Structure of Polymer Blends Based on Solvent-Crazed Polymers

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Abstract: Blends based on polymers (PET, HDPE) prepared by deformation via the mechanism of classical and delocalized solvent crazing are described. The second component of polymer blends may be represented by various polymers such as PMMA, PS, PBMA, PEG, polyaniline, etc. The above polymers are characterized by a high level of mutual dispersion of components. Structure and mechanical properties of the blends are studied.

INTRODUCTION

Deformation of amorphous glassy and semicrystalline polymers in the presence of adsorptionally active liquid environments proceeds via the

mechanism of solvent or wet crazing. This process is accompanied by polymer dispersion into fine aggregates of oriented macromolecules (fibrils), which are separated by microvoids. The dimensions of craze fibrils and microvoids do not exceed 20 nm. Correlation between the conditions of tensile drawing, the nature of the polymer and liquid environment, and the parameters of the fibrillar-porous structure of the crazes has been established, and this knowledge allows one to consider solvent crazing as a promising method for the development of highly dispersed porous materials with controlled structure.[1–3]

There are two modes of solvent crazing: classical localized crazing and delocalized or intercrystallite solvent crazing. Classical localized crazing is a typical mode of deformation of amorphous glassy polymers (e.g., polyethylene terephthalate (PET), polyvinylchloride (PVC), polycarbonate (PC)) in the presence of surface-active liquid environments. Delocalized crazing is observed during tensile drawing of semicrystalline polymers (e.g., high-density polyethylene (HDPE), polypropylene (PP), polyamide-6 (PA-6), and polyamide-12 (PA-12)) in the presence of surface-active or plasticizing liquids.[4] Even though, depending on the mode of solvent crazing, the mechanism of polymer stretching is different, in both cases, highly disperse porous materials with a volume porosity up to 50–60% are obtained.

Highly dispersed and porous polymer materials prepared via solvent crazing can serve as suitable matrices or substrates for the preparation of nanocomposites[5] and polymer blends.[6,7] The advantages of the proposed approach are that, as this method does not require any thermodynamic compatibility between components, one can use quite different polymers and additives and prepare a wide range of polymer blends.

METHODS FOR THE PREPARATION OF POLYMER-POLYMER BLENDS VIA SOLVENT CRAZING

Let us consider the preparation of polymer-polymer blends via solvent crazing. All methods can be conditionally divided into two groups. The first group involves the preliminary introduction of monomers into the porous structure and further in situ polymerization, and the second approach concerns the direct introduction of polymers into the solvent-crazed matrix.

The method of in situ polymerization is well known for the preparation of semi-interpenetrating and interpenetrating polymer networks.[8,9] However, synthesis of interpenetrating polymer networks requires marked swelling of matrix polymers in liquid monomers; hence, the number of possible polymer pairs, especially for semicrystalline polymers, is limited.

The general scenario of the preparation of polymer-polymer blends based on solvent-crazed polymer matrices involves the introduction of

the monomer into the porous structure of crazes. This introduction can be accomplished either by direct tensile drawing of the polymer in liquid monomer containing the initiator of polymerization or by tensile drawing of the polymer in physically active liquid and subsequent substitution of the crazing liquid in the pores by the liquid monomer or its solution, when, for some reasons, tensile drawing in this particular liquid monomer is not allowed.

According to this scheme, polymer-polymer blends based on solvent-crazed HDPE, PP, PA-12, or PET matrices were prepared. As the second polymer component, polystyrene (PS), polymethylmethacrylate (PMMA), poly(butyl methacrylate) (PBMA), and electroconducting polymers like polyacetylene and polyaniline (PANi) were used.[10–15]

For the preparation of polymer-polymer blends based on HDPE, PP, and PA-12 with PS, PMMA, and PBMA, porous polymer matrices were prepared by tensile drawing in the presence of proper monomers containing initiating agents (benzoyl peroxide) and, in some cases, cross-linking agents (ethylene glycol dimethacrylate).

Polymer-polymer blends based on HDPE and PET matrices containing PANi were prepared by tensile drawing of polymers in the presence of plasticizing (heptane) and surface-active (butanol) liquid environments, respectively. Then, the active liquid in the crazes was substituted by an aqueous solution of aniline in 1 M HC1, and subsequent electropolymerization of the monomer in the volume of porous matrix was carried out.

