

# Oligomer–Polymer Blends Based on Solvent-Crazed Polymers<sup>1</sup>

E. G. Rukhlya<sup>a</sup>, O. V. Arzhakova<sup>a</sup>, L. M. Yarysheva<sup>a</sup>, A. L. Volynskii<sup>a</sup>, and N. F. Bakeev<sup>b</sup>

<sup>a</sup> Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119992 Russia

<sup>b</sup> Enkolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,  
Profsoyuznaya ul. 70, Moscow, 117393 Russia  
e-mail: katrin310@yandex.ru

Received July 18, 2006;

Revised Manuscript Received December 14, 2006

**Abstract**—The feasibility of preparation of oligomer–polymer blends by means of the solvent crazing technique is considered. An analysis of the mechanical behavior of polymers and porosity of deformed films led to the conclusion that polyethylene glycol and polypropylene glycol in their liquid state are adsorption-active environments effective toward PET and HDPE. The stretching of PET and HDPE in these environments follows the mechanisms of classical and delocalized solvent crazing, respectively. The blends based on PET and HDPE containing polyethylene glycol 400, polypropylene glycol 400, and polypropylene glycol 3000 with an amount of the hydrophilic component of 25–45% were prepared. Most blends retained their stability with time. The exception is the PET–PEG 400 blend, which exhibited a sustained release of the liquid component.

DOI: 10.1134/S156009040705003X

## INTRODUCTION

Crazing is one of the modes of plastic deformation of polymers. The development of crazing is strongly facilitated by drawing of polymers in adsorption-active liquid environments. This phenomenon is of particular interest to researchers inasmuch as the deformation of polymers via the crazing mechanism is accompanied by the initiation and growth of crazes, special regions that possess a unique fibrillar–porous structure with pore and fibril diameters of 2–20 nm [1–3]. In this context, solvent crazing of polymers in the presence of an adsorption-active medium (AAM) can be treated as an effective means of the preparation of finely divided porous materials [1–4]. When drawing is carried out in a solution that contains various low-molecular-mass compounds, these compounds can effectively penetrate into the porous structure of crazes. As a result, it becomes possible to manufacture nanocomposites in which both polymer and incorporated additives are dispersed on the nanometer scale [5].

A fundamental difference of this process for the manufacture of nanocomposites from the traditional methods of mixing components in melts or solutions is that the thermodynamic compatibility of the components is not necessarily required for the incorporation of additives into the polymer structure. The critical condition in this case is the size of molecules or particles of the additive. Examples of the preparation of nanocomposites based on solvent-crazed polymers with different low-molecular-mass additives have been reported.

The molecular size of the admixed compounds did not exceed 3 nm [6].

Attempts to prepare polymer–polymer blends with the interpenetrating network structure by means of solvent crazing of polymers have succeeded as well [7, 8]. A monomer and an initiator were introduced into the matrix of the crazed polymer at the first stage, and in situ polymerization was carried out then.

However, it seemed interesting to prepare polymer blends by means of a simpler procedure via the direct drawing of a polymer in the medium of another polymer. The most attractive option concerns the preparation of highly dispersed blends based on polymers with strongly different properties, for example, hydrophilic and hydrophobic polymers. In this case, it may be expected that the materials thus prepared will possess interesting nontrivial properties. However, the compatibilization of such incompatible components presents a serious problem. Moreover, there are polymer pairs that cannot be blended by means of the traditional mixing procedures. For example, it is difficult to compatibilize PET with hydrophilic polymers, such as polyethylene glycol (PEG) or polypropylene glycol (PPG), for the purpose of obtaining a blend with a high level of dispersion.

Indeed, the melting temperature of PET is 254°C, whereas the temperatures of thermal degradation of PEG and PPG in air are 180 and 220°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.

<sup>1</sup>This work was supported by state contract no. 02.434.11.2005, and the grant “Leading Scientific Schools,” NSH-4897.2006.3.

