Structure and Stability of Oligomer–Polymer Blends Based on Poly(ethylene terephthalate) Deformed by Crazing Mechanism

A. Yu. Yarysheva[a], V. V. Polyanskaya[a], E. G. Rukhlya[b], A. I. Dement'ev[a], A. L. Volynskii[b], and N. F. Bakeev[b]

[a] *Department of Chemistry, Moscow State Pedagogical University, Nesvizhskii per. 3, Moscow, 119021 Russia*

Department of Chemistry, Moscow State University, Moscow, 119991 Russia

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Abstract—Deformation of poly(ethylene terephthalate) films in high-viscosity poly(ethylene glycol) (PEG 600) and poly(propylene glycol) (PPG 3000) is investigated. It is established that the deformation is realized by the classical crazing mechanism, is accompanied by the formation of a finely dispersed fibrillar–porous structure and results in the formation of blends with high concentrations of the incorporated components (as high as 52–57 wt %). The stability of samples that occur in the free state after stretching is studied. Prolonged release of PEG 600 from the crazed poly(ethylene terephthalate) matrix is revealed, the intensity of which depends on the ambient humidity.

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INTRODUCTION

Stretching amorphous glassy polymers in adsorption-active liquid media (**AAMs**) occurs via the classical crazing mechanism [1–4], which is realized in local deformation zones that are referred to as crazes. The structure of crazes consists of fibrils connecting the opposite walls of crazes and voids between them filled with an ambient liquid. The deformation mechanism and the structure of resulting crazes depend on the adsorption activity and viscosity of a medium in which the stretching is implemented [5].

The application of high-viscosity nonvolatile liquids as AAMs is of special interest because, under these conditions, one can monitor the kinetics of the migration of the medium from the pore volume to gain insight into the stability of these systems and the structural rearrangements taking place in crazed matrices [6, 7]. Crazes consist of voids with diameters of no larger than 20 nm separated by oriented polymer fibrils with the same sizes; i.e., deformed polymers represent highly dispersed colloidal systems. As was revealed in [1–4], when the stress is removed, the fibrils are folded and stick to one another. The structural rearrangements cause the polymer to shrink and lead to the liquid being squeezed from the crazes.

Previously, for poly(ethylene terephthalate) (**PET**) deformed in high-viscosity media, such as ethylene glycol, water–alcohol solutions of ethylene glycol and glycerol [6, 7], and poly(ethylene glycol) with a molecular mass of 400 [8], the prolonged release of liquids captured by the polymer was observed for a long time (several years). This property of systems composed of dispersed polymer matrices and high-viscosity AAMs present in crazes may be of practical

interest because, at present, there is a need for materials with controlled long-term release of functional ingredients. These systems are of great importance for medicine, cosmetology, the food industry, and agriculture. At present, they are mainly produced by encapsulating functional agents as emulsions, gels, and block copolymers containing active components [9–11].

Note that the prolonged release of liquids from crazed matrices is observed for viscous hygroscopic compounds. Therefore, it is of interest to investigate polymer stretching, the kinetic of the release of different high-viscosity one-component AAMs, and the effect of ambient humidity as a factor that allows one to control the latter process.

EXPERIMENTAL

The objects for the study were 100-μm films of amorphous glassy nonoriented PET. Dumbbell-like samples with working region sizes of 6.15×20 mm were deformed in the media of poly(ethylene glycol) with a molecular mass of 600 (**PEG 600**, Loba Chemie) and poly(propylene glycol) with a molecular mass of 3000 (**PPG 3000**, Aldrich). Then, the samples were released from the clamps of a stretching unit, residual liquid was removed from the film surface, and the samples were weighed. The content of a liquid phase (oligomer) in the films was calculated as follows: $(m_t - m_0)/m_t$, where m_t is the mass of a film with an oligomer (PEG 600 or PPG 3000) immediately after the stretching and m_0 is the mass of an initial PET film. The stability of the blends was estimated from the amount of liquid medium contained in the deformed
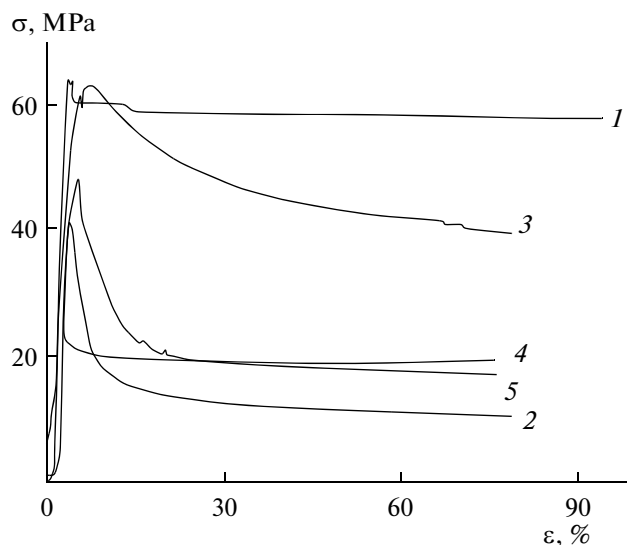
Fig. 1. Stress-strain curves for PET films deformed in (*1*) air, (*2*) PEG 600, (*3, 5*) PPG 3000, and (*4*) isopropanol at deformation rates of (*1–4*) 2, and (*5*) 0.1 mm/min.