The method of direct introduction of polymers into porous structure seems to be far more attractive. We studied the feasibility of the introduction of polymers with a molar mass below 3000 g/mol. We selected poly(ethylene glycol) (PEG) with a molar mass of 400 g/mol (PEG-400) and poly(propylene glycols) (PPGs) with a molar mass ranging from 400 to 3000 g/mol (PPG-400 and PPG-3000). At ambient conditions, the above polymers exist in liquid state and can serve as adsorptionally active environments with respect to PET and HDPE.

Figure 1 presents the stress-strain curves for PET recorded during its stretching in air (curve 1) and in PEG and PPG (curves 2–4). As follows from the stress-strain diagrams, tensile drawing of polymers in the presence of PEG and PPG is accompanied by a marked drop in tensile stress as compared with that observed during stretching in air. This behavior is quite similar to the mechanical response of polymers upon their tensile drawing in the presence of adsorptionally active environments, including iso-propanol (curve 5).

Direct stretching of PET in the presence of PEG and PPG allows preparation of polymer-polymer blends with appreciably different properties (hydrophobic and hydrophilic polymers). Let us mention that the conventional methods of polymer blending from melts or solutions fail to achieve this result. Indeed, the melting temperature of PET is equal
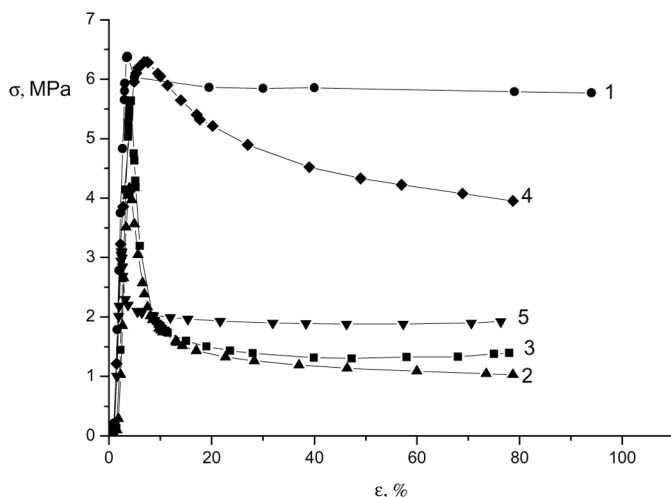
Figure 1.   Stress-strain curves for PET recorded during its stretching in air (1), in PEG400 (2), PPG400 (3), PPG3000 (4), and iso-propanol (5).

to 254°C, and the temperature of chemical degradation of PEG and PPG in air is equal to 180° and 220°C, respectively. Therefore, preparation of such composites via melt blending is impossible. The above polymers do not have common solvents, and their mixing from solutions is also prohibited.

COMPOSITION OF POLYMER-POLYMER BLENDS BASED ON SOLVENT-CRAZED POLYMERS

Obviously, the composition of polymer-polymer blends based on solvent-crazed polymers should be primarily controlled by the porosity of the solvent-crazed matrix, which, in turn, depends on the mode of solvent crazing (classical or delocalized solvent crazing) and on the nature of the liquid environment and tensile strain of the solvent-crazed polymer. Figure 2 presents the porosity plotted against tensile strain of PET and HDPE. Curve 1 shows the changes in porosity with increasing tensile strain for PET samples when stretching in the presence of an adsorption-ally active liquid environment proceeds via the development of classical solvent crazing. Curve 2 illustrates changes in porosity for HDPE when deformation proceeds via delocalized solvent crazing.

In the case of delocalized solvent crazing, porosity linearly increases with increasing tensile strain. In the case of classical solvent crazing, porosity passes its maximum. At higher strains, the observed decrease
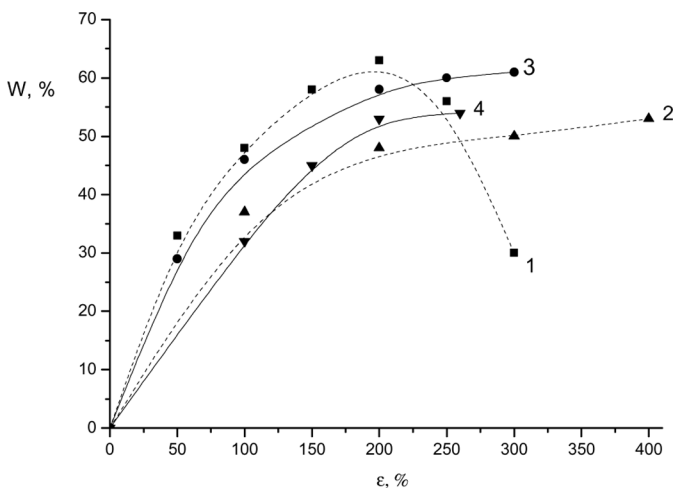
Figure 2. Porosity W of polymer vs. tensile strain ε for the deformation of films of PET (1) and HDPE (2) in n-heptane and PET (3) and PE (4) in PPG3000.

