



Specific features of the environmental crazing of poly(ethylene terephthalate) fibers



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ABSTRACT

Tensile drawing of glassy PET fibers via environmental crazing is studied. Direct microscopic observations show that this process includes the development of macroscopic porosity due to the initiation and growth of multiple crazes with their specific fibrillar-porous structure. Environmental crazing of fibers is characterized by the early collapse of the thermodynamically unstable structure of crazes. This process commences at the stage of craze widening and proceeds until the crazes lose their porosity and become fully monolithic. The collapse is provided by the coagulation of the flexible nanoscale craze fibrils via their interaction by side surfaces. The collapse is markedly intensified when the active liquid is removed from the volume of crazes and, as a result, the crazed fibers acquire a specific surface relief with alternating thick and thin regions corresponding to the bulk unoriented polymer and the collapsed crazes. Practical advantages of the stage of the collapse of the crazed nanoporous structure of crazes for the creation of the fiber-based nanocomposite materials are discussed.

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1. Introduction

According to the general knowledge [1–7], crazing is the mode of the plastic deformation of solid polymers which is accompanied by the stress-induced development of the macroscopic porosity. When polymers are subjected to the action of the applied stress in the presence of an adsorptionally active liquid environment (AAL), their deformation proceeds via the development of numerous discrete zones of strain accommodation with their unique structural organization which are coined as crazes [1–3]. The inner structure of crazes consists of the oriented craze fibrils produced by the mechanism of the Taylor meniscus instability and the ends of fibrils are firmly fixed in the adjacent regions of the bulk polymer [6–8]. The typical diameter of the craze fibrils is equal to several nanometers (below 20 nm), and the spacing between the neighboring fibrils (pores or cavities) also lies within the nanometric scale [2,9,10]. However, the actual inner structure of crazes is far from the idealized case when fibrils are modeled as firm individual rods bridging the opposite craze walls but appears as a fibrillated weblike network [11]. Noteworthy is that the glass transition

temperature of the polymer material in the nanoscale fibrils can be markedly depressed as compared with that of the bulk polymer [12,13], and this factor also contributes to structural organization and further evolution of the crazed material.

As compared with the deformation of solid polymers in air via the mechanism of crazing (so-called *dry crazing*) [1–3], tensile drawing of polymers in adsorptionally active liquid environments (*solvent crazing or environmental crazing*) is characterized by its own specific features provided by the action of a liquid environment on polymers [10,14–16]. In contrast to dry crazing, deformation via environmental crazing proceeds over a broad interval of tensile strains without fracture up to the stage of orientational strengthening, thus opening advantageous possibilities for the detailed study of this phenomenon and characterization of the structural evolution of the nanoporous fibrillated craze matter [15,17].

The process of environmental crazing (EC) includes several well-defined stages [10]. Fig. 1 shows the general scenario of environmental crazing of solid polymers in its comparison with the corresponding stress–strain diagram and the (porosity)–(tensile strain) curve.

At the early stages of stretching (at low tensile strains below the yield point), surface defects existing in the polymer sample give rise to the initiation of multiple crazes with their unique fibrillar-porous structure, which serve as the regions of strain accommodation (Fig. 1). The initiated crazes start to grow in the direction

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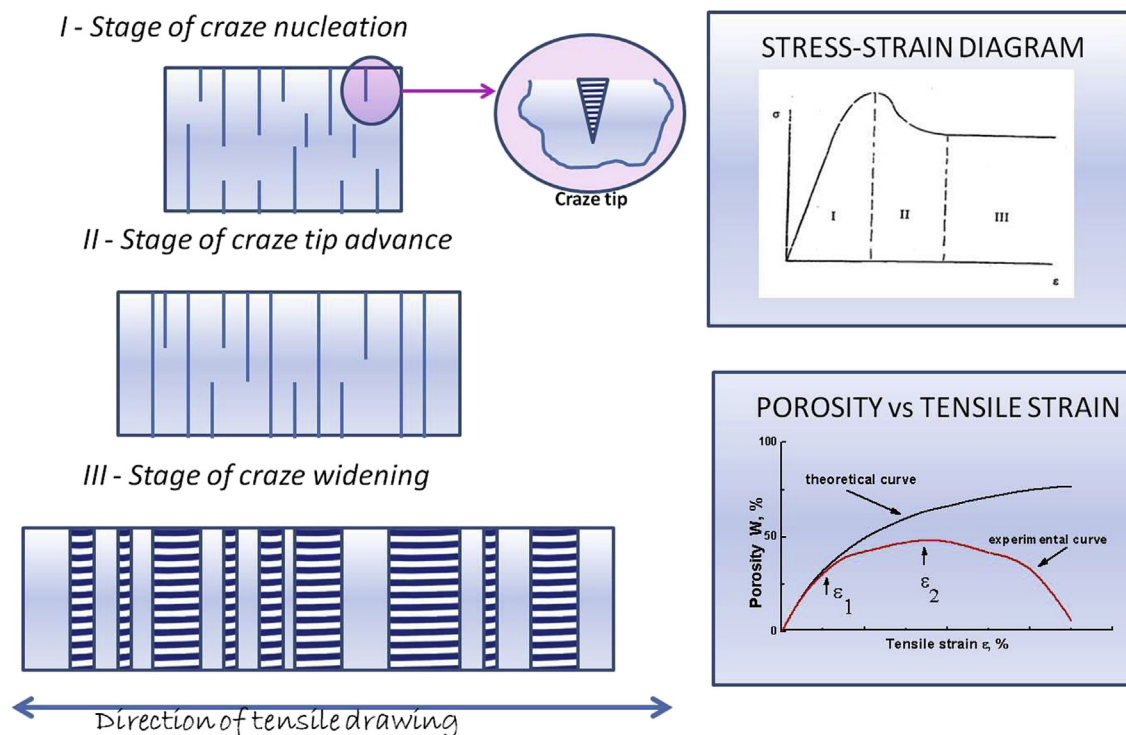


