

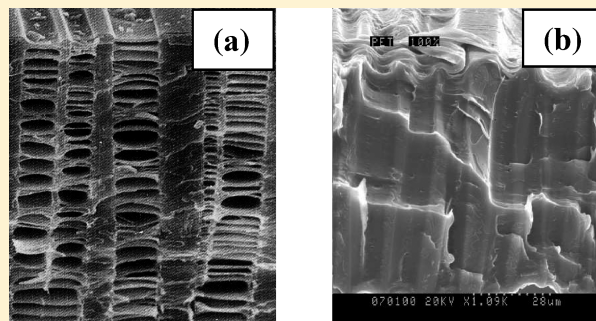
Penetration of Poly(ethylene oxide) into the Nanoporous Structure of the Solvent-Crazed Poly(ethylene terephthalate) Films

Ekaterina G. Rukhlya,^{*,†} Ekaterina A. Litmanovich,[†] Anatolii I. Dolinnyi,[‡] Larisa M. Yarysheva,[†] Aleksandr L. Volynskii,[†] and Nikolai F. Bakeev[†]

[†]Faculty of Chemistry, M. V. Lomonosov Moscow State University, Leninskie gory 1, Moscow 119991, Russia

[‡]A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, Leninsky prospekt 31, 119991 Moscow, Russia

ABSTRACT: Tensile drawing of the poly(ethylene terephthalate) (PET) samples in semidilute solutions of poly(ethylene oxide) (PEO) with the molecular mass ranging from 4×10^4 to 1×10^6 proceeds via the mechanism of solvent crazing. This process is accompanied by the penetration of PEO into the porous structure of crazes, and this conclusion is proved by the data on the composition of the resultant blends as well as by the direct electron microscopic observations. Effective diameter of pores in the nanoporous structure of the solvent-crazed PET samples is estimated by the method of pressure-driven liquid permeability. Structure of PEOs is studied by the methods of dynamic light scattering and capillary viscometry as a function of the molecular mass and polymer concentration in the solutions. Penetration of PEO into the solvent-crazed nanoporous structure proceeds under so-called “confined” conditions when the hydrodynamic radius of a polymer coil is comparable or higher than the effective dimensions of pores in the crazes. Penetration of the PEO macromolecules into the porous structure of the solvent-crazed PET-based sample via diffusion under the action of the concentration gradient is compared with the flow-assisted penetration in the course of the tensile drawing of the PET samples in the PEO solutions. Content of PEO in the pores of the solvent-crazed polymer samples is higher than that in the surrounding solution, and this fact can be explained by the adsorption of PEO on the highly developed surface of the fibrillated polymer in crazes. Penetration of PEO into the porous structure upon tensile drawing proceeds much quicker (minutes) as compared with the attainment of the equilibrium content of the polymer under the action of the concentration gradient (days).



INTRODUCTION

Cold drawing of amorphous glassy and semicrystalline polymers in the presence of adsorptionally active liquid media (AALM) proceeds via the nucleation and growth of the local deformation regions referred to as crazes, and the whole process has been coined as solvent crazing.^{1–6} This specific mode of the plastic deformation of polymers involves stress-induced disintegration of the polymer material in crazes into fine aggregates composed of oriented macromolecules (craze fibrils), which are spaced by voids (pores) of the same dimensions. To summarize, solvent crazing involves the development of a highly dispersed fibrillar–porous structure with dimensions of pores and craze fibrils of about 2–20 nm, and crazing by itself can be treated as a universal method for the development of the nanoscale porosity.^{1–4} It is important to mention that parameters of the resultant porous materials such as porosity, specific surface, and pore dimensions, can be easily controlled by varying conditions of tensile drawing (tensile strain, temperature, strain rate, geometry of the sample, etc.).

Another fascinating aspect of solvent crazing is concerned with the fact that the formed porous structure of the solvent-crazed polymer appears to be loaded with the surrounding liquid medium; when this medium comprises the solutions of low-molecular-mass

compounds, they can also penetrate the porous structure of crazes together with the solvent. In this connection, the phenomenon of solvent crazing can be used for the preparation of diverse composites with the nanoscale level of dispersion between the components, and this factor is controlled by the parameters of the specific fibrillar–porous structure of the crazes.^{7,8}

This approach based on solvent crazing allowed preparation of various polymer–polymer blends by in situ polymerization of monomers within the parent matrix of the solvent-crazed polymer.^{9–11} When tensile drawing of the polymer sample is performed in the solutions of high-molecular-mass compounds, feasibility of solvent crazing and preparation of polymer blends did not seem to be so evident because of the high viscosity of polymer solutions and comparable dimensions of macromolecular coils and pores in the solvent-crazed polymer. However, the pioneering work in this direction¹² showed that tensile drawing of PET and HDPE in the presence of liquid oligomers, poly(ethylene glycol) and poly(propylene glycol), which are AALMs, proceeds via the