in porosity is related to structural rearrangements and collapse of highly dispersed polymer fibrils in crazes. The mechanism behind this phenomenon has been studied in detail by Volynskii and Bakeev (1984, 1995) and Yarysheva et al. (1993, 2004). However, the nature of liquid environment can markedly change the stability of crazes at high tensile strains. When stretching is performed in highly viscous solvents, collapse of porous structure at high strains is less pronounced. This observation is illustrated by curve 3 (Figure 2) when stretching is performed in PEG. In this case, porosity increases with increasing tensile strains, and no collapse of fibrillar-porous structure of crazes is observed.

As follows from Figure 2, porosity of solvent-crazed polymers during tensile drawing in the presence of active liquid environments can achieve 50–60%. Hence, the content of the second component in polymer blends based on solvent-crazed polymers can be rather high. In addition to porosity, composition of polymer blends based on solvent-crazed polymers is also controlled by the conditions of monomer polymerization and by the occupation of the formed porous structure by the second polymer.

Figure 3 shows the effect of tensile strain on the composition of polymer-polymer blends based on solvent-crazed HDPE matrices prepared by delocalized solvent crazing and solvent-crazed PET matrices prepared by classical crazing. Typical HDPE-PANi, PET-PANi,[15] PET-PEG, and HDPE-PEG blends are presented. As follows from Figure 3, the content of the second component in polymer blends is determined by porosity.
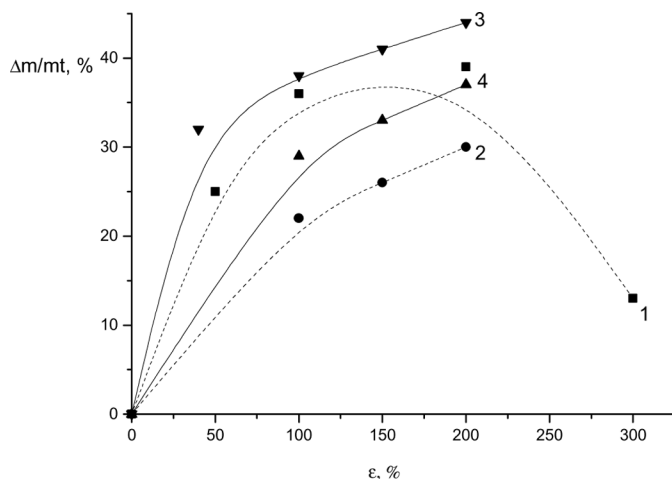
Figure 3. The content of the second component in polymer blends ($\Delta m/mt$) PET-PANi (1), HDPE-PANi (2), PET-PPG3000 (3), and HDPE-PPG3000 (4) vs. tensile strain (ε) polymer in the presence of a liquid environment.

Let us mention that delocalized solvent crazing of semicrystalline polymers allows preparation of polymer-polymer blends containing 40% of the second component. Note that spontaneous swelling of bulk polymers in the same monomers does not allow this result.

As shown in Figure 3, direct introduction of polymers via tensile drawing allows preparation of polymer blends with high concentration of the second component. However, solvent-crazed polymers after their stretching in adsorptionally active liquid environment are known to experience shrinkage, their porosity markedly decreases, and the liquid environment is partially or fully removed from the craze structure.[1–3,16] In this connection, it seems interesting to study the stability of the prepared blends in time.

Figure 4(a) and 4(b) show the migration or release of PPG (curves 1 and 2) and PEG-400 (curve 3) from their blends with PET and HDPE in free state (in air). Initial points correspond to the content of PEG and PPG in the blends immediately after stretching. As follows from Figure 4, the amount of released component does not exceed 2–5%, and the system comes to its equilibrium state within several days for the PET-based blends and within 25–30 days for HDPE-based blends. The only exception is provided by the PET-based blend containing PEG-400. In this case, migration of the second component is high, and this system does not achieve its equilibrium state even within eight months.

