymer 1) in solutions containing macromolecules of another chemical nature (polymer 2) involves their efficient penetration in the nanoporous structure of developing crazes. Furthermore, the actually introduced amount of polymer 1 can significantly exceed its amount calculated under the assumption that the pores are filled with a solution of the concentration that is equal to the concentration of the surrounding solution, in which polymer 1 is being deformed [3]. This phenomenon was demonstrated by 100% stretching of polymer 1 (poly(ethylene terephthalate), or PET) in a solution of polymer 2 (poly(ethylene oxide), or PEO).

At the same time, it is well known that the nanoporous structure of a polymer being deformed in an adsorptive medium undergoes complex evolution during crazing (Fig. 1). Early in the stretching, crazes with fibrous porous structure grow, which causes a general increase in the porosity and specific surface area of the polymer (Fig. 1a). In the course of such deformation, the initial block polymer continuously transforms to the finely dispersed material of crazes. Obviously, this process cannot last too long, and the system finds a way to get rid of the excess surface area. When a considerable part of the polymer passes to the oriented fibrillated state, the porous structure begins to collapse (Fig. 1b). And lastly, when much of the polymer changes to the material of crazes, the polymer experiences lateral contraction (Fig. 1c). Such lateral contraction of the polymer is accompanied by a decrease in its porosity, average pore size, and specific surface

area. During crazing, the emerging porous structure is being filled with the surrounding liquid; therefore, in the course of the decrease in the polymer porosity, a part of the liquid trapped in the bulk of the polymer early in the stretching seeps to the environment (a phenomenon of syneresis).

In other words, during crazing, the mass transfer of the liquid component reverses; namely, its ingress into the bulk of the polymer early in the stretching is replaced by its migration from the pore space at the stage of the collapse of the porous structure. Naturally, these structural rearrangements cause the extremal behavior of the porosity W of the crazed polymer as a function of the polymer strain ε in the adsorptive medium (Fig. 2).

In this work, we made the first attempt to study specific features of the mass transfer of PEO dissolved in an adsorptive medium in the course of PET crazing in PEO solutions.

Figure 3 presents the PEO content of the crazed nanoporous PET matrix versus strain ε. Figure 3 shows that the amount of PEO incorporated in the fibrous porous structure of the crazed polymer depends on the PET strain in PEO solutions and on their molecular weight. It proved that the amount of relatively low-molecular-weight (4000) PEO increases with increasing PET strain in the PEO solution throughout the studied strain range. It may seem strange because the porosity of PET being deformed in a solution of PEO with a molecular weight of 4000 passes through a maximum at a strain of about 250% (Fig. 2, curve *1*).

That is, whereas the total amount of the PEO-containing crazing liquid within the strain range ~200–300% decreases because of the collapse of the fibrous porous structure of crazes, the amount of PEO introduced into PET increases (compare Figs. 2 and 3). This paradox can be explained by considering the scheme of structural rearrangements accompanying the polymer crazing (Fig. 1). It is well seen that, by the beginning of the collapse of the porous structure of crazes (Fig. 1b), the polymer contains sufficiently
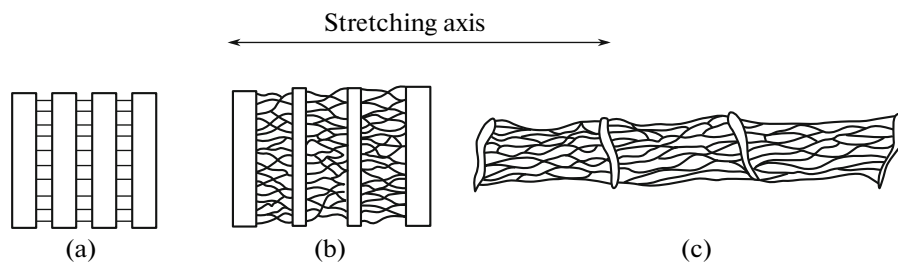
Moscow State University, Moscow, 119992 Russia