Received: April 7, 2011

Revised: June 1, 2011

Published: June 13, 2011

mechanism of solvent crazing and this approach allowed preparation of the polymer–oligomer blends. Moreover, it was demonstrated in refs 13–16 that tensile drawing of PET and HDPE in semidilute solutions of flexible-chain polymers (for example, poly(ethylene oxide)) with higher molecular masses also proceeds via the mechanism of solvent crazing and this process is accompanied by the penetration of macromolecules into the nanoporous structure of crazes. However, the effect of the conditions of solvent crazing (conditions of tensile drawing), concentration and molecular mass of the added polymer on the efficacy of this penetration has not been studied yet.

The problems concerning structure and dynamics of polymer chains in the nanoporous materials are crucial for many areas of science and technology associated with diffusion, flow, adsorption, and selective separation of various compounds. Transport of macromolecules through nanosized channels is the basis of diverse biological processes. Special interest is focused on the penetration of polymers into the nanoporous materials under so-called hindered conditions (in the confined spaces) when dimensions of a macromolecular coil is comparable or smaller than the pore diameter.^{17–19}

Problems related to the penetration of polymers into the nanoporous materials via diffusion of macromolecules have been studied in more detail,^{20–23} but simulation of the flow of polymers into the small-sized nanoporous materials appears to be a challenging problem. Model description of the hydrodynamic flow of dilute and semidilute solutions of flexible-chain polymers under confined conditions and the effect of the flow rate, shape and dimensions of pores, molecular mass and concentration of a polymer in its solution have been discussed according to the scaling approach.²⁴ Penetration of macromolecules from their solutions into the small-sized pores under the action of the external force can take place only when flow of a solvent achieves a certain critical level, and its value is controlled by the interplay between friction forces acting between macromolecules and the solvent, on one hand, and by the elastic retraction force of the polymer, on the other hand.

So far numerous publications have been devoted to the theoretical studies on the penetration of macromolecules into the pores of diverse geometry. As a confined pore space, spherical voids, cylindrical or cone-shaped pores or, finally, narrow slits confined by two walls have been analyzed.^{19–25} However, the diversity of existing porous materials cannot be exhausted by the above-mentioned fixed geometry, especially, for the biological objects with their sophisticated organization of porous channels.^{26,27} Complications of experimental studies are likely to be related to the limited number of nanoporous materials with well-characterized structure whose parameters can be modified without any changes in the nature of the polymer. In this connection, it seems interesting to study penetration of macromolecules into the nanoporous materials based on the solvent-crazed polymers. The advantages of solvent crazing for the preparation of nanoporous materials are primarily related to the fact that parameters of the formed porous structure can be changed by varying conditions of tensile drawing, nature of a polymer and a liquid medium.

The objective of this work is concerned with the mechanism of penetration of the PEO macromolecules into the nanoporous structure of the solvent-crazed PET matrix. This study is also important from the practical viewpoint because solvent crazing can be treated as a new method for the preparation of various polymer blends with the high level of mutual dispersion between the components.

MATERIAL AND METHODS

In this work, we used the films of amorphous unoriented PET with a thickness of 100 μm . As the second component, we used PEO with the molecular mass varying from 2×10^4 to 1×10^6 (Aldrich; degree of polydispersity was 1.1). At room temperature, high-molecular-mass poly(ethylene oxides) are solid; hence, they can be incorporated via solvent crazing into the PET films only from their solutions. The PET samples with a gage size of 6.15×20 mm were stretched with a constant strain rate of 6 mm/min in the ethanol–water solutions (ethanol:water = 7:1) of PEO. The solvent-crazed samples were wiped off in order to remove the residual PEO from their surface; then, to remove the residual solvent, the samples were dried under isometric conditions until their constant weight was attained. The content of PEO in the blends was estimated gravimetrically.

Porosity W of the solvent-crazed PET was defined as $W = (\Delta V \times 100\%)/(V_0 + \Delta V)$, where ΔV is the increase in the volume of the sample after its tensile drawing by a given tensile strain, and V_0 is the initial volume of the polymer sample. Structure of the PET samples and the PET–PEO blends was studied by the electron microscopic observations on a Hitachi S-520 scanning electron microscope. Prior to the SEM observations, the samples were fractured in the liquid nitrogen along and perpendicular to the direction of tensile drawing. The fractured surfaces were decorated with gold on an Eiko IB-3 unit by the method of ionic plasma sputtering.