The objective of this study was to prepare polymer-polymer blends from incompatible pairs of polymers, such as PET-PEG and PET-PPG, and from the blends of HDPE with these hydrophilic polymers by means of solvent crazing of polymer matrixes.

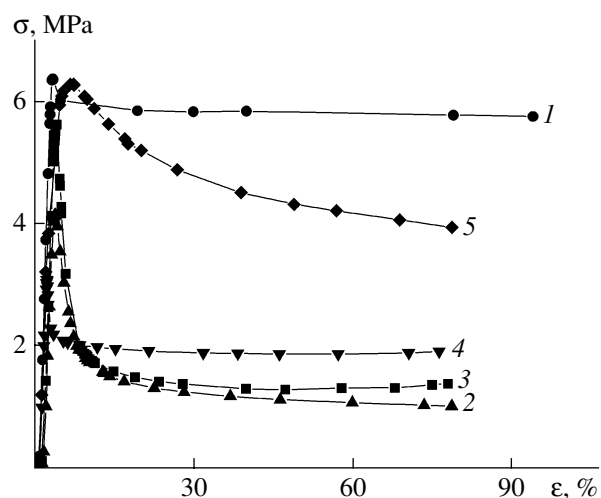
### EXPERIMENTAL

The objects of study were commercial films of unoriented glassy amorphous PET with a thickness of 100  $\mu\text{m}$  and HDPE films with a thickness of 25–60  $\mu\text{m}$ . The samples were cut as rectangular specimens (strips) with a gauge size of 20  $\times$  40 mm. The test samples were stretched at a draw rate of 0.2 mm/min in the presence of PEG (Loba Chemie) or PPG (Merck). Mechanical tests were performed on an Instron 4301 universal tensile machine; the tests were conducted with a strain rate of 0.2 mm/min in air and liquid environments. The porosity  $W$  of crazed films was determined by measuring the geometric dimensions of the specimens and expressed as an increment in volume of the film  $\Delta V$  divided by its total volume  $V_t$ :  $W = \Delta V/V_t$ . To determine the amount of PEG and PPG in the blend, the specimens were dried, released from the clamps, and weighed after the removal of residual liquid from the film surface. The of PEG and PPG contents of the blends were measured as an increment in the specimen mass  $\Delta m$  divided by the total mass  $m_t$  of the deformed specimen.

### RESULTS AND DISCUSSION

In this work, we studied the feasibility of the introduction of liquid oligomer compounds with  $M \leq 3000$  into the structure of solvent-crazed polymers. As oligomer compounds, PEG with  $M = 400$  (PEG 400) and PPG with  $M = 400$ –3000 (PPG 400 and PPG 3000) were selected. Under standard conditions, the above high-molecular-mass compounds are liquids. In this context, it seems interesting to reveal whether they can serve as AAMs toward PET and HDPE. The ability of liquid environments to change the mechanism of polymer deformation (as compared with polymer drawing in air) was judged by visual observation of the appearance of crazes as well as by studying the mechanical response of polymers during their drawing and changes in the porosity of the deformed samples.

Tensile drawing of PET (amorphous glassy polymer) in the presence of PEG and PPG proceeds via the mechanism of classical crazing, as indicated by the formation of numerous crazes in the specimens. Moreover, the deformation of PET in PEG and PPG is accompanied by a decrease in the draw stress, similar to deformation via the classical crazing mechanism in typical AAMs (aliphatic alcohols and hydrocarbons) [1, 3]. Figure 1 presents the stress-strain diagrams measured for PET films during their stretching in air, PEG, PPG, and in the presence of a typical AAM (isopropanol). As follows from Fig. 1, stress-strain curves corresponding