Fig. 1. Schematic representation of different stages of environmental crazing: I – the region of craze initiation, II – the region of craze tip advance, III – the region of craze widening or thickening. Correlation of the EC stages with the corresponding stress–strain diagram and (porosity)–(tensile strain) curve.

perpendicular to the direction of the applied stress (the stage of craze tip advance) [18,19]. At this stage, the width of crazes is low (several fractions of microns) and remains virtually unchanged. New crazes are initiated [20,21] until one or several initiated crazes at the stage of craze tip advance propagate through the whole cross section of the sample, and stress relaxation takes place (the yield tooth). Evidently, this process is strongly controlled by the geometry of the polymer sample, in particular, by its thickness. For example, as was shown in Ref. [22], the duration of this stage is naturally longer for thicker samples because the time required for crazes to pass the cross section of the sample is naturally longer. As a result, the density of the initiated crazes increases.

Once the initiated crazes pass through the whole cross section of the sample, the stage of craze widening or craze thickening comes into play when the growing crazes increase their width along the direction of tensile drawing and the craze walls are drifted apart. Naturally, this is the stage when most of the initial bulk polymer is transformed into the oriented state within the craze fibrils. The macroscopic porosity W of the sample increases with increasing ϵ according to the following law as $W = (\epsilon/(\epsilon + 1)) \times 100\%$ (the theoretical curve in Fig. 1) where W is the volume of the crazed regions per the overall volume of the sample, and ϵ is the tensile strain. The development of the marked macroscopic porosity with increasing tensile strain is possible only when the volume of nanoporous crazes is continuously filled up with the surrounding adsorptionally active liquid. It is important to mention that, according to the abundant experimental data collected by diverse physicochemical methods (X-ray analysis, TEM, pressure driven liquid permeability, etc.) [3,8,23], the diameter of the craze fibrils and the distance between the neighboring fibrils are of the same order and lie within the range of ~ 1 – 20 nm. The length of the craze fibrils is obviously equal to the distance between the craze walls. Thus, the craze fibrils can be treated as specific asymmetric colloidal particles with the fixed ends, and the whole craze can be

compared to a specific colloidal system with a high level of surface energy.

The final stage of environmental crazing is concerned with the collapse of the nanoporous structure of crazes which takes place at high tensile strains when most of the polymer appears to be transformed into the oriented fibrillated state within crazes [10]. The onset of this stage can be detected from the deviation of the experimental W – ϵ curve from the theoretical dependence (ϵ_1 in the experimental W – ϵ plot in Fig. 1). This phenomenon can be explained as follows: the collapse of the nanoporous craze structure commences when, with increasing ϵ , the craze walls are drifted apart by a relatively long distance so that the fibrillar aggregates bridging the opposite craze walls become relatively long. As the length of the craze fibrils increases, they acquire a sufficient flexibility and the neighboring fibrils can contact each other by their lateral surfaces. This contact of the neighboring fibrils leads to their coagulation which provides so-called collapse of the nanoporous structure of crazes. Evidently, at this stage, the liquid entrapped within the nanoporous crazes is squeezed out or expelled from the sample (syneresis). Finally, the W – ϵ plot passes the maximum at a certain tensile strain (depicted as ϵ_2 in Fig. 1) and starts to decrease. Our earlier studies on the EC phenomenon for polymer films show that this stage of environmental crazing is strongly controlled by the geometry of the sample, in particular, by the thickness. For thicker films, the onset of the collapse and the maximum in W – ϵ plot are observed at much higher tensile strains: for example, $\epsilon_1 = 75\%$ and $\epsilon_2 = 175\%$ for the films with a thickness of $50 \mu\text{m}$, and $\epsilon_1 = 220\%$ and $\epsilon_2 = 280\%$ for the films with a thickness of $300 \mu\text{m}$ [22]. Hence, for all stages of environmental crazing, the geometry of the sample is proved to be the critical factor that should be necessarily taken into account.

In this connection, of special interest is the study of environmental crazing for polymeric fibers as the samples with an alternative (critically different from the films) geometry. However, so

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