samples; i.e., the $\left(m_t^* - m_0\right)/m_0$ values were determined, where m_t^* is the mass of a medium-containing film at time moment t after the stretching.

The porosity of the deformed polymer W was calculated from a change in the geometric sizes of the films and expressed as a ratio between the volume increment ΔV resulting from the stretching and the total volume $V_0 + \Delta V$ of a deformed sample $W = [\Delta V/(V_0 + \Delta V)] \times 100\,(\%)$. The samples were exposed to ambient humidities of 0, 84, and 100% in desiccators. The shrinkage of the samples was calculated as the ratio of a change in the linear sizes of the films after the shrinkage to a change in the sizes resulting from the stretching $(l_d - l_{sh})/(l_d - l_0)$, where l_0 is the initial sample length, l_d is the deformed sample length, and l_{sh} is the sample length after the shrinkage. At least six samples were prepared for each measurement; the average measurement errors were 1.5 and 3% for the porosity and the mass of the samples, respectively. All of the experiments were performed at room temperature (22–25°C).

RESULTS AND DISCUSSION

Let us consider the peculiarities of PET deformation in liquid oligomers PEG 600 and PPG 3000. Unlike typical low-viscosity and volatile AAMs that are commonly used for polymer crazing, these compounds have a substantially higher viscosity. For example, the viscosity of typical AAMs (lower aliphatic alcohols or hydrocarbons) is no higher than 10 cP, while the viscosity of PPG 3000 is as high as 630 cP.

The adsorption activity of a liquid and the efficiency of crazing are commonly assessed based on the data on the mechanical behavior of polymers and changes in the porosity of deformed samples. Figure 1 illustrates the stress–strain curves for PET films in (*1*) air; (*2*) PEG 600; (*3*) PPG 3000; and (*4*) a typical AAM, isopropanol, at a deformation rate of 2 mm/min. As can be seen from the presented data, the stress–strain curves for the PET films in PEG and isopropanol are close to one another. Hence, the efficiency of PET crazing, which is estimated from a reduction in the stress of the stretching in a medium relative to that in air, may be considered to be equal in PEG 600 and in the typical low-molecular-mass medium.

In PPG 3000, the tensile stress at a deformation rate of 2 mm/min (Fig. 1, curve *3*) decreases to a lower extent than in PEG 600 (Fig. 1, curve *2*) because of its high viscosity, which creates transport confinements for the penetration of the liquid into the tip of a growing craze, thus hindering the development of the porous structure. Unlike PEG 600, the deformation of PET films in PPG 3000 at this stretching rate is realized through a mixed mechanism. At low elongations, a neck develops in a sample, i.e., the stretching occurs as it does in air. However, in the course of stretching, the stress decreases in the sample, the neck ceases to develop, and the further deformation is realized by the crazing mechanism with the nucleation and development of a large number of crazes. Because the transport of a liquid medium depends on its viscosity, the stretching in high-viscosity media is characterized by a critical stretching rate at which the deformation mechanism changes. The critical stretching rate of the passage from the mixed to the crazing mechanism is 0.1 mm/min for PET deformation in PPG 2000, with the stretching under these conditions being accompanied by a noticeable reduction in the stress (Fig. 1, curve *5*).