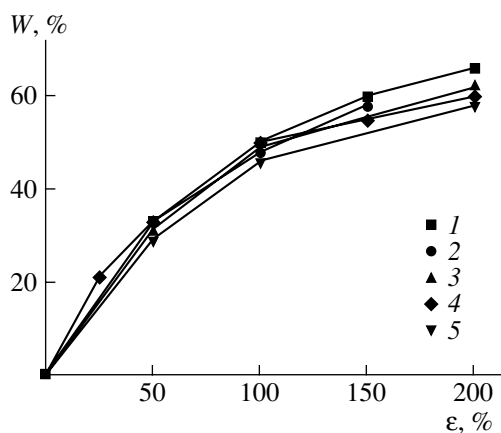


**Fig. 1.** Stress-strain diagrams (stretching at room temperature) corresponding to the drawing of PET in (1) air, (2) PEG 400, (3) PPG 400, (4) isopropanol, and (5) PPG 3000.

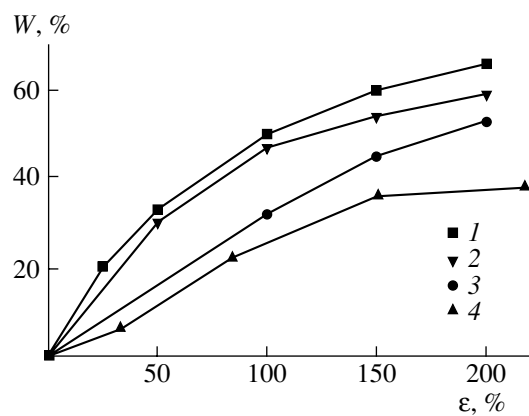
to the drawing of PET in PEG 400 and PPG 400 are similar to the stress-strain curve of PET in isopropanol. The efficacy of solvent crazing of PET in the presence of PEG 400 and PPG 400 is estimated as the decrease in the yield stress of polymer in the presence of AAM as compared with that in air. This parameter appears to approach the efficacy of solvent crazing of polymers in typical AAMs. For PPG 3000, the decrease in the draw stress is less pronounced. Evidently, this tendency is due to a much higher viscosity of this liquid medium, a factor that impedes the effective penetration of the medium into the structure of the formed crazes.

Data on the porosity of the solvent-crazed films prepared by drawing in a PEG or PPG medium are of special interest because this quantitative information allows one to predict the content of an additive that can be incorporated into the polymer structure for the preparation of nanocomposites or polymer blends. These results make it possible to assess the mechanism of tensile drawing in polymers and to assess the efficacy of solvent crazing as a means of introduction of modifying additives into polymers.

Figure 2 presents the porosity  $W$  plotted against tensile strain  $\epsilon$  of the solvent-crazed PET films after their drawing in various liquid environments. Curve 1 corresponds to the theoretical dependence of porosity on tensile strain during solvent crazing under the assumption that all deformation proceeds via increasing the volume of the deformed films (in other words, via the development of porosity). Curves 2–4 demonstrate the experimental data on the porosity of PET films during their stretching in PEG 400, PPG 400, and PPG 3000. For comparison, Fig. 1 presents the dependence (curve 5) of the porosity of the solvent-crazed PET films on tensile strain during stretching in a typical AAM (isopro-



**Fig. 2.** Porosity  $W$  vs. tensile strain  $\varepsilon$  of solvent-crazed PET samples: (1) calculated curve, (2) heptane, (3) PPG 400, (4) PEG 400, and (5) PPG 3000.



**Fig. 3.** Porosity  $W$  vs. tensile strain  $\varepsilon$  of solvent-crazed HDPE samples: (1) calculated curve, (2) PPG 400, (3) PPG 3000, and (4) PEG 400.