Porous structure of the solvent-crazed PET films was studied by the method of the pressure-driven liquid permeability. The PET films were stretched in the ethanol–water solutions (ethanol:water = 7:1); to prevent shrinkage, the samples were fixed by their contour in the metallic frameworks, and their permeability with respect to the ethanol–water solutions was measured on an FMO-2 membrane cell at a pressure of 2 MPa. Effective dimensions of pores in crazes were calculated from the data on liquid permeability and volume porosity W of the solvent-crazed samples through the Pouseille equation.²⁸

Relative viscosity of the water–ethanol solutions of PEO was measured on an Ubbelohde viscometer (viscosity of the mixed solvent was 2.33 cP; no corrections for kinetic energy). Prior to measurements, all solutions were thermostated at 20 $^\circ\text{C}$ for 15 min. Temperature was maintained with an accuracy of ± 0.2 $^\circ\text{C}$.

Light scattering of the PEO solutions was measured on a Photocor Complex photometer (Photocor Instruments, USA) equipped with a He–Ne laser as a light source (10 mW, $\lambda = 633$ nm). Scattering angle was 90 $^\circ$. Concentration of PEO in the solution was 0.7, 0.15, 0.1, and 0.09% for PEO with $M = 4 \times 10^4$, 1×10^5 , 4×10^5 , and 1×10^6 . Polymer solutions were filtered through porous filters “Millipore” with pore dimensions of 0.2 μm . Hydrodynamic radii of macromolecules R_h were calculated from the diffusion coefficients D through the Einstein–Stokes equation

$$R_h = \frac{kT}{6\pi\eta D}$$

where

k is the Boltzmann constant,
 T is the temperature,
 D is the coefficient of self-diffusion,
 η is the viscosity of the medium.

RESULTS AND DISCUSSION

Solvent crazing offers the universal means for the development of nanoscale porosity in various polymer films and fibers.^{3–6} This approach allows preparation of the nanoporous polymer matrix by tensile drawing of the polymer sample in the selected liquid media. This deformation is accompanied by a spontaneous development

of porosity which increases up to 60% and pore dimensions range from 2 to 20 nm. Moreover, this process can take place only when the formed nanoporous structure is continuously filled with the surrounding liquid. In other words, solvent crazing makes it possible not only to prepare the nanoporous polymer matrix but also to load it up with the second component.

This work is focused on the feasibility of the introduction of the second polymer component into the porous solvent-crazed matrix.

The Dimensions of Pores in the Solvent-Crazed PET Films. PET was used as a matrix polymer for the preparation of the materials with nanoporous structure because, for this polymer, the mechanism of solvent crazing has been studied in detail.

Tensile drawing of PET was carried out in the ethanol–water (7: 1 by volume) solutions of PEO. All studies were performed for the solvent-crazed PET samples stretched by a tensile strain of 100% with a constant strain rate. In this case, overall porosity of the solvent-crazed samples was 48–50%.

Effective pore dimensions for the PET sample stretched by 100% in the ethanol–water solution were calculated according to the procedure described in ref 28 from the data on volume porosity and pressure-driven liquid permeability. To gain information on pore dimensions for the “native” solvent-crazed samples (or, in other words, for the samples whose structure remains virtually unchanged after their tensile drawing), the solvent was not removed from the solvent-crazed samples and their contour was fixed by an O-shaped metallic framework in order to prevent any shrinkage. Liquid permeability through the porous samples was measured with respect to the same water–ethanol solutions, in which tensile drawing via solvent crazing was performed. The estimated effective pore diameter in the crazes appeared to be equal to about 8.4 nm.

Characteristics of PEO Solutions. For the introduction of the second component, we selected polymers with a narrow molecular mass distribution but their chemical nature was different from PET: hydrophilic poly(ethylene oxides) (PEOs) with the molecular mass ranging from 4×10^4 to 1×10^6 . This choice of PEO was primarily associated with the fact that this polymer is available as homopolymers with the narrow molecular-mass distributions because polydisperse polymers are multicomponent systems with their complex flow and diffusion behavior.

Moreover, it seems interesting to prove the feasibility of the preparation of polymer–polymer blends from unlike polymers with appreciably different natures which cannot be prepared by mixing from melts or solutions. Indeed, the melting temperature of PET is 254 °C, whereas the temperatures of thermal degradation of PEO in air are 180 °C, respectively. Evidently, it is unfeasible to prepare a blend from these components via their mixing in melt. The mixing of such different polymers in solution is likewise impossible because they do not have common solvents.

The PEO solutions were characterized by the methods of dynamic light scattering (R_h) and capillary viscometry ($[\eta]$). The crossover or overlap concentration (c^*) was calculated from the data on the intrinsic viscosity of the solutions according to the Debye criterion:

$$c^* = 1/[\eta]$$

The corresponding data on the crossover concentration, correlation length, and hydrodynamic radius of the macromolecular coil are listed in Table 1 as a function of the concentration of PEO in the solution and its molecular mass.