Note that, after the yield stress is reached, the stress–strain curves for PET stretching in PEG 600 and, especially, PPG 3000 (Fig. 1, curves *3, 5*) decrease more smoothly than in isopropanol. A reduction, which is observed in the stress during PET stretching after the yield stress has been achieved, is explained by the growth of individual crazes or their ensembles throughout the cross-section of a sample. The range of the stationary development of deformation at a constant stress is attained when all nucleated crazes have been grown throughout the cross-section of a sample. Therefore, the onset of the plateaus in the stress–strain curves during the crazing of polymers in AAMs is governed by the growth rate of crazes. This value is, in turn, dependent on the stress σ_N in a local zone of deformation, i.e., at the tip of a developing craze. When a polymer is deformed at a constant stretching rate, the stress in a tip of a craze is inversely proportional to the number crazes that have been nucleated; i.e., $\sigma_N = \sigma/N$, where N is the number of
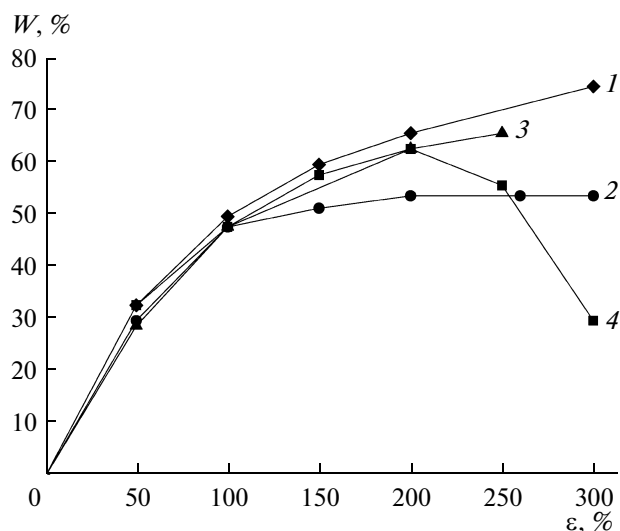
Fig. 2. Porosity-elongation curves for PET films: (*1*) theoretical dependence and dependences experimentally measured in (*2*) PEG 600, (*3*) PPG 3000 and (*4*) 1 : 7, vol/vol, water–ethanol solution.

Fig. 3. Variations in amount of PEG 600 in a PET matrix as depending on elongation.

crazes and σ is the tensile stress detected in the stress–strain curve. In the literature, this effect of the number of crazes on their growth rate was called the multiplicity effect [12]. The growth rate of crazes also depends on the rate of liquid transport to the craze tip and is governed by the viscosity of the liquid. The higher the viscosity of an applied AAM the lower the craze growth rate. PET deformation in PPG 3000 and PEG 600 is accompanied by the nucleation of a large number of crazes and, because the viscosity of these oligomers is much higher than the viscosity of isopropanol, the stress–strain curves exhibit a smoother decrease in the stress in the oligomers than in isopropanol.

Polymer deformation via the crazing mechanism is distinguished by an enlargement of a sample volume in the course of stretching due to the development of a porous structure. The dependences of the porosity of PET films deformed in different media on the elongation are demonstrated in Fig. 2. Curve *1* reflects variations in the theoretical porosity. The theoretical porosity is some ideal porosity, which is calculated assuming that the entire deformation leads to a rise in the volume; i.e., the length of a sample, which is determined by the elongation, increases, while the width and thickness of a sample remain unchanged. Thus, the theoretical porosity may be calculated as follows: $W = [\varepsilon/(1 + \varepsilon)] \times 100$ (%), where $\varepsilon = \Delta l/l_0$ is the degree of deformation (elongation). The concept of the theoretical porosity is introduced to assess to what extent the real deformation of a polymer differs from the ideal one that would take place in the absence of the structure collapse and, as well as to estimate the stabilizing effect of a medium on the deformation process.