panol). As is seen, with increasing the tensile strain of solvent-crazed PET, porosity of the samples increases in all environments. At low tensile strains (below 100%), experimental porosity–tensile-strain dependences corresponding to the tensile drawing of PET films in PEG and PPG virtually coincide with the theoretical estimates and with the experimental curves obtained for the solvent-crazed PET samples during their stretching in isopropanol. A slight difference between theoretical and experimental curves is seen only at high tensile strains of the solvent-crazed samples. This decrease in porosity was likewise observed during the drawing of polymer films in typical AAMs [3, 4]. This tendency is provided by the development of coagulation processes in the craze structure. However, it should be mentioned that, in the case of the tensile drawing of PET in PEG and PPG, the decrease in porosity at high tensile strains (as compared with theoretical values) does not exceed 10%. This behavior suggests that both PEG and PPG appear to be efficient AAMs toward PET and that all polymer deformation proceeds via the development of classical crazing. This fact allows the preparation of the materials with a high porosity and, hence, with a high content of the second component.

Let us consider the tensile drawing of HDPE in the presence of the same liquid environments (PEG and PPG). HDPE is a typical semicrystalline polymer, and its stretching in an AAM proceeds via the mechanism of delocalized solvent crazing [9]. In this case, polymer deformation is homogenous throughout the entire polymer volume and no individual crazes are formed. Analysis of the mechanical response of polymer does not allow ascertainment of the mechanism of deformation, because, during tensile drawing of HDPE in PEG and PPG, no marked stress decrease is observed (as compared with that during drawing in air). Therefore, the mechanism of deformation of HDPE in PEG and PPG can be established by studying the changes in the poros-

ity of polymer samples during tensile drawing. If the volume of the deformed polymer films increases with increasing the tensile strain, this fact indicates that polymer deformation proceeds via the mechanism of solvent crazing.

Experimental data on the porosity were compared with the theoretical dependences describing the changes in porosity with increasing the tensile strain (Fig. 3). As follows from Fig. 3, deformation of HDPE in PPG is accompanied by a marked gain in porosity (curves 3, 4). This fact indicates that PPG with  $M \leq 3000$  is an effective AAM with respect to HDPE and that polymer deformation proceeds via the mechanism of solvent crazing.

Tensile drawing of HDPE in PEG 400 (curve 2) is not accompanied by a marked increase in porosity. Polymer deformation is similar to that in air. This behavior is related to the fact that this liquid poorly wets a hydrophobic polymer, such as HDPE. To circumvent this factor, we used the mixture of PEG 400 with isopropanol, which is known to be a good AAM for HDPE. As was found, the addition of 20% of alcohol was sufficient to change the mechanism of deformation. In this case, the porosity of a polymer specimen increases during its tensile drawing (curve 2), thus indicating that deformation proceeds via the mechanism of solvent crazing.

Therefore, liquid oligomers such as PEG and PPG can serve as effective crazing-promoting agents for the selected polymers (PET and HDPE). In this context, their penetration into the crazed polymer matrix appears to be extremely efficient. As a result of simple drawing of polymers in the presence of oligomers, one can prepare highly dispersed blends composed of incompatible components: PET and HDPE, on one hand, and PEG and PPG, on the other hand.

With allowance for the fact that tensile drawing is performed in liquid polymers, the data on porosity