Table 1. Characteristics of PEOs in the Ethanol–Water Solutions^a

molecular mass of PEO	$[\eta]$, dL/g	c^* , g/100 mL	R_h , nm	ξ at $c = 5.5\%$, nm	ξ at $c = 20.0\%$, nm
4×10^4	0.6	1.67	5.2	2.2	0.8
1×10^5	1.0	1.00	9.2	2.5	1.0
4×10^5	3.1	0.32	20.0	2.4	0.9
1×10^6	6.6	0.15	53.0	2.4	0.9

^a Note: $[\eta]$ is the intrinsic viscosity, R_h is the hydrodynamic radius of a polymer coil; c^* is the crossover concentration; ξ is the correlation length when the polymer concentration c is equal to 5.5 and 20.0%.

As follows from Table 1, introduction of the PEO macromolecules proceeds under so-called confined conditions when the hydrodynamic radius of a coil is comparable or even higher than pore dimensions in the crazes.

Transport characteristics of the flexible-chain polymers are known to depend on the polymer concentration in the solution. In a dilute solution, macromolecules exist as individual separated coils but, in a semidilute solution, the coils are overlapped; hence, the structure of this solution appears as a fluctuation network of entanglements. The concentration controls not only the dynamic (the mechanism of flow and diffusion) but also thermodynamic characteristics (osmotic pressure) of the polymer solution. According to the data summarized in Table 1, the crossover concentration (c^*), at which transition from dilute to semidilute water–ethanol solutions of PEO takes place, decreases from 1.7 to 0.2% with increasing molecular mass from 4×10^4 to 1×10^6 .

In this work, concentration of the PEO solutions used for the tensile drawing of PET was higher than 5%, or, in other words, we used semidilute solutions. According to the scaling concepts, in the description of the dynamics of the semidilute solutions of the flexible-chain polymers, the key parameter is the correlation length ξ . The correlation length means the average distance between two consecutive (along the chain) contacts with other neighboring chains and a macromolecule by itself is visualized as a sequence of blobs with the size ξ . In the case of the semidilute solutions of the flexible-chain polymers, the kinetic unit involved in the diffusion under the action of concentration gradient and flow under the action of the mechanical field is a blob with the size ξ rather than a whole macromolecule.

Correlation length for the PEO macromolecules in the water–ethanol solution is calculated through the equation for the flexible-chain polymers in a good solvent:

$$\xi = R_h(c/c^*)^{-3/4}$$

For concentrations 5–20% of PEO solutions, used in this work, values of ξ change from 2.5 to 0.9 nm (Table 1) and is smaller than the diameter of pores in the crazes, which is equal to 8.4 nm.

Features of Penetration of the PEO Macromolecules into the Pores upon Tensile Drawing of the PET Films. Tensile drawing of the PET films in the semidilute solutions is accompanied by the nucleation and development of numerous crazes, and this observation directly proves that deformation proceeds via the mechanism of classical solvent crazing.

As was shown earlier, tensile drawing of PET is accompanied by the penetration of PEO into the formed porous structure of crazes.^{13–15} However, analysis of the stress–strain behavior of

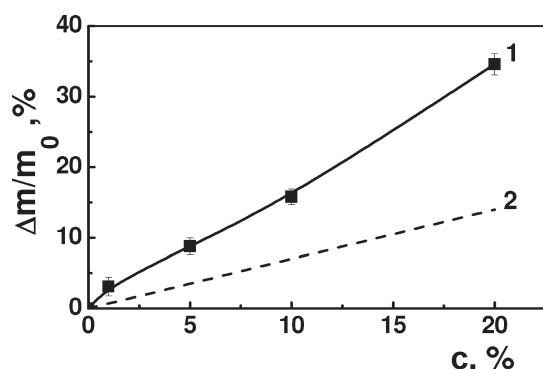


Figure 1. Content of PEO ($\Delta m/m_0$) with $M = 4 \times 10^4$ (1) in the solvent-crazed PET plotted against concentration of PEO in the solution (c). The strain rate is 6 mm/min, and the tensile strain is 100%. Curve 2 corresponds to the content of PEO in the solvent-crazed PET under the assumption that concentration of PEO in the porous structure of the solvent-crazed PET is equal to that in the solution.

the PET upon its tensile drawing in the PEO solutions shows that, despite high viscosity of the polymer solutions, tensile drawing of PET in the PEO solutions is virtually similar to that in the PEO-free solutions.¹⁶ This fact makes it possible to assume that, in the course of the tensile drawing of the PET samples, PEO is “filtered off” and only pure solvent or AALM is delivered into the tip of the growing crazes. In this connection, it seems interesting to study the efficacy of the transport of macromolecules into nanopores of the solvent-crazed polymer or, in other words, to estimate the content of PEO in the resultant blends.

