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Features of Uniaxial Tension of Amorphous Poly-L-Lactic Acid in Liquid Media

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Polylactic acid (PLA) is a polymer that is eco-friendly, biocompatible, biodegradable, and produced from renewable bioresources [1, 2]. Usually it represents a copolymer of optical isomers of L- and D-lactic acid. The greatest interest is raised by poly-L-lactic acid with a small (2−10%) and controllable content of D-isomeric chains.

However, despite all its advantages, i.e., the reasonably high elasticity modulus, possibility of remaking of mouldings and extrusion by traditional methods, transparency, etc., polylactic acid is quite fragile at temperatures lower than the glass transition temperature (50−70°C), and the maximal degree of its deformation usually does not exceed 10−15% [1, 3]. For elimination of these disadvantages, one adds softeners to poly-L-lactic acid [4, 5], subjects it to short-term thermal treatment at the glass transition temperature [6], and orients at high temperatures [7].

The purpose of this research is studying the mechanical behavior and structure of an amorphous poly-L-lactic-acid film during its uniaxial deformation in various liquid media (aliphatic hydrocarbons and alcohols).

In this work, it is shown for the first time that the deformability of amorphous glass poly-L-lactic acid considerably increases in the presence of liquid adsorption-active media: to 100−150% in *n*-heptane and to 500% in ethanol. Large plastic deformations are developed by the crazing mechanism and accompanied by the formation of a fibrillar−porous structure. The tension to high degrees of deformation (more than 300%) in alcohols results in intense crystallization of PLA films.

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As objects of investigation, we used an industrial nonoriented film of amorphous PLA Cargill DOW, United States ($M_w = 2 \times 10^5$, PDI of 1.603, glass transition temperature of 63°C, and thickness of 300 μm). The films in the form of bilateral blades with the working part of 6×20 mm in size was uniaxially deformed on an Instron device with the speed of 25%/min at the temperature of 20−25°C in air and in *n*-heptane (analytically pure), ethanol (96%, chemically pure), and isopropanol (chemically pure).

The structure of deformed samples was investigated by the method of small-angle X-ray scattering (SAXS) on the Nanostar installation (Bruker AXS) with a two-dimensional coordinate detector on CuK_α radiation at the primary-beam point collimation; the angular resolution is 7′. The morphology was investigated by a Carl Zeiss optical polarizing microscope (Jena) and a JEOL JSM-6390LA scanning electronic microscope (cleavages were prepared by the technique of fragile fracture in liquid nitrogen and gold deposition). The thermal properties of samples were studied by the method of differential scanning calorimetry (DSC) using Metler_TA4000 calorimeter (cell DSC-30) in the temperature range of 25−200°C with a heating rate of 10 °C/min.

In Fig. 1, we show the dynamometric curves obtained during the uniaxial deformation of a PLA film in air and in liquid media. They have a traditional shape of curves with a forced-elasticity limit. We observed a sharp decrease in its value to 15−20 MPa in liquid media in comparison with the process in air (61 MPa). The second fact found is an increase in rupture elongations at the transition from the deformation in air (11%) to the tension in heptane (100−150%) or alcohols (400−500%).

The photographs of the surfaces of PLA samples under different degrees of deformation are shown in the inset to Fig. 1. In all images, the cracks oriented perpendicularly to the direction of tension, which rep-
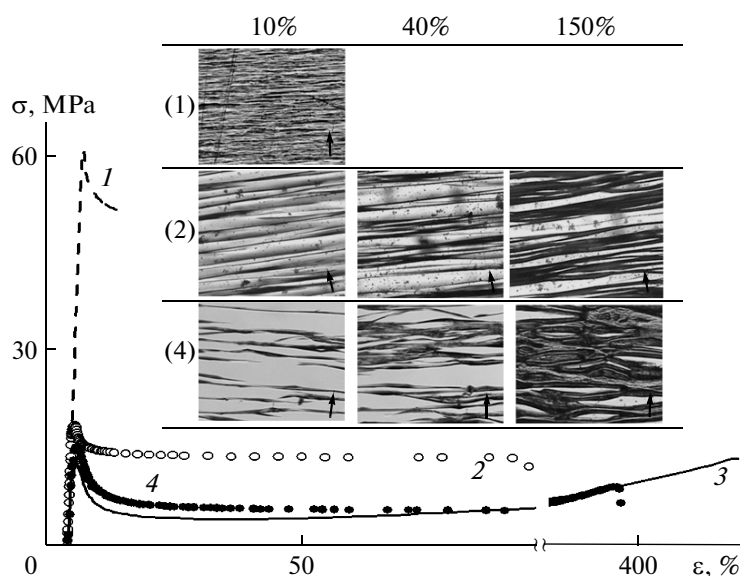
Fig. 1. Dynamometric curves for a PLA film obtained (*1*) in air and in media of (*2*) heptane, (*3*) ethanol, and (*4*) isopropanol. In the inset are optical photographs (magnification of 100 times) of the surface of polymer deformed to 10, 40, and 150% (1) in air, (2) in heptane, and (4) in isopropanol. The arrows in photographs designate the direction in which the extension was carried out.

resent crazes, are seen. Their morphology and concentration depend on the nature of the medium in which the PLA film is deformed.