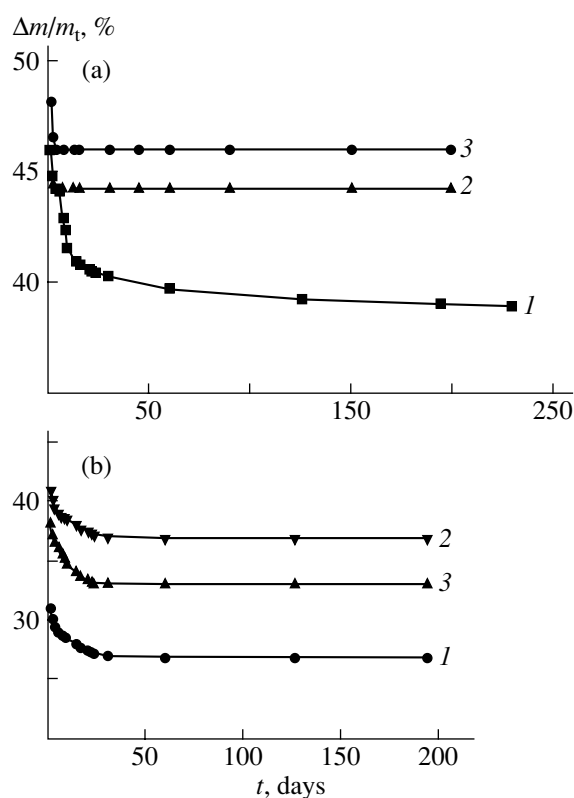
should reflect the composition of the resultant blends. However, as is known [1, 3, 10], when solvent-crazed films are released from the clamps, they experience shrinkage, which is accompanied by a decrease in porosity and by a partial or complete release of the incorporated additive from the crazed structure. In this context, we studied the stability of free-standing PET and HDPE films in time after their stretching in PEG and PPG. Drawing conditions were selected in such a manner that the porosity of the solvent-crazed PET and HDPE samples would be virtually the same (tensile strain is 100% and 200% for PET and HDPE, respectively); hence, the amount of the second component in the resultant blends should be the same. The stability of the deformed samples with time (for more than 8 months) was estimated via monitoring porosity changes and the amount of the liquid component (PEG or PPG) in the blend.

Figure 4 shows the changes in the relative mass content of PEG (curve 1) and PPG (curves 2, 3) in the free-standing PET and HDPE films in air with time. The initial points on the curves correspond to the PEG or PPG content of the PET-PEG or PET-PPG blends immediately after drawing and release from the clamps.

Above all, it should be noted that the overall concentration of oligomers in the blends remains high over 8 months. The curves illustrating the PEG or PPG content of the blends contain two regions: at the initial stage, one can observe a fast release (or so-called burst release) of the oligomer component from the volume of the samples; then, concentration of the second component in the free-standing composite films in air remains virtually the same.

The blends based on solvent-crazed PET containing PPG 400 and PPG 3000 demonstrate the best stability. In this case, the mass loss does not exceed 2% and equilibrium is attained within 5–7 days. The release of the liquid component from the PET films containing PEG 400 is higher, and the system does not attain its equilibrium state even within 8 months. A similar phenomenon of the sustained release of a liquid component from PET films deformed in viscous low-volatility liquids was observed in [11, 12]. This release of the liquid component from the fibrillar-porous structure of crazes as a highly dispersed colloidal system is presumably due to its thermodynamic instability and to the occurrence of coagulation processes. In turn, the intensity of coagulation processes is provided by the ability of a liquid to reduce polymer surface energy and to stabilize the highly dispersed fibrillar-porous structure of crazes. In this context, it may be assumed that the invariability of composition of the PET-PPG blends (as compared with the PET-PEG blend) is due to a greater ability of PPG to reduce the polymer surface energy and, hence, to provide a higher stability of the highly dispersed structure of crazes.

In the case of the HDPE-PEG and HDPE-PPG blends (Fig. 4b), equilibrium in the system is attained



**Fig. 4.** Relative changes in the mass of free-standing (a) PET and (b) HDPE samples in air with time after their tensile drawing in (1) PEG 400, (2) PPG 3000, and (3) PPG 400.

within 60 days; then, the materials remain stable with time. The mass loss by the liquid component does not exceed 3–5%. This implies that highly viscous and non-volatile liquids, such as PEG and PPG, are able to stabilize the highly dispersed porous structure of crazes in solvent-crazed HDPE even under the stress relaxation conditions. Therefore, the crazing of HDPE in the presence of PEG and PPG allows preparation of stable blends with a sufficiently high content of hydrophilic component in the porous matrix.