Stretching axis

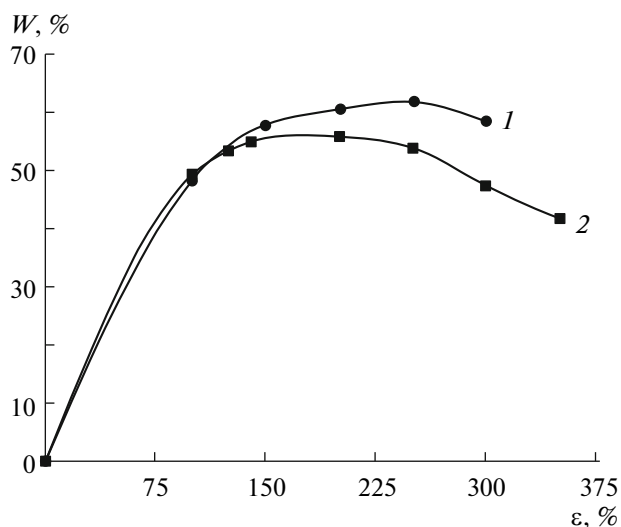**Fig. 1.** Structural rearrangements accompanying the polymer crazing in an adsorptive medium (see text for details).

Fig. 2. Porosity W vs. strain ε of PET in solutions of PEO with molecular weights of (*1*) 4000 and (*2*) 40 000.
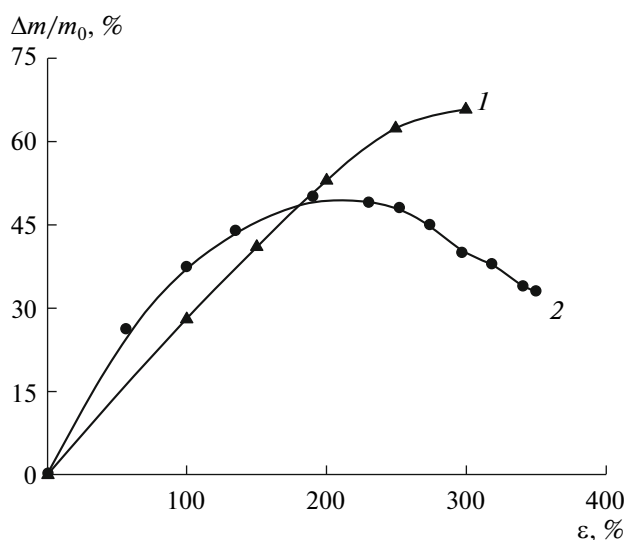

Fig. 3. Content of PEO incorporated in the structure of PET by PET crazing in solutions of PEO with molecular weights of (*1*) 4000 and (*2*) 40 000 vs. strain ε.

many blocks of the initial undeformed polymer located between crazes.

As noted above, the collapse of the porous structure of crazes is accompanied by the release of a part of the adsorptive medium into the environment. However, at this stage of crazing (Fig. 1b), there are a rather large number of blocks of the undeformed polymer being in contact with the adsorptive medium even under mechanical loading. As a result, the crazing of these undeformed polymer blocks continues, and additional portions of the PEO solution enter the polymer. Thus, the total amount of the liquid in the polymer (Fig. 2) is controlled by two opposite processes: the egress of the liquid from collapsing crazes and the ingress of the liquid into the polymer owing to the crazing of the intact unoriented part of the polymer.

The increase in the amount of PEO in the porous structure of PET is explained by the fact that the release of the liquid into the environment occurs by filtration through the fibrous porous structure of crazes. As a result of this "solution filtration" of a sort, the pure solvent is liberated into the environment and PEO macromolecules are incorporated in the struc-

ture of PET crazes. This phenomenon was detected previously when studying the migration of dyes while deforming polymers in their solutions [4].

Figure 2 also suggests that the amount of higher-molecular-weight (40 000) PEO in PET decreases at high strains. This means that the relatively high-molecular-weight PEO entering the porous structure of the polymer early in the deformation (during the nucleation and growth of crazes) migrates from the structure of the crazed polymer in the course of its collapse. It can be assumed that this phenomenon is related to the structure of the PEO solution. In the case of PEO with a molecular weight of 40 000 in a 20% solution, the concentration c_e of formation of continuous entanglement network is exceeded. When the mass transfer reverses at high polymer strains, it is because of the entanglement network that the PEO solution is transported into the environment. At the same time, in a 20% solution of PEO with a molecular weight of 4000, the concentration c_e is not reached. Therefore, this PEO has no continuous entanglement network and is adsorbed on the well-developed surface

of crazes, and the almost pure solvent is filtered off into the environment (i.e., there is syneresis).

Thus, the mass transfer of the liquid component in the porous structure of crazes is complex, which is caused by the structural evolution of crazes. As this work showed, this process involves the mass transfer of the second polymer component (PEO) dissolved in the adsorptive medium.

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