Figure 1 (curve 1) shows the content of PEO (its molecular mass is 4×10^4) in PET plotted against concentration of PEO in the solution. As follows from Figure 1, with increasing PEO concentration in the solution, content of PEO in the solvent-crazed PET increases. This evidence allows us to conclude that the PEO macromolecules are able to penetrate the porous structure of crazes in the course of the tensile drawing of PET in the AALM.

In the ethanol–water solutions of PEO with higher molecular masses (1×10^5 and 1×10^6), tensile drawing of PET also proceeds via solvent crazing. This deformation is also accompanied by the weight gain of the samples and this fact attests penetration of the PEO macromolecules into the formed nanoporous structure of crazes. For the PET samples stretched in 18.6% solution of PEO with $M = 1 \times 10^5$ and in 5.5% solution of PEO with $M = 1 \times 10^6$, weight gain is equal to 30 and 13%, respectively.

Penetration of PEO into the porous structure of the solvent-crazed PET is visualized and proved by our electron microscopic observations; we studied the solvent-crazed PET samples after their tensile drawing in the pure AALM and the solution of PEO with $M = 1 \times 10^6$. Figure 2 presents the SEM images of the fractured surface of the solvent-crazed PET samples after their stretching in the ethanol–water solutions: the pure AALM (a) and in the 5.5% solution of PEO with $M = 1 \times 10^6$ (b). Tensile drawing of PET in the pure AALM and in the PEO-containing solution is accompanied by the nucleation of multiple crazes which propagate through the whole cross section of the sample in the normal direction with respect to the direction of tensile drawing. The SEM images of the fractured surface of the solvent-crazed PET sample clearly show well-pronounced crazes with their specific fibrillar–porous structure containing numerous voids. To the contrary, solvent crazing of PET in the PEO-containing

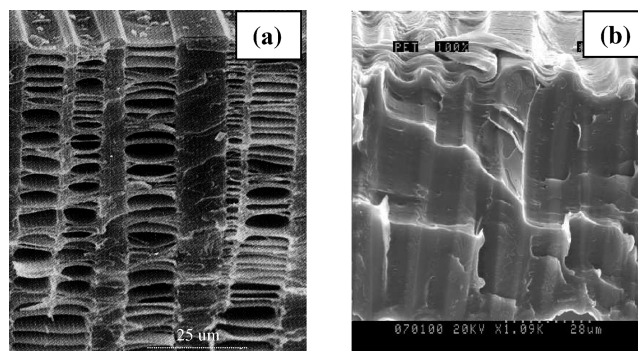


Figure 2. SEM images of the solvent-crazed PET samples after their stretching in AALM (a) and in 5.5% solution of PEO with $M = 1 \times 10^6$ (b).

solutions leads to the formation of crazes filled with the second polymer (PEO). Hence, the SEM observations prove that tensile drawing of PET in the PEO-containing solution is accompanied by the penetration of PEO into the porous structure of crazes.

Analysis of the data shown in Figure 1 allows another important conclusion concerning the content of PEO in the solvent-crazed PET matrix. According to changes in the geometrical dimensions of the samples in the course of the tensile drawing, porosity of the solvent-crazed PET stretched by 100% is equal to 50%. Figure 1 (curve 2) presents the content of PEO in the solvent-crazed PET under the assumption that concentration of PEO in crazes is equal to that in the surrounding solution. The experimental content of PEO in the pores of the solvent-crazed polymer (Figure 1, curve 1) appears to be higher than that in the surrounding solution over the entire interval of concentrations.

Transport of high-molecular-mass compounds into nanoporous materials is controlled by the interplay between the dimensions of macromolecules and kinetic elements of polymer chain.

Table 1 shows that only individual macromolecules of PEO with a molecular mass of 40×10^4 from their dilute solutions are able to penetrate the pores of the solvent-crazed PET because the dimensions of pores are comparable to the molecular size of PEO. In this work, concentration of the PEO solutions used for the tensile drawing of PET was higher than 5% or, in other words, we used semidilute solutions. Penetration of the macromolecules from semidilute solutions into the nanoscale pores is described by the expression $\xi^{-1} \leq D$ which predicts that macromolecules can enter pores if their size is bigger than the blob size (D).^{17,18}

As follows from the data listed in Table 1, the PEO solutions with a concentration of 5–20% are semidilute solutions and the correlation length ξ calculated for all molecular masses and concentrations (from 2.5 to 0.9 nm) is smaller than the diameter of pores in the crazes, which is equal to 8.4 nm. This is the reason behind the penetration of the PEO macromolecules with a molecular mass of 1×10^6 into the porous structure of crazes in the course of the tensile drawing of the PET samples in the semidilute PEO solutions via the mechanism of solvent crazing.