The observed distinctions are apparently connected both to the stress level at which the crazes nucleate and to the compatibility of the medium with the polymer. From the published data, it is known [1] that neither *n*-heptane (the solubility parameter is 7.4 cal$^{1/2}$ cm$^{-3/2}$), nor the aliphatic alcohols (the solubility parameter of ethanol is 12.9 cal$^{1/2}$ cm$^{-3/2}$) used in this work are the solvents for the PLA (the solubility parameter is 10.0−10.3 cal$^{1/2}$ cm$^{-3/2}$); i.e., they represent liquid adsorption-active media. However, it was experimentally revealed in this work that the PLA swells a bit in the ethanol medium at room temperature—in two weeks, the alcohol content in the polymer amounted to 7 wt %. The mechanical-stress action favors the accelerated penetration of alcohol in PLA and, first of all, in the volume forming crazes, which, apparently, affect the mechanism of their further development.

Scanning electron microscopy (SEM) was used for investigating the morphology of fragile cleavage in a PLA film deformed in ethanol by 30%. It is revealed that it represents the structure formed by the mechanism of classical crazing [8]. It is important to note that the crazes are penetrable for liquids. Actually, the samples deformed in liquid media are easily painted by the solution of rhodamine-C dye. In this case, the PLA bulk regions remain unpainted.

We used the SAXS method for investigating the structure of films deformed under various conditions. In Fig. 2, we show the small-angle X-ray diffraction patterns of the initial PLA film and also those after its deformation by 25% in heptane and ethanol media and the typical curves of distributions of intensity of the X-ray scattering in the meridional and equatorial directions. It can be seen that, contrary to the initial isotropic amorphous film, the deformed samples give two types of reflexes in mutually perpendicular directions: the narrow stroke on the meridian from the walls of crazes and the scattering extended along the equator from the system of oriented fibrils separated in the space connecting the walls of crazes.

Similar SAXS pictures are characteristic for glass polymers containing crazes [9, 10]. However, there is a significant distinction from previously studied systems with classical crazes. It has proved to be that the equatorial component of scattering of the deformed PLA has a diffusive character; although, it is common to observe an interference peak on a similar curve that characterizes the distance between the centers of fibrils. The absence of a peak on the scattering curve can point to both irregular arrangement of individual fibrils in crazes and to wide distribution of values of the diameter of fibrils.