Indeed, the real porosity evaluated from the geometric sizes of a film in the deformation range of no
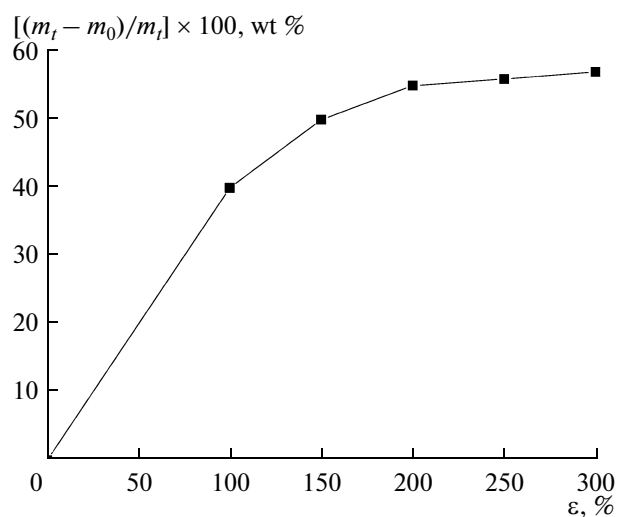
higher than 100% is lower than the theoretical one. Figure 2 (curves *2*, *3*) illustrates the dependences of the porosity on the elongation of samples deformed in high-viscosity PEG 600 and PPG 3000. A similar dependence plotted for PET films deformed in a typical AAM (water–ethanol solution) has a pronounced extremal pattern with a maximum at an elongation of 200% (curve *4*). A reduction in the porosity at higher elongations is explained by the fact that, as the elongation grows, fibrils that connect the opposite walls of crazes become more mobile and flexible due to both an increase in their length and a diminish in the hindrances from the nonoriented bulk polymer. The exposure of the samples to isometric conditions prevents the fibrillated polymer from the longitudinal shrinkage in crazes; however, it does not exclude fibrils sticking to one another, which in turn leads to the collapse of the craze structure and a decrease in the polymer porosity. The absence of an abrupt fall in porosity at high elongations of PET films in PEG 600 and PPG 3000 to compare with the low-viscosity water–ethanol solution is obviously associated with the deceleration of the structural rearrangements in the crazes due to the high viscosity of the former two media. Thus, PEG and PPG stabilize the porous structure of deformed PET.

Figure 3 shows the data on the content of PEG 600 in the crazed PET matrix as depending on the elongation. The porosity of the films (Fig. 2) was measured under isometric conditions, while the content of the oligomer was determined for films that occur in a free state, when shrinkage begins in a sample as a result of stress relaxation. Therefore, it would be incorrect to compare their absolute values. Nevertheless, it is obvious that the curves that characterize the dependences of the porosity of PET in PEG 600 (Fig. 2, curve *2*) and the content of PEG 600 in PET (Fig. 3) on the
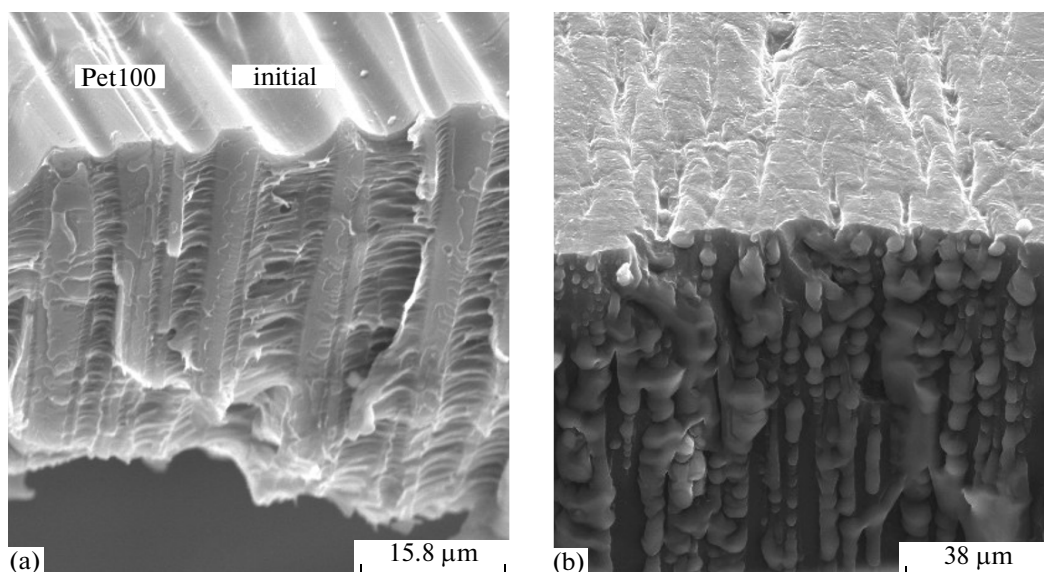
Fig. 4. Micrographs of cleavages of PET films deformed by 100% in (a) 7 : 1, vol/vol, water-ethanol solution and (b) PEG 600.

elongation are of the same character. As the elongation rises, the fraction of the polymer that is transformed into crazes and, accordingly, the porosity and the amount of the liquid filling the formed pores increase.