The curve illustrating the migration of PEG from its blend contains two regions. Within the initial time period, burst release of PEG is
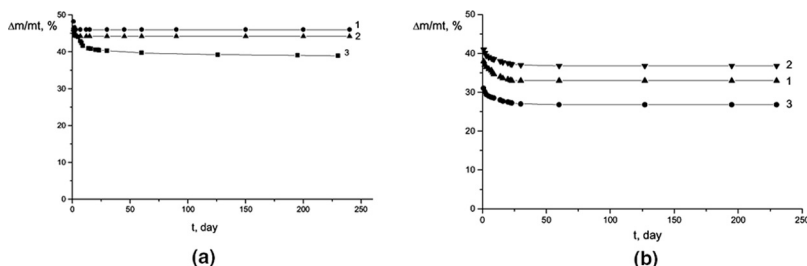
Figure 4. Migration of the second component (Δm/mt) PPG400 (1), PEG400 (2), and PPG3000 (3) from polymer blends PET (a) and HDPE (b) vs. time (t).

observed (up to 7%). Then, the migration rate slows down and proceeds at a constant rate for a rather long time period. A similar phenomenon of prolonged release was observed for PET-based blends containing low-viscous components.[17,18]

Therefore, solvent crazing of polymers allows preparation of polymer blends with a high content of the second component (25–45%) via in situ polymerization of monomer in the matrix of solvent-crazed polymer and via direct introduction of polymers during tensile drawing.

THE STRUCTURE OF POLYMERS DEFORMED VIA THE MECHANISM OF CRAZING

The structure of polymer samples prepared via the mechanism of classical and delocalized solvent crazing is characterized by certain common and different features. When the tensile drawing of a polymer in the presence of a surface-active liquid environment proceeds via the mechanism of classical solvent crazing, polymer deformation is localized in narrow local zones (crazes), and the transition of the polymer into the oriented state is accompanied by the dispersion of polymer into fine craze fibrils, the voids between which are filled with the liquid. The main operating mechanism in the case of classical crazing in surface-active liquid environments is the surface drawing of craze fibrils. The structural changes takes place in the solvent-crazed polymer with increasing tensile strain. Early stages of classical crazing involve the nucleation of crazes with a fibrillar-porous structure and craze tip advance in the direction perpendicular to the direction of principal stress. At this stage, individual crazes are separated by the regions of bulk undeformed polymer. With increasing tensile strain, the diameters of craze fibrils and the pores between the neighboring fibrils remain invariable, the fractional content of the polymer in the crazes increases, and the length of the regions of undeformed polymer
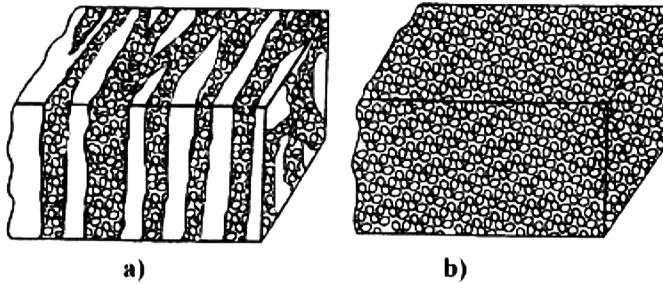
Figure 5. Schematic representation of blend structure based on the solvent-crazed polymer matrix prepared via the mechanism of classical crazing (a) and delocalized crazing (b).

between the crazes decreases. Finally, at tensile strains approaching the natural draw ratio of a given polymer, the entire polymer is transformed into the oriented fibrillar state within the craze volume. At high tensile strains, the specific features of solvent-crazed structure are associated with the manifestation of coagulation interaction between individual fibrils.

However, in the case of classical solvent crazing, one should take into account the fact that, with increasing tensile strain, density of crazes increases. Furthermore, one can observe their branching and merging. Finally, all crazes appear to be interconnected and form a certain network, as shown in Figure 5(a).

In contrast to classical solvent crazing, the development of delocalized solvent crazing is not accompanied by the formation of individual pores, and one can barely follow their evolution during stretching. Even though the morphology of pores in the porous samples prepared by delocalized crazing is still unclear, the development of macroscopic porosity takes place throughout the entire volume of the polymer sample (Figure 5(b)).

At a microscopic level, the porosity is primarily localized within the amorphous regions of the semicrystalline polymer, which are first involved in the plastic deformation of the polymer. For most semicrystalline polymers, their amorphous phase is continuous, and the as-nucleated pores appear to be interconnected and uniformly distributed in the whole volume of polymer sample.

