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Amorphization of poly(vinyl alcohol) in the mesoporous matrix based on high-density polyethylene

Alena Yu. Yarysheva,*[a] Aleksandr Yu. Kopnov,[a] Anna K. Berkovich,[a] Artem V. Bakirov,[b,c] Larisa M. Yarysheva,[a] Olga V. Arzhakova[a] and Sergey N. Chvalun[b,c]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 0174; e-mail: alyonusha@gmail.com*
[b] *N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences, 117393 Moscow, Russian Federation*
[c] *National Research Center 'Kurchatov Institute', 123098 Moscow, Russian Federation*

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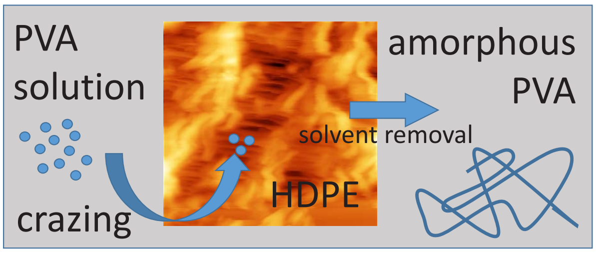
Poly(vinyl alcohol) (PVA) was incorporated into the mesoporous structure of high-density polyethylene (HDPE) directly upon the tensile drawing of films *via* crazing in water–ethanol PVA solutions. The structure and thermophysical properties of the HDPE–PVA nanocomposites were explored by differential scanning calorimetry and X-ray analysis. PVA was found to exist in an amorphized state within the mesoporous structure of the HDPE host matrix since its crystallization is prevented by the spatial confinements.



Keywords: poly(vinyl alcohol), mesoporous polymers, crystallization of polymers, crazing, high-density polyethylene, nanocomposites.

Fundamental characteristics of substances (phase transition temperatures, heat of fusion, and crystallization) are known to undergo dramatic changes when their structural elements (phases) are reduced to nanoscale dimensions. As the surface-to-volume ratio increases, the crystallization of polymers in nanolayers, thin films, emulsions, block copolymers, templates, nuclear track membranes, *etc*., can be accompanied by changes in the mechanism of crystallization, including the crystal nucleation and the morphology of the crystallites as well as the orientation of macromolecules.[1–13] In addition to the fundamental aspects of this problem, investigation of the crystallization of semicrystalline polymers under confined conditions also has an important applied value because various properties of polymers, polymer composites, and membranes (swelling, gas and vapor permeability, ionic conductivity, wettability, and even antibacterial activity) are controlled by their phase state. Tensile drawing of high-density polyethylene (HDPE) in physically active liquid environments (PALEs) proceeds *via* the mechanism of environmental crazing which is accompanied by the development of volume porosity up to 60 vol%. Figure 1 shows the atomic force microscopic (AFM) image of the HDPE film after tensile drawing in the PALE. Prior to deformation, the initial HDPE films are characterized by the so-called layered row-nucleated structure[14] when the crystalline lamellae are oriented primarily perpendicular to the extrusion direction. Upon environmental crazing, the corresponding AFM images of the HDPE films show the well-defined fibrils oriented along the direction of tensile drawing, and slit-like pores between them.

Analysis of the AFM images allows the construction of the cross-section profiles along the direction of tensile drawing. For the HDPE film after tensile drawing by 200%, the long period is estimated to be 195 ± 72 nm. The mean distance between the peaks corresponding to the fibrils (this parameter characterizes the sum of the pore width and fibril diameter) is equal to 35 ± 8 nm. Hence, deformation of HDPE *via* the environmental crazing provides the development of a mesoporous structure according to the IUPAC classification.[15]

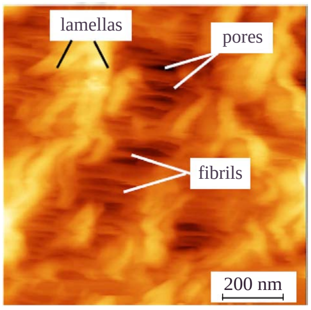


Figure 1 AFM image of the HDPE films after tensile drawing by 200% *via* environmental crazing (the extrusion axis and stretching direction are horizontal).

In the course of environmental crazing, the mesoporous structure of HDPE films (host matrix) is continuously filled by PALEs which are common organic solvents or the solutions of low-molecular and high-molecular-weight compounds.[16–20] In this work, PVA was selected as a guest component since this choice permits to gain a deeper insight into the effect of nanoconfined 3D space on the crystallization of semicrystalline PVA.[†] When a volatile PALE is removed from the sample, the composite system is formed, with the pore walls of the host HDPE matrix preventing the aggregation of the guest PVA

[†] The HDPE–PVA nanocomposites were prepared by tensile drawing of HDPE films (gauge size 48 × 20 mm^2) with a strain rate of 5 mm min^{-1} in the water–ethanol (3:2) solutions of PVA (11 wt%). After tensile drawing, the samples under isometric conditions were blotted with filtering paper and dried in a pressurized air stream for 30 min and then in vacuum for 24 h.

