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Hydrophilization of polypropylene films by poly(ethylene oxide) *via* intercrystallite crazing

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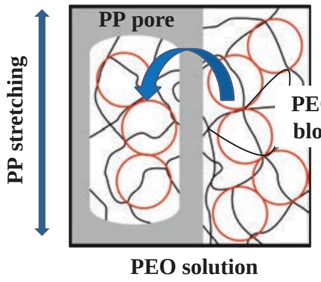
Nanocomposite materials based on the incompatible polymers polypropylene and poly(ethylene oxide) were prepared. The stretching of polypropylene films in water–ethanol solutions of poly(ethylene oxide) proceeds *via* intercrystallite crazing, and it is accompanied by the penetration of poly(ethylene oxide) macromolecules into the porous structure of a polypropylene matrix. The incorporation of a hydrophilic component provides an efficient hydrophilization of the initial hydrophobic polypropylene films.



Keywords: poly(ethylene oxide), polypropylene, nanocomposite, crazing, wettability.

Usually, polymers are thermodynamically incompatible and their blends experience macro- and microphase separation due to their low mixing entropy. Physicomechanical properties of multicomponent polymer blends are largely controlled by the phase separation and mutual dispersion of the components.[1–3] Preparation of nanocomposites as sustainable multicomponent systems offers an advantageous solution of the challenging problem concerning the poor compatibility of polymers. Nanocomposites can be prepared by the successive polymerization of two monomers without copolymerization.[4,5] At the same time, an alternative approach to the preparation of polymer–polymer nanocomposites involves the development of a porous polymeric matrix and the incorporation of monomers and polymer components into the as-formed porous structure.[6]

In this work, we prepared a porous host matrix by the deformation of polymer films in physically active liquid environments (PALEs) *via* an intercrystallite crazing mechanism.[7,8] When a polymer is stretched in a PALE containing a dissolved target additive (or additives),[9–13] this additive can penetrate into the nanoporous structure of crazes. The removal of the PALE as a volatile component from the system leads to the formation of a stable nanocomposite of the host polymer and an incorporated additive.

The aim of this work was to prepare new composite materials based on commercial polymers hydrophobic polypropylene (PP) and hydrophilic poly(ethylene oxide) (PEO) and to characterize their wettability. The improved wetting characteristics of polymers, including PP, which is used for tissue engineering, assist the nonspecific binding of proteins and cells, and they can increase the adhesion of a polymer matrix.[14] However, practical applications of PP are limited by its high hydrophobicity. Plasma treatment,[15] graft polymerization,[16] and hydrophilic additives[17–19] are currently used for the hydrophilization of PP. Here, we prepared hydrophilic PEO–PP nanocomposites by the introduction of hydrophilic PEO into a hydrophobic PP matrix *via* environmental crazing.[†]

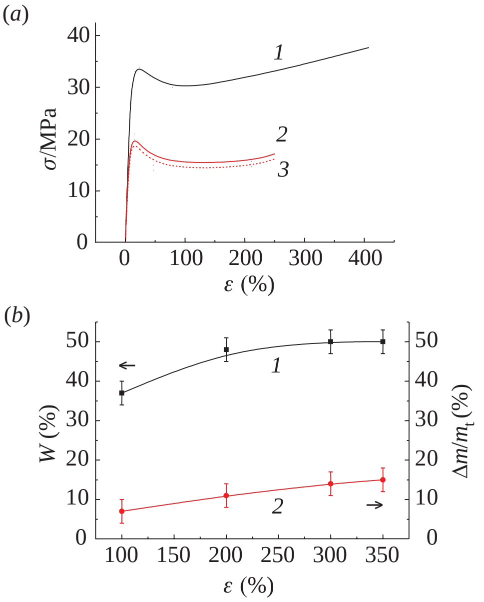


Figure 1 *(a)* Engineering stress–strain curves for PP films illustrating their deformation in (*1*) air, (*2*) water–ethanol solution, and (*3*) PEO water–ethanol solutions, (curve *1* until fracture, curves *2*, *3* for the tensile strain below 250%); *(b)* (*1*) volume strain W and (*2*) PEO content $\Delta m/m_t = (m_t - m_0)/m_t$, where m_0 is the weight of an initial PP film and m_t is the weight of the PP–PEO composite plotted against the tensile strain (ε) of the PP films.

[†] Nanocomposites were prepared according to the following protocol: the films of isotactic PP with a thickness of 90 μm (M_w = 250 kDa, M_w/M_n = 3.5) were stretched in a water–ethanol (1 : 7, v/v) solution of PEO (Aldrich) (10 wt% PEO with M = 200 kDa). The strain rate was 5 mm min^{-1}. After stretching, the residual PEO was removed from the surface by blotting paper; then, the samples were evacuated to remove the volatile solvent (1 × 10^{-2} mbar).