THE STRUCTURE OF POLYMER-POLYMER BLENDS BASED ON SOLVENT-CRAZED POLYMERS

Polymer-polymer blends based on porous matrices prepared via the mechanism of classical and delocalized solvent crazing were studied by
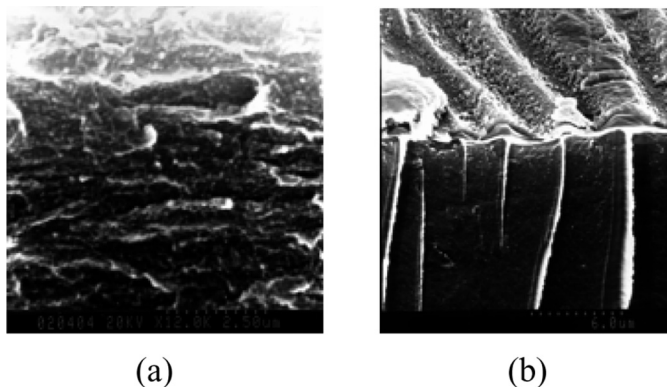
(a)   (b)

Figure 6. SEM images of the fractured surface of HDPE-PANi (a) and PET-PANi (b).

direct electron-microscopic observations. These observations showed that the second polymer separates into an individual phase. This phase separation is well demonstrated by scanning electron microscopy (SEM) images for chips of the blends of PET and HDPE with PANi (Figure 6). As is well seen, the spherical particles of PANi are uniformly distributed within HDPE porous matrix prepared via the mechanism of delocalized solvent crazing. All particles are distributed in the porous structure of crazes in solvent-crazed PET.

Within the framework of the adopted classification, the polymer-polymer blends are similar to consecutive semi-interpenetrating polymer networks.

In the case of delocalized solvent crazing, the network of crystallites allows one to consider the initial semicrystalline polymer, in a certain sense, as a cross-linked structure. In the cases when the in situ polymerization of the monomer in solvent-crazed polymers is carried out in the presence of the cross-linking agent, the resulting polymer-polymer blends may be referred to as interpenetrating polymer networks.

In the case of classical solvent crazing, both polymers form continuous phases in the blend. On one hand, we deal with the interconnected porous structure of crazes filled with the incorporated polymer. The other phase is composed of fibrils based on oriented polymer and undrawn polymer regions between crazes. The above regions of undrawn polymer bridged by polymer fibrils serve as cross-links.

However, the structure of polymer-polymer blends based on solvent-crazed matrices prepared by solvent crazing appears to be far more complex than that of two-component interpenetrating polymer networks. In this case, the important feature of the above blends is the possibility of

imparting the molecular orientation to one or both components, and this molecular orientation may be controlled by varying the tensile strain of the solvent-crazed matrix. The development of crazes in the polymer via the mechanism of crazing is known to be accompanied by the transition of the polymer to a highly disperse oriented state in craze fibrils. Because of this, the polymer in the craze fibrils of solvent-crazed matrix is characterized by molecular orientation. In the case of the blend based on HDPE and polyacetylene,[13] both polymers are characterized by molecular orientation. Furthermore, polymer blends prepared via classical solvent crazing show asymmetric location of pores and the second component. This fact is directly proved by studying the electric conductivity of the blends based on PET and PANi, which demonstrate a well-pronounced anisotropy provided by the different location of pores in the sample.

Polymer blends prepared via the mechanism of solvent crazing are characterized by a high level of dispersion, which is dictated by the highly dispersed structure of crazes. First, the polymer matrix exists in its highly dispersed oriented state. Second, the dimensions of incorporated component within the solvent-crazed structure do not exceed 100–200 nm.

Hence, the polymer-polymer blends based on solvent-crazed polymer matrices prepared via two different modes of solvent crazing are characterized by similar composition, character of microphase separation of the components, and degree of dispersion. A marked difference between them is related to the fact that, in the case of delocalized crazing, the second component is uniformly distributed in the entire volume of polymer samples, whereas in the case of classical crazing, the second component is localized in the straight canals (crazes) separated by the regions of undeformed bulk polymer.

CONCLUSION

Solvent crazing allows preparation of polymer blends based on a wide range of incompatible polymers. The specific highly disperse porous structure of solvent-crazed polymers prepared via different modes of solvent crazing allows one to prepare polymer-polymer blends with unusual structures. With respect to the character of phase separation, these blends are similar to semi-interpenetrating polymer networks and are characterized by a high level of dispersion of the components.

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