Scanning electron microscopy was used to examine the structure of film cleavages oriented normal to the thicknesses and parallel to the stretching axes of the films. A typical micrograph of PET deformed in a water−ethanol solution and dried under isometric conditions is depicted in Fig. 4a. It is known [1−4] that the complete removal of a liquid medium, even under isometric conditions that prevent deformed samples from longitudinal shrinkage, is accompanied by noticeable changes in the fibrillar−porous structure of polymers. The sticking of fibrils results in the formation of large strands connecting the opposite walls of crazes and voids between them, the sizes of which (up to 1 μm) are larger than the diameters of pores and fibrils, which are characteristic of the native structure of crazes (below 20 nm), by several orders of magnitude [1−4].

The use of high-viscosity nonvolatile liquids, such as PEG 600 (Fig. 4b), as AAMs makes it possible to observe the structure of a deformed polymer without removing the medium. As the samples are scanned in high vacuum, the micrographs demonstrate the transfer of liquid PEG to the cleavage surface at the sites where crazes are located. It can be seen that the structure of the surface layer of the films differs from their internal structure. The droplets of released PEG are seen in the bulk of the polymer films, but they are actually absent on the film surface. Hence, in the high-viscosity medium, the coagulation of the fibrillar−porous structure also proceeds on the surface with the formation of a thin denser layer, which isolates internal pores from an ambient space, which was pre-

viously observed for PET deformed in typical AAMs. This layer is not monolithic because the prolonged release of the liquid medium captured during crazing is observed for PET samples deformed in PEG 600.

The stability of the polymer−oligomer blends may be estimated from variations in the masses of deformed samples with time. After the samples were released from the clamps of the stretching unit, they were exposed to air with room humidity (nearly 30%) and wiped before each weighing to remove PEG transferred to the surface. In order to assess the effect of the elongation on the migration of a high-viscosity medium from a polymer matrix, the amount of PEG released from the samples over a certain time was related to the amount of PEG captured during the stretching and measured at the initial time moment, $\Delta M_t/M_0$. As can be seen from the data presented in Fig. 5, the curves consist of two regions. During initial several days, a drastic rise in the amount of released PEG 600 is observed, while the subsequent region is flat and exhibits a very slow release of the oligomer.

During the initial several days, PEG 600 is released more intensely from PET deformed by 300%. However, in the course of time, the intensity of the oligomer release from the structure of crazes diminishes, and the relative amount of released PEG slightly depends on the elongation. Note that the same character of the prolonged release of media from crazed PET matrices was observed for other high-viscosity hygroscopic liquids [6−8].

Since, as was mentioned above, the prolonged release of oligomers from PET may be of practical significance, a question arises as to the factors that can affect this process. PEG is a very hygroscopic compound (at 100% humidity, PEG 600 absorbs as much as 200% water relative to its own mass over 7 days);
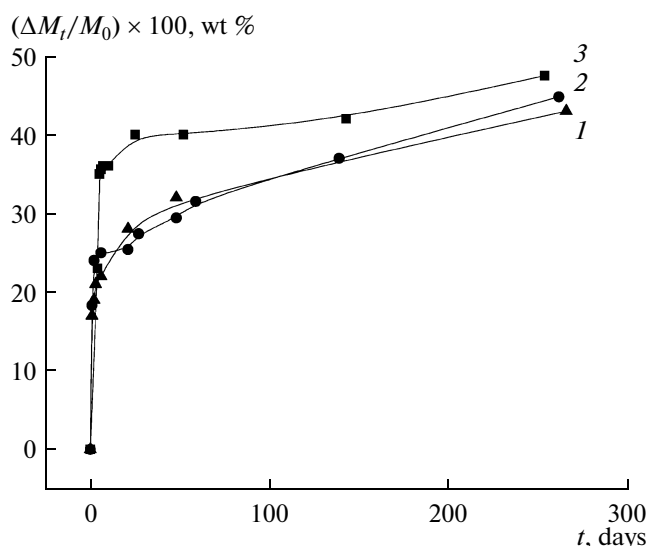
$(\Delta M_t/M_0) \times 100$, wt %

Fig. 5. Kinetics of PEG 600 release from PET samples deformed to elongations of (*1*) 100, (*2*) 200, and (*3*) 300%.