In the environmental crazing mechanism, deformation proceeds at a lower stress, as compared with that in air, and it is accompanied by the development of a marked porosity.[7] Figure 1(*a*) shows that, as compared with stretching in air (curve *1*), the deformation of PP in a water–ethanol mixture (curve *2*) or a PEO solution (curve *3*) is accompanied by a decrease in the tensile stress without changes in elastic modulus, and this behavior is accompanied by the surface activity of the water–ethanol mixture.[‡]

Upon the deformation of PP films in air, no volume changes were observed. At the same time, porosity increased up to 50% upon the deformation of PP films in PEO solutions and in a pure solvent by a tensile strain of 300% [Figure 1(*b*)]. The presence of PEO in solutions exerted no effect on the porosity. Therefore, the deformation of the PP films in the PEO solutions proceeded *via* environmental crazing.

The structure of the PP films after their tensile drawing in the water–ethanol solutions *via* environmental crazing was studied by AFM.[20] The porous structure parameters of the PP films were estimated: the pore lengths were 36 ± 8, 47 ± 12 and 55 ± 15 nm at tensile strains of 100, 200 and 300%, respectively. The pore width did not exceed 23 ± 5 nm even at high tensile strains (300%).

The environmental crazing of PP films in PEO solutions is accompanied by the penetration of PEO molecules into the porous structure of the PP host matrix. Figure 1(*b*) shows the PEO content of the nanocomposite plotted against the tensile strain. The porosity of the PP films increased with tensile strain (curve *1*), and the PEO content of the composite became higher to achieve 15% at high tensile strains (curve *2*). The absence of water from the nanocomposites was confirmed by TGA measurements.

Penetration of macromolecules into nanoporous materials is controlled by the interplay between the macromolecular coil radius R_h and pore size D and by the concentration of a polymer solution. In dilute solutions, macromolecules occur as individual coils and do not penetrate into nanopores at $D \leqslant R_\mathrm{h}$. In semidilute solutions, the macromolecular coils are overlapped, and the whole structure is characterized in terms of a fluctuation entanglement network. According to scaling concepts,[21,22] the key parameter of the dynamics of semidilute solutions is the correlation length ξ. Therefore, in semidilute solutions, a macromolecule can be represented as a sequence of blobs with size ξ. The concentration corresponding to the development of the entanglement network is referred to as the crossover concentration c^*. The condition providing the penetration of macromolecules from semidilute solutions into pores with diameter D is $\xi \leqslant D$; otherwise speaking, macromolecules can penetrate into pores if the blob size is smaller than the pore diameter.[21,22]

The crossover concentration of a solution of PEO was calculated according to the Debye criterion $c^* = 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity. The hydrodynamic radius of a macromolecular coil was calculated as $R_\mathrm{h} = 0.0202(M_\mathrm{w}{}^{0.58})$.[23] The correlation length ξ of PEO macromolecules in solution was estimated using the equation $\xi = R_\mathrm{h}(c/c^*)^{-3/4}$ for flexible-chain polymers in good solvents. For PEO (200 kDa), the hydrodynamic radius is 24 nm, which is higher than or comparable to the above pore dimensions of a PP matrix.[20] However, the correlation length (0.09 nm at c = 10%) enables the penetration of PEO macromolecules into the pores of a host PP matrix and the formation of PP–PEO nanocomposites.

We studied the properties of the nanocomposites based on PP and PEO. Water contact angles (WCAs) were measured for the initial and crazed PP films and the PP–PEO composite.[§] Due to the development of a patterned surface, WCAs increased from 98° for the initial PP film to 115° for crazed PP. The enhancement of hydrophobicity due to surface roughness is a well-known phenomenon.[24] As a result of the incorporation of PEO, the WCA of the PP–PEO composite decreased to 70–75°, thus attesting hydrophilization. Hence, the incorporation of PEO into a PP host matrix offers an efficient tool for the controlled modification of PP-based materials. In this context, it will be of interest to develop the UV-induced crosslinking of PEO in the presence of pentaerythritol triacrylate[25] to provide PEO immobilization in a PP matrix for the preparation of stable PEO–PP nanocomposites.

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[‡] Mechanical properties of the test samples were studied upon their tensile drawing at a constant rate of 5 mm min^{-1} on an Instron 1122 tensile machine; the gage size of the samples was 10 × 4 mm.

[§] Water contact angles (WCAs) were measured by a sessile droplet method using a KRUSS DSA30E drop shape analysis system.