



# Influence of liquid media on the craze initiation in amorphous polylactide

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## ABSTRACT

The influence of various liquid media (aliphatic alcohols, water-alcohol solutions, saturated hydrocarbons, and organosilicon liquids) on the development of uniaxial deformation and nucleation of crazes in amorphous polylactide (PLA) films has been studied. It has been found that in the presence of the liquids the tensile stress during the polymer deformation decreases by 3–4 times. According to the Griffith's theory, linear dependences (with an accuracy of  $R^2 = 0.96–0.97$ ) have been revealed between the yield point or the flow stress of PLA and the square root of product of the elasticity modulus of the polymer in a liquid and the interfacial surface energy at the polymer-liquid medium interface calculated using the Owens-Wendt equation. The data obtained may be used to predict the critical mechanical stress at which crazes will be initiated in PLA.

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## 1. Introduction

Polylactide (PLA) is a commercial biopolymer, the monomer of which, lactic acid, is obtained from vegetable raw materials. It represents an environmentally safe and nontoxic material. The high interest in studying different properties of PLA is due to its biocompatibility, complete degradability under the action of different microorganisms, and the ability to undergo gradual bioresorption in a living organism to complete dissimilation. Owing to the above-mentioned properties, PLA is a promising polymer to be used as a matrix for producing composites applied in medicine, as a packaging material, etc. [1,2].

However, the application of PLA is limited by its brittleness. Its average breaking strain is commonly equal to 5–20% depending on the isomeric composition of the polymer, a method of production and a history of the sample (preliminary annealing, hydrolysis, etc.), and the conditions of mechanical tests [2,3]. One of the main reasons for the embrittlement of PLA is its ability to rapid physical aging [4], which seems to be accompanied by structuring and leads to a change from necking to crazing mechanism during uniaxial deformation.

Crazing is frequently considered as one of the main failure mechanisms of glassy and partially crystalline polymers [5–7]. In this case, after the formation of crazes, the surfaces of which are bridged by many fine fibrils with the diameter of 5–30 nm, the true fracture crack develops. Moreover, the appearance of the crazes substantially changes the properties of the polymer material, e.g., its transparency and barrier properties are deteriorated, the rate of degradation changes, etc. The determination of criteria, which may be used to predict the conditions for nucleation of crazes, is an important and urgent problem.

Crazing is substantially facilitated in the presence of adsorption-active media (AAMs), in which a polymer is not noticeably swelable, but its interfacial surface energy markedly decreases at a polymer-medium interface [8]. Commonly, similar processes are referred to as the solvent-crazing or environmental stress crazing (cracking) [8–10]. As has been found previously [11,12], the uniaxial deformation of commercial polylactide films in ethanol and *n*-heptane develops via the solvent-crazing mechanism. In this case, the nucleation of crazes and the stretching of the polymer occur at lower stresses, with the breaking tensile strain substantially increasing (up to 550% in alcohol). Since PLA is frequently used in contacts with liquid media, it is of importance to determine the conditions of a craze initiation in the presence of AAMs for PLA and open the possibilities of controlling this process.

There are several approaches to determining criteria of craze

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nucleation in the presence of liquid media. The most widely used approach is based on the determination of the difference between the solubility parameters of a medium and a polymer, with this difference being related to parameter RED (relative energy difference) [2,13]. According to this criterion, liquids with the RED value of about 1 are most efficient initiators of craze formation. In some works [14,15] the local plasticization of polymers by liquid media has been considered as one of the main reasons for the appearance of crazes. In this case, a decrease of the glass-transition temperature of a polymer in crazes under the action of a medium [14] or the rate of medium diffusion into the polymer volume [15] become the main parameters that determine the activity of a liquid as the craze-initiating agent. It has been shown that the critical strain of craze formation decreases with a reduction in the glass-transition temperature determined for a polymer swollen in a considered liquid medium to an equilibrium state, as well as in the viscosity and the molar volume of the liquid. In the work [16] it has been stated that “good” solvents are “poor” crazing agents and “intermediate” solvents tend to be “good” crazing agents.

Another criterion consists in the determination of the critical values of the inelastic deformation energy density or the inelastic deformation itself [17]. In this case, crazes arise on reaching these critical values in a polymer. Criteria describing the nucleation and development of crazes in liquid media on the basis of determining the surface properties of a polymer during the formation of a new surface are most commonly used. These approaches have resulted from the development of the ideas presented in the work [18] and “meniscus instability theory” [19] for the formation of crazes in air, as well as in the works [20,21] based on the Griffith theory of brittle fracture. One of the most evident proofs of the effect of adsorption of liquid media on the deformation behavior of polymers is the study of their stretching in aqueous solutions of homologous fatty alcohols [8]. It has appeared that the passage to each next homolog decreases the concentration, at which a certain reduction in the polymer strength is observed, decreases by 3–3.5 times in accordance with the Duclaux-Traube rule.

The aim of this work is to study the influence of liquid media of different chemical natures (aliphatic alcohols, water-alcohol solutions, saturated hydrocarbons, and organosilicon liquids) on the mechanism of the uniaxial stretching of polylactide films; determine the conditions, under which the deformation develops by the solvent-crazing mechanism; and find correlations between the mechanical parameters of the polymer and some properties of the liquid media. This study is important for predicting mechanical behavior of polylactide during its using in contact with liquid media.

## 2. Materials and methods

Initially, a PLA film 110–140  $\mu\text{m}$  thick was obtained by the hot-pressing procedure from pellets of the 4032D grade (Nature-Works LLC, United States) characterized by molecular mass  $M_w$ , 160 kDa; polydispersity index, 1.7; the content of D-isomer units, 2%; glass-transition temperature, 60–63  $^{\circ}\text{C}$ ; and melting temperature, 168  $^{\circ}\text{C}$ . The PLA pellets were melted and pressed in a mold, then a sample was rapidly quenched with water at 15  $^{\circ}\text{C}$ . During quenching, the polymer film surface had no direct contact with water. This approach yielded amorphous isotropic samples. Before the experiments, the obtained PLA films were exposed under room conditions for at least 2 weeks.

As-prepared PLA films were subjected to uniaxial stretching in air and liquid media of different natures. The media were selected from organic liquids that are most frequently used as adsorption-active media and induce crazing in polymers. Therewith, it was taken into account that AAMs must not cause substantial polymer

swelling (the degree of swelling must not be higher than 10%). As a result, water (degassed and deionized); saturated hydrocarbons, namely, *n*-heptane (analytical grade) and *n*-decane (reagent grade); aliphatic alcohols, i.e., ethanol (96%), isopropanol, *n*-butanol, and *n*-pentanol (reagent grade); and organosilicon compounds, namely, hyperbranched polyethoxysiloxane (HPEOS) ( $M_w = 30$  kD, density