Using the Porod method modified for oriented systems [9, 10], the diameter of fibrils connecting the walls of crazes was determined. We accepted that the concentration of fibrillized material in PLA crazes amounts to 0.25, the same as for PET deformed by the crazing mechanism in liquid media [11]. The calcu-
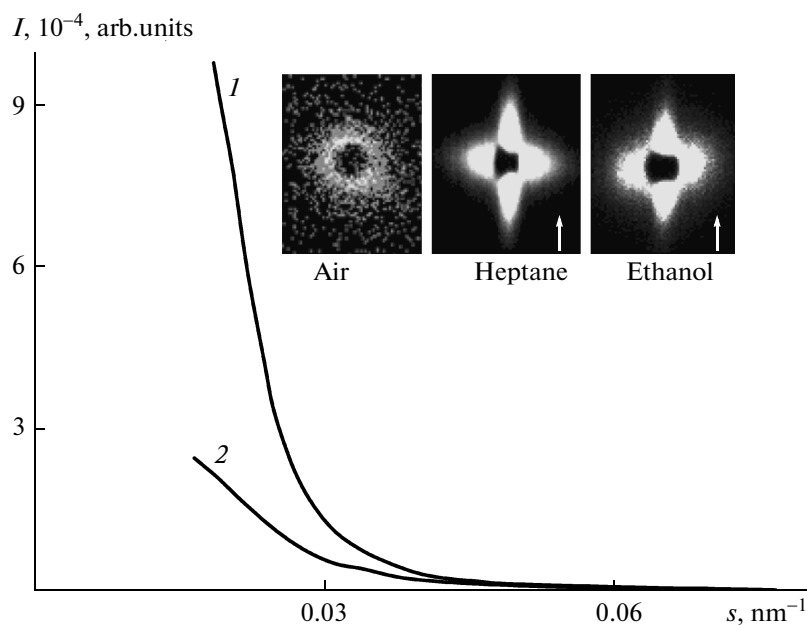
Fig. 2. (*1*) Meridional and (*2*) equatorial distributions of SAXS intensity for PLA deformed by 25% in heptane (transferred into *n*-decane); shooting was carried out in liquid. As the coordinate of scattering, we used the scattering-vector modulus $s = 2\sin(\varphi/2)/\lambda$, where φ is the scattering angle, and $\lambda = 0.154$ nm is the wavelength of X-ray radiation. In the inset are the small-angle X-ray diffraction pattern of the original film and those deformed in heptane medium (then, transferred to *n*-decane) and ethanol (then, transferred to *n*-butanol) by 25%. The arrow shows the direction of the PLA tension.
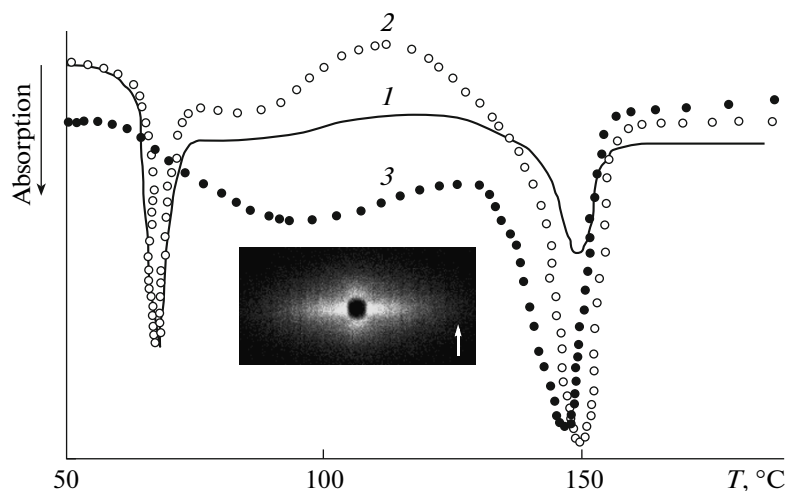
Fig. 3. DSC curves for (*1*) original PLA films and those for deformed by (*2*) 100 and (*3*) 400% in the ethanol medium. In the inset is the small-angle X-ray diffraction pattern for the sample (*3*). The arrow shows the direction of the tension of the polymer.

lated diameter of fibrils of amorphous PLA amounted to about 17 nm.

Now we consider the features of the PLA-film structure stretched to high degrees of deformation (above 350%) in the aliphatic-alcohol medium. In Fig. 3, we show the DSC curves for the initial amorphous PLA film and for that deformed by 100 and 400% in the ethanol medium. It can be seen that the behavior

of the sample with the degree of deformation of 100% is similar to the original film: in the region of 90–130°C, the polymer is crystallized after which the melting process begins, the temperature peak of which occurs in the region of 150°C. The degree of crystallinity for these samples determined with taking into account the crystallization processes happened directly in the DSC cell was lower than 10%. The behavior of a PLA film deformed by 400% in ethanol

is somewhat different. Two distinct transitions are observed: the vitrification in the form of a step with the mean glass transition temperature a little higher than that for the initial PLA (by about 75−80°C), and the melting peak near 150°C. Its degree of crystallinity amounted to 35% (we note that the time of contact of the sample with ethanol during the experiment was less than 20 min). Previously, similar behavior was observed for amorphous PET films during their orientation extension in hexadecane [11] and aliphatic alcohols [12]. This fact was explained by the local plasticizing action of the liquid medium and the increased mobility of the polymeric material on the craze−bulk-polymer interface.

In the inset of Fig. 3, we show the SAXS pattern for a sample crystallized during the extension by 400% in ethanol. In it there is a very intense anisotropic diffusive scattering extended in the direction perpendicular to the deformation direction. It can testify to the presence of lengthened (slotlike) pores in the material.

Thus, we show in the study that the uniaxial tension of amorphous PLA at the presence of liquid adsorption-active media of various nature proceeds by the mechanism of classical crazing accompanied by the formation of a fibrillar-porous structure with a diameter of fibrils of about 20 nm, and its deformability considerably increases. For high degrees of deformation, a significant reorganization of the crazed structures, which is accompanied by the crystallization of the polymeric film, is observed.

The obtained results enable us to use all previously accumulated knowledge and the investigated possibilities of the crazing process in liquid media [8] with reference to amorphous polylactic acid with the purpose of introducing various functional fillers (dyes, antipyrines, pharmacological substances, and others) in it and fabrication of hybrid and composite materials.

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