Adsorption of the PEO Macromolecules in the Pores of the Solvent-Crazed PET Films. However, it is necessary to understand the reasons behind the increase in the content of PEO in the pores as compared with its concentration in the surrounding solution upon the tensile drawing of PET via the mechanism of solvent crazing. Because of the conformational hindrances experienced by macromolecules in the small-sized pores, one can expect that concentration of the polymer in the

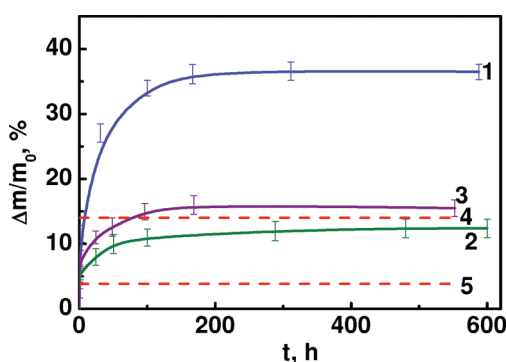


Figure 3. Content of PEO in the solvent-crazed PET films plotted against exposure time in the PEO solutions; molecular mass of PEO is 4×10^4 (1, 2) and 1×10^6 (3); concentration is 5.5 (2, 3) and 20.0% (1). Curves 4 and 5 correspond to the content of PEO when the porous structure of the solvent-crazed PET filled with the polymer solution of the same concentration (20.0% and 5.5%, respectively) as in the surrounding solution.

pores should be lower than that in the surrounding solution. This conclusion has been proved by^{17,19,29} for the macromolecules in the nanopores under the assumption that interaction between the added polymer and pore walls is absent.

The question arises whether the increased content of PEO in the pores is observed only for the solvent-crazed structure of PET or this tendency is solely provided by the conditions of the transport of macromolecules upon tensile drawing? To clarify this problem, we studied the diffusion of PEO into the nanoporous structure of crazes under the action of the concentration gradient. The experiments were performed according to the following scenario: the PET films were stretched with the same strain rate in the PEO-free ethanol–water solution; then, the stretched samples fixed in the clamps were placed into the PEO solutions and allowed to stay under isometric conditions (to prevent shrinkage). For PEOs with different molecular masses, their concentration in the semidilute solutions varies from 5.5% to 20%.

Figure 3 shows the content of PEO with $M = 4 \times 10^4$ and 1×10^6 in the solvent-crazed PET plotted against exposure time (curve 1–3). For comparison, Figure 3 also shows the reference curve (the dotted line) illustrating the content of PEO, which is calculated under the assumption that the formed pores of the solvent-crazed PET are completely filled with the surrounding polymer solution (with the account for the volume porosity of the films and polymer concentration in the solution).

The content of PEO in the solvent-crazed PET is seen to be higher than that in the surrounding solution. Moreover, the equilibrium content of PEO with $M = 4 \times 10^4$ in the solvent-crazed PET sample is the same, independently of the mode of its introduction into the polymer matrix, either diffusion under the action of concentration gradient or stress-induced penetration in the course of the tensile drawing. The corresponding data are shown in Table 2. For PEO with $M = 1 \times 10^5$ and 1×10^6 , the content of PEO in the solvent-crazed PET sample appears to be virtually the same. Only for the highly viscous solutions (20% solution of PEO with $M = 1 \times 10^5$ and 5% solution of PEO with $M = 1 \times 10^6$), the equilibrium content of the diffusion-loaded PEO in the solvent-crazed PET is somewhat higher than the content of PEO delivered in the course of the tensile drawing.

Therefore, according to the data presented in Figures 1 and 3 and in Table 2, penetration of macromolecules into the

Table 2. Content (m/m_0) of PEO in the Solvent-Crazed PET Samples as a Function of the Molecular Mass of PEO and Polymer Concentration (c) in the Solutions^a

molecular mass of PEO	c , %	m/m_0		m/m_0
		(calculated) ^b	(experiments on the diffusion of the polymer solutions into the porous PET-based matrix)	(experiments on the tensile drawing of PET in the polymer solutions)
2×10^4	20	14.9	33	34
4×10^4	5.5	3.8	12	12
	9.3	6.5	16	16
	20.0	14.9	36	36
1×10^5	5.5	3.8	7	7
	9.3	6.5	17	17
	18.6	13.5	34	30
1×10^6	5.5	5.5	17	13

^a PEO was loaded by diffusion into the solvent-crazed porous matrix and in the course of the tensile drawing of PET in the PEO-containing solutions with a strain rate of 0.2 mm/min. ^b m/m_0 (calculated) is the content of PEO calculated under the assumption that the porous structure is filled with the surrounding PEO solution.

nanoporous structure of crazes due to the diffusion under the action of the concentration gradient as well as due to the flow under the action of hydrodynamic pressure into the nanoporous structure of the polymer formed directly upon tensile drawing leads to the increased content of PEO in the resultant blends as compared with the theoretical value calculated under the assumption that the porous structure of crazes is filled with the solution of the same concentration as in the surrounding medium. Let us mention that the content of PEO in the pores of the solvent-crazed PET samples is virtually independent of the mode of the loading of PEO. However, penetration of PEO into the porous structure upon tensile drawing proceeds much quicker (minutes) as compared with the attainment of the equilibrium content of the polymer under the action of the concentration gradient (days).