$\left[(m^*_t - m_0)/m_0\right] \times 100$, wt %

Fig. 6. Time variations in relative content of PEG 600 in PET samples (100% elongation) upon passing them from conditions of 30 to (*1*) 100 and (*2*) 84% humidity.

therefore, the stability of the obtained system was investigated as depending on the ambient humidity. Figure 6 illustrates a curve characterizing the content of PEG in PET related to the mass of the initial film $\left(m^*_t - m_0\right)\big/m_0$. It can be seen that the curve, which smoothly decreases with time, abruptly falls when samples, which have been previously exposed to room conditions with a humidity of 30–32%, are placed into desiccators with humidities of 84 and 100%. This fall becomes evident within just 24 h, and the higher the ambient humidity the greater the fall.

When the samples were dried under room conditions, the content of the liquid component in them became still lower (the final regions of curves *1* and *2* in Fig. 6 correspond to the "dry" samples), i.e., water absorbed by poly(ethylene glycol) also contributes to the measured masses of the samples, and the real loss of the oligomer at an increased humidity appears to be even greater. The oligomer is not completely removed from the crazed matrix. Even after being exposed to 100% humidity for 3 months, the samples contained about 6% PEG 600.

Unfortunately, the porosity of the samples after shrinkage cannot be experimentally determined because of the nonuniform thickness of the films subjected to shrinkage. The results obtained may be explained by comparing them with the published data on the effects of the viscosity and the surface activity of a medium on the stability of a fibrillar–porous structure [1–3]. The amount of water absorbed by PEG enlarges with humidity. This process leads to a reduction in the viscosity of the medium present in the crazed matrix, because the viscosity of water is much lower than that of PEG (135 and 1 cP for PEG 600 and
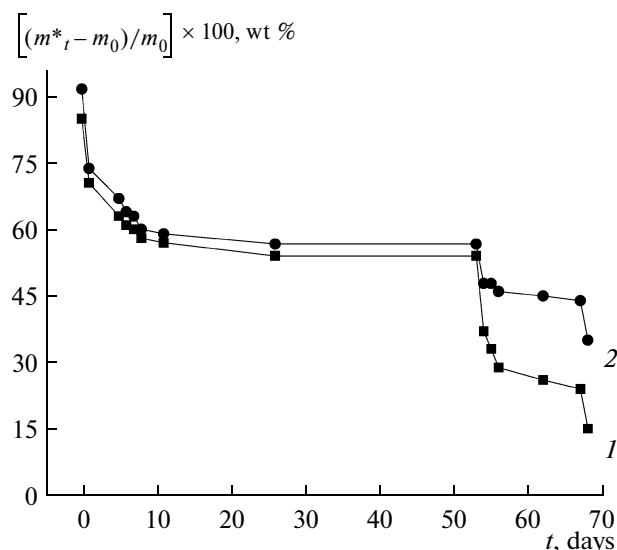
water, respectively). It may be believed that an increase in water content in PEG also decreases the adsorption activity of the medium, because, as compared to PEG, water does not wet PET and is a poor crazing agent for it [14]. Both of these factors, a reduction in the viscosity and a decrease in the adsorption activity of the medium, affect the stability of deformed samples. Coagulation processes occur faster and more efficiently in the structure of crazes, which results in more intense squeezing of the liquid medium.

Since PPG 3000 has another chemical nature and, in contrast to PEG 600 is low-hygroscopic (PPG absorbs no more 2–3% water under the conditions of 100% humidity), a question arises as to the stability of PET films that are deformed in PPG 3000 and occur in the free state under the conditions of different humidities after stretching. At room humidity, the shrinkage and a slight release of the liquid (no more than a few percent) only take place in an initial region (during initial several days) of the curve that characterizes the content of PPG in PET films. After that, the sample mass remains unchanged; i.e., the resulting system is stable (Fig. 7).

It might be assumed that the stability of craze structure is only associated with the higher viscosity of PPG 3000 to compare with PEG 600. However, the same loses of a liquid phase were observed in [8] for PET deformed in PPG 400, which has a lower viscosity. For example, in the cases of PEG 400 [8] and PEG 600, the release of the oligomers during the initial 24 h was 12–15%, while, for PPG 400 [8] and PPG 3000, this value was no larger than 3–5%. Therefore, we may believe that the higher stability of the craze structure of PET deformed in PPG with different molecular masses is associated not only with their high viscosity,
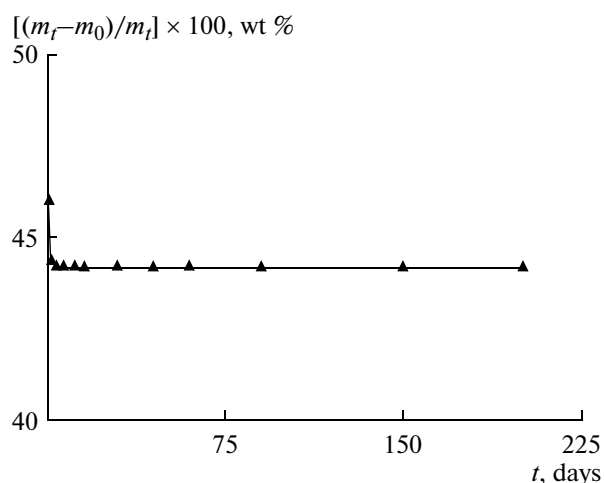
$[(m_t-m_0)/m_t] \times 100$, wt %

Fig. 7. Release of PPG 3000 from PET sample (100% elongation) under the conditions of room humidity (30−32%).

but also with their ability to more efficiently reduce the free energy of the polymer to compare with PEG.

However, despite the higher stability of the structure and the absence of the prolonged release of the liquid component for PET deformed in PPG, variations in humidity also affect this system. The conditioning of PPG 3000-containing PET films at 100% humidity showed that the system that had been previously stable released 8–9% liquid phase during 7–10 days. Then, in the course of a two-month follow-up period of measurements, the sample mass remained unchanged; i.e., the system was equilibrated again.

Thus, it has been established that PET deformation in the media of high-viscosity PEG 600 and PPG 3000 is realized through the mechanism of classical crazing. Unlike typical AAMs, in these media, high porosity values can be achieved at high elongations. PET−PPG blends are characterized by a higher stability of their composition than PET−PEG blends. The release of liquid media from the formed structures has been studied as depending on the elongation and ambient humidity. It has been demonstrated that variations in these parameters enable one to regulate the intensity of oligomer release from crazed PET.

REFERENCES

1. Volynskii, A.L. and Bakeev, N.F., *Vysokodispersnoe orientirovannoe sostoyanie polimerov* (Highly Dispersed Oriented State of Polymers), Moscow: Khimiya, 1984.
2. Kramer, E.J., *Adv. Polym. Sci.*, 1983, vols. 52-53, p. 2.
3. Volynskii, A.L. and Bakeev, N.F., *Solvent Crazing of Polymers*, Amsterdam: Elsevier, 1995.
4. Yarysheva, L.M., Volynskii, A.L., and Bakeev, N.F., *Vysokomol. Soedin., Ser. B*, 1993, vol. 35, p. 813.
5. Volynskii, A.L., Shitov, N.A., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1981, vol. 23, p. 978.
6. Volynskii, A.L., Arzhakov, M.S., Karachevtseva, I.S., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A,* 1994, vol. 36, p. 85.
7. Yarysheva, L.M., Karachevtseva, I.S., Volynskii, A.L., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A,* 1995, vol. 37, p. 1699.
8. Rukhlya, E.G., Arzhakova, O.V., Yarysheva, L.M., et al., *Vysokomol. Soedin., Ser. B*, 2007, vol. 49, p. 920.
9. Madene, A., Jacquot, M., Scher, J., and Desobry, S., *Int. J. Food Sci. Technol.*, 2006, vol. 41, p. 1.
10. Allen, C., Maysinger, D., and Eisenberg, A., *Colloids Surf. B*, 1999, vol. 16, p. 3.
11. Kwon, G.S. and Okano, T., *Adv. Drug Delivery Rev.*, 1996, vol. 21, p. 107.
12. Volynskii, A.L., Lukovkin, G.M., Yarysheva, L.M., et al., *Vysokomol. Soedin., Ser. A*, 1982, vol. 24, p. 2357.
13. Volynskii, A.L., Bekman, I.N., Shelekhin, A.B., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A*, 1988, vol. 30, p. 1731.
14. Sinevich, E.A., Prazdnichnyi, A.M., and Bakeev, N.F., *Vysokomol. Soedin., Ser. A,* 1994, vol. 36, p. 937 .