The table presents the data on the porosity  $W$  and mass fraction  $\Delta m/m_i$  of PEG or PPG in solvent-crazed PET with a tensile strain of 100% after their deformation via the mechanism of classical crazing and in solvent-crazed HDPE films with a tensile strain of 200% after their deformation via the mechanism of delocalized solvent crazing. As follows from the table, the drawing of PET and HDPE in PEG and PPG not only is accompanied by a marked increase in porosity but also provides a simple means for the preparation of stable oligomer-polymer blends. The content of the second component (PEG or PPG) in the blend achieves 25–45%.

Thus, liquid oligomers (PEG and PPG) are adsorptionally active environments toward PET and HDPE

Characteristics (porosity  $W$  and mass content of  $\Delta m/m_1$ ) of oligomer–polymer blends prepared via the drawing of PET and HDPE to strains  $\epsilon$  of 100 and 200%, respectively

Blend	$\epsilon$ , %	$W$ , %	$\Delta m/m_1$ , %
PET–PEG 400	100	50	39*
PET–PPG 400	100	50	46
PET–PPG 3000	100	46	44
HDPE–PEG 400	200	38	27
HDPE–PPG 400	200	59	33
HDPE–PPG 3000	200	53	37

\* Equilibrium is not attained.

and promote the development of polymer deformation via the mechanism of solvent crazing. This fact allows preparation of stable oligomer–polymer blends containing components with quite different natures, and the amount of the second component can reach 45%. In other words, the drawing of polymers in liquid media can be offered as a promising method for the physical modification of polymers and preparation of oligomer–polymer blends.

## REFERENCES

1. A. L. Volynskii and N. F. Bakeev, *Highly Dispersed Oriented State of Polymers* (Khimiya, Moscow, 1984) [in Russian].
2. E. J. Kramer, *Adv. Polym. Sci.* **52–53**, 2 (1983).
3. A. L. Volynskii and N. F. Bakeev, *Solvent Crazing of Polymers* (Elsevier, Amsterdam, 1995), p. 410.
4. L. M. Yarysheva, A. L. Volynskii, and N. F. Bakeev, *Polymer Science, Ser. B* **35**, 1000 (1993) [*Vysokomol. Soedin., Ser. B* **35**, 913 (1993)].
5. A. L. Volynskii, O. V. Arzhakova, L. M. Yarysheva, and N. F. Bakeev, *Polymer Science, Ser. C* **44**, 83 (2002) [*Vysokomol. Soedin., Ser. C* **44**, 1701 (2002)].
6. V. S. Loginov, Candidate's Dissertation in Chemistry (Moscow, 1978).
7. A. L. Volynskii and N. F. Bakeev, in *Advances in Interpenetrating Polymer Networks*, Ed. by D. Klemperer and K. S. Frisch (Technomic, Basel, 1991), p. 53.
8. L. M. Yarysheva, I. D. Kurashvili, T. E. Grokhovskaya, et al., *Polymer Science, Ser. A* **39**, 20 (1997) [*Vysokomol. Soedin., Ser. A* **39**, 26 (1997)].
9. A. L. Volynskii, O. V. Arzhakova, L. M. Yarysheva, and N. F. Bakeev, *Polymer Science, Ser. B* **42**, 70 (2000) [*Vysokomol. Soedin., Ser. B* **42**, 549 (2000)].
10. L. M. Yarysheva, I. D. Kurashvili, T. E. Grokhovskaya, et al., *Polymer Science, Ser. A* **46**, 1048 (2004) [*Vysokomol. Soedin., Ser. A* **46**, 1713 (2004)].
11. A. L. Volynskii, M. S. Arzhakov, I. S. Karachevtseva, and N. F. Bakeev, *Polymer Science, Ser. A* **36**, 70 (1994) [*Vysokomol. Soedin., Ser. A* **36**, 85 (1994)].
12. L. M. Yarysheva, I. S. Karachevtseva, A. L. Volynskii, and N. F. Bakeev, *Polymer Science, Ser. A* **37**, 1044 (1995) [*Vysokomol. Soedin., Ser. A* **37**, 1699 (1995)].