Let us consider the effect of the initial concentration of PEO in the solution on the PEO content in the solvent-crazed PET matrix and on the time required for the attainment of the equilibrium weight gain. Comparing curves 1 and 3 (Figure 3) for PEO with $M = 4 \times 10^4$, one can conclude that with increasing concentration of PEO in the solution, the rate of the attainment of the equilibrium state increases. For example, in the 20% tion of PEO, equilibrium is attained within 7 days; for the 5.5% solution, equilibrium is not attained even within 12 days. This increase in the diffusion rate with increasing polymer concentration has been repeatedly observed for the penetration of semidilute solutions of the flexible-chain polymers into the nanoporous materials.^{20,22} In the dilute solutions, the diffusion rate of a flexible-chain polymer is controlled by the size of its coil; according to the scaling approach, at the concentrations above the crossover concentration, the kinetic unit responsible for the transport characteristics of macromolecules is a blob which corresponds to the correlation length or to a chain fragment between junctions. In the semidilute solution, with increasing concentration, the number of entanglements per one polymer chain increases; hence, the number of the blobs in the chain increases. Therefore, even with a slight increase in the concentration of the solution, the concentration of blobs markedly increases. Since the osmotic pressure of a semidilute solution is controlled by the concentration

of blobs,¹⁷ the concentration dependence of the osmotic pressure becomes stronger than that in the dilute solutions [$\pi_{\text{semidilute}} \sim c^{9/4}$].

Let us discuss in more detail the dependence of the equilibrium content of PEO in the solvent-crazed PET matrix on the concentration of the PEO-containing solution and on the molecular mass of PEO when PEO is introduced into the parent PET-based matrix directly in the course of the tensile drawing of the polymer samples or via diffusion into the solvent-crazed PET matrix. Table 2 presents the corresponding data on the equilibrium content of PEO (m/m_0) with $M = 2 \times 10^4$, 4×10^4 , 1×10^5 , and 1×10^6 .

As follows from Table 2, as the concentration of PEO (2×10^4 and 1×10^5) in the solutions increases, the PEO content in the pores of the solvent-crazed PET increases both for the loading via diffusion under the concentration gradient and due to the loading via tensile drawing in the polymer solution.

The following question arises: what is the nature of the accumulation and concentration of PEO in the pores of the crazes due to the PEO sorption from the solution as well as due to the flow into the porous polymer structure in the course of the solvent crazing? Evidently, this phenomenon is related to the specific structural features of crazes, namely, to their highly developed specific surface which approaches nearly $100 \text{ m}^2/\text{g}$.^{3–6} One can assume that penetration of the PEO-containing solution into the pores is accompanied by the adsorption of the PEO macromolecules on the highly developed surface of the fibrillated polymer in the crazes.

To investigate the generality of the observed phenomena in the experiments were conducted using polymers of a different nature. For this purpose, along with PET, HDPE (high density poly(ethylene)) is used, the deformed via the mechanism of solvent-crazing. For the introduction of porous craze, along with the PEO used other flexible chain polymers—poly(vinylpyrrolidone) (PVP). It was found that in all cases, the content of the polymer injected exceeded the theoretically calculated value determined based on the porosity of the flexible polymer and the concentration of the surrounding solution. As a result, the deformation of PET and HDPE via the mechanism crazing in solutions of macromolecular compounds were obtained by polymer–polymer blends of PET–PEO, HDPE–PEO, and PET–PVP containing a second component to 40%.

CONCLUSION

Therefore, tensile drawing of the PET samples proceeds via the mechanism of solvent crazing and this process is accompanied by the penetration of the PEO macromolecules into the porous structure of the crazes. The PEO macromolecules are captured by the flow of the low-molecular-mass fluid and worm into the porous structure of the crazes in the course of the tensile drawing of the parent polymer. The PEO content in the pores of the solvent-crazed polymer is controlled by the overall porosity of the parent polymer as well as by the concentration of the feed polymer in the surrounding solution. However, penetration of PEO into the porous structure upon tensile drawing proceeds much quicker (minutes) as compared with the attainment of the equilibrium content of the polymer under the action of the concentration gradient (days).