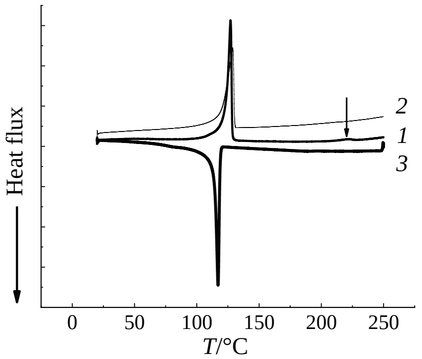


Figure 2 DSC scans of (*1*) first melting, (*2*) second heating, and (3) cooling of the HDPE–PVA nanocomposite (the content of PVA is 18 wt%); the heating and cooling rate is 10 K min^{-1}.

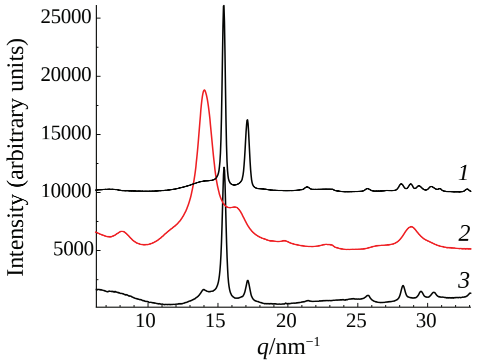


Figure 3 Wide-angle diffractograms of (*1*) HDPE, (*2*) PVA, and (*3*) HDPE–PVA nanocomposite prepared by tensile drawing of HDPE by 200% in the PVA solution.

component, and this component appears to be dispersed at the nanoscale level within the host matrix.

Thermophysical characteristics of the HDPE–PVA nanocomposites were explored by differential scanning calorimetry (DSC). Upon the first and second heating/cooling runs, the corresponding DSC scans showed no melting and crystallization peaks of PVA. Only during the first heating there was a weakly pronounced step (marked with an arrow in Figure 2) near the PVA melting point at 218 °C with a thermal effect, which, normalized by the PVA content, corresponds to 5% degree of crystallinity. For the HDPE component, the melting peak coincided with that of the pristine HDPE: the melting temperature was 128 °C, and the degree of crystallinity was 63% (Figure 2).[‡] Therefore, when, upon ‘free’ crystallization, the degree of crystallinity of PVA was equal to 57%, PVA incorporated into the mesopores of the host HDPE matrix appeared to be amorphized, and this phenomenon was earlier observed for poly(ethylene oxide).[21–24]

Figure 3 presents the wide-angle X-ray scattering (WAXS) curves of the neat HDPE, PVA, and HDPE–PVA nanocomposite. The X-ray scattering curves of HDPE and the HDPE–PVA composite show the well-pronounced reflections of HDPE: (*110*), (*200*), (*210*), and (*020*) at 15.4, 17.1, 21.4, and 25.7 nm^{-1} respectively. A weak peak at 13.9 nm^{-1} can be identified as (*010*) of the HDPE monoclinic phase or the most intensive reflection of PVA. However, the crystallinity indices of the neat HDPE and the HDPE–PVA composite virtually coincide: ~73 and ~75%, respectively.[§] This evidence supports the conclusion concerning the amorphized state of PVA in the HDPE host matrix according to the DSC data.

According to the WAXS data, the degree of crystallinity of the neat HDPE and HDPE in the composite is by 10–12% higher than that calculated from the DSC data. However, this value was calculated from the scattering of the whole material, including the scattering from the amorphous phase of HDPE and HDPE–PVA samples.

Obviously, the mesoporous HDPE matrix suppresses the crystallization of PVA. Amorphization of PVA in HDPE-based composites can present an evident interest for the development of innovative gas separation and ion-conducting materials where the content of the amorphous phase is the critical factor.

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[‡] The degree of crystallinity of the polymer was calculated as $\chi = [\Delta H / \Delta H_{100\%}] \times 100$ (%), where ΔH is the experimental heat of fusion of the polymer at a heating rate of 10 K min^{-1}, and $\Delta H_{100\%}$ is the heat of fusion of an ‘ideal’ crystal (293 J g^{-1} for HDPE and 136.7 J g^{-1} for PVA).

[§] To evaluate the change in the degree of crystallinity, the deconvolution of the X-ray diffraction patterns was performed using the ORIGIN PRO software by considering the Gaussian function as the shape of the resolved peaks. The crystallinity index (CI) of the samples was calculated as CI = $S_c/S_t \times 100$ (%), where S_c is the area of the crystalline domain, and S_t is the area of the total domain.