

Incorporation of an Abnormally High Amount of Poly(ethylene glycol) into Poly(ethylene terephthalate) during Tensile Drawing in Liquid Media¹

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Abstract—Tensile drawing of PET via the mechanism of solvent crazing in adsorption-active media containing poly(ethylene glycol) with $M < 1 \times 10^6$ is accompanied by their penetration into the porous structure of the matrix polymer. In this case, the amount of PEG in PET exceeds its concentration calculated on the assumption that the porous structure is filled with the polymer solution. This excess is evidently due to the adsorption of PEG on the highly developed surface of crazes.

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We studied the feasibility of the preparation of polymer–polymer nanocomposites via the incorporation of another polymeric component into a crazed polymer matrix. Earlier, such attempts were accomplished via the introduction of a monomer into the polymer matrix and its subsequent in situ polymerization. Polymer–polymer nanocomposites having unique mechanical, physicochemical, and other properties were prepared on the basis of incompatible polymer pairs, such as HDPE–PS, HDPE–PMMA, and PP–PS [1–3]. However, this approach to the preparation of nanocomposites is very complicated and laborious.

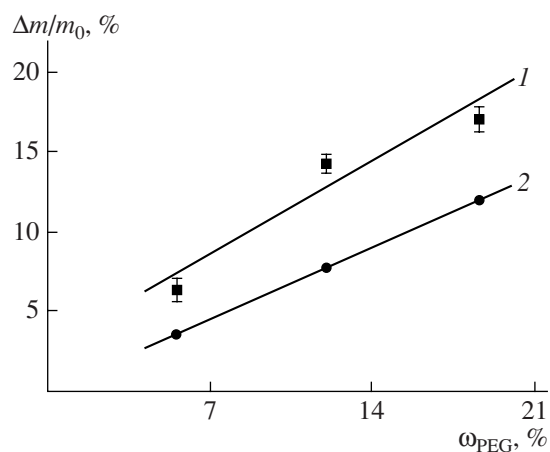
As was shown earlier [4], the solvent crazing of PET and HDPE allows the introduction of high-molecular-mass compounds, such as PEG and PPG with $M = 400$ – 3000 , into crazed polymer matrices. It seemed interesting to investigate the feasibility of the introduction of polymers with a higher molecular mass into the crazed polymer matrix produced during the tensile drawing in a liquid medium. Note that the mean-square radius of a macromolecular coil for PEG with $M = 1.2 \times 10^6$ in the solution is about 60 nm [5], whereas the effective pore diameter in solvent-crazed PET as estimated by means of the small-angle X-ray scattering and pressure-driven liquid permeation techniques does not exceed 5–10 nm [6].

As was shown in [7], PEG macromolecules with $M < 1.3 \times 10^6$ are able to penetrate into some inorganic sorbents (porous glasses) with a pore diameter of 5–10 nm. However, this process was carried out from dilute solutions under static conditions and took a long time. In this study, the second incompatible polymer component (PEG) was introduced into the crazed polymer matrix (PET) under dynamic conditions or, in other words, directly during the drawing of the polymer in the solvent and the development of the porous structure in the specimen. For this purpose, PET films were stretched in PEG solutions in ethanol–water mixtures (PEG concentration was 5.5, 12, and 18.6%). The composition of the solvent was selected in such a manner that it would dissolve PEG in an appreciable amount (water : ethanol ratio = 1 : 7.5) on the one hand and cause the effective crazing of PET on the other hand.

After the deformation of PET films (thickness, 100 μm ; width, 6.15 mm; and length, 20 mm) in the presence of the above solution of PEG with $M = 4 \times 10^5$ at a strain rate of 6 mm/min by a tensile strain of 100%, the specimens were removed from the clamps of the stretching device and dried to a constant weight to gravimetrically determine the amount of PEG introduced into PET.

Surprisingly, it turned out that PEG with such a high molecular mass effectively penetrated into the porous

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Relative amount of PEG with $M = 4 \times 10^5$ incorporated into a PET specimen during its drawing in aqueous alcohol solution versus the PEG concentration in this solution: (1) measured experimentally and (2) predicted on the assumption that the porous structure of crazes is completely filled with the PEG solution.

structure of PET during crazing. Moreover, the amount of PEG that penetrates during crazing is much higher than the anticipated quantity calculated on the assumption of complete pore filling with the polymer solution of the given concentration that was taken as a crazing

medium (figure). In other words, there is a certain mechanism of the enrichment of the solution in PEG that penetrates into the porous structure of PET during its solvent crazing upon deformation in the solution of the second component. The cause of this phenomenon seems to be related to the adsorption of the second polymer component on the highly developed surface of pores and will be elucidated in the further investigation.

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