First discovered in the phenomenon of penetration of macromolecular flexible-chain polymers in the porous structure of crazes formed in the process of drawing of polymers in solutions of macromolecular compounds in the AAL via the mechanism of crazing be a general nature and can be considered as a perspective method of creating polymer–polymer blends.

AUTHOR INFORMATION

Corresponding Author

*E-mail: katrin310@yandex.ru.

ACKNOWLEDGMENT

This work was supported by the Russian Foundation for Basic Research. Project No. 09-03-00430-a), by the Grant of the State Support of the Leading Scientific Schools, NSh-4371.2010.3, and by the State Contracts, Project Nos. P1484 and 02.740.11.0143.

REFERENCES

- (1) Kambour, R. P. *J. Polym. Sci., Macromol. Rev.* **1973**, *7*, 1.
- (2) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *S2–S3*, 2.
- (3) Volynskii, A. L.; Bakeev, N. F. *Highly Dispersed Oriented State of Polymers*; Khimiya: Moscow, 1984.
- (4) Volynskii, A. L.; Bakeev, N. F. *Solvent Crazing of Polymers*; Elsevier: Amsterdam, New York, and Tokyo, 1995, 410.
- (5) Volynskii, A. L.; Bakeev, N. F. *Structural Self-Organization of Amorphous Polymers*; Physmatlit: Moscow, 2005.
- (6) Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Polym. Sci. Ser. B* **1993**, *35*, 913.
- (7) Volynskii, A. L.; Yarysheva, L. M.; Bakeev, N. F. *Nanotechnol. Russ.* **2007**, *2*, 58.
- (8) Volynskii, A. L.; Mikushev, A. E.; Yarysheva, L. M.; Bakeev, N. F. *Russ. Chem. J.* **2005**, *XLIX*, 118.
- (9) Volynskii, A. L.; Bakeev, N. F. *Advances in Interpenetrating Polymer Networks*; Technomic Publishing: Lancaster, PA, 1991, *3*, 53.
- (10) Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Polym. Sci. Ser. A* **1997**, *39*, 26.
- (11) Volynskii, A. L.; Rukhlya, E. G.; Yarysheva, L. M.; Bakeev, N. F. *Nanotechnol. Russ.* **2007**, *2*, 44.
- (12) Rukhlya, E. G.; Arzhakova, O. V.; Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Polym. Sci. Ser. B* **2007**, *49*, 118.
- (13) Rukhlya, E. G.; Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Polym. Sci. Ser. B* **2007**, *49*, 245.
- (14) Yarysheva, L. M.; Rukhlya, E. G.; Volynskii, A. L.; Bakeev, N. F. *Perspekt. Mater.* **2008**, *6*, 203.
- (15) Rukhlya, E. G.; Arzhakova, O. V.; Dolgova, A. A.; Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Int. J. Polym. Anal. Charact.* **2007**, *12*, 65.
- (16) Rukhlya, E. G.; Yarysheva, L. M.; Volynskii, A. L.; Bakeev, N. F. *Polym. Sci. Ser. A* **2010**, *52*, 614.
- (17) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*. Cornell University Press. Ithaca, NY, 1979.
- (18) Grosberg, A. Yu. Khokhlov, A. R., *Statistical Physics of Macromolecules*; American Institute of Physics: New York, 1994.
- (19) Sakaue, T.; Raphael, E. *Macromolecules* **2006**, *39*, 2621.
- (20) Guillot, G.; Leger, L.; Rondelez, F. *Macromolecules* **1985**, *18*, 2531.
- (21) Teraoka, I.; Langley, K. H.; Karasz, F. E. *Macromolecules* **1993**, *26*, 287.
- (22) Grull, H.; Shaulitch, R.; Yerushalmi-Rozen, R. *Macromolecules* **2001**, *34*, 8315.
- (23) Caspi, Y.; Zbaida, D.; Cohen, H.; Elbaum, M. *Macromolecules* **2009**, *42*, 760.
- (24) Daoudi, S.; Brochard, F. *Macromolecules* **1978**, *11*, 751.
- (25) Cifra, P.; Teraoka, I. *Polymer* **2002**, *43*, 2409.
- (26) Krasilnikov, O. V.; Rodrigues, C. G.; Bezrukov, S. M. *Phys. Rev. Lett.* **2006**, *97*, 018301–1.
- (27) Movileanu, L.; Cheley, S.; Bayley, H. *Biophys. J.* **2003**, *85*, 897.
- (28) Yarysheva, L. M.; Galperina, N. B.; Arzhakova, O. V.; Volynskii, A. L.; Bakeev, N. F.; Kozlov, P. V. *Polym. Sci. Ser. B* **1989**, *31*, 211.
- (29) Cassasa, E. F. *J. Polym. Sci. B5* **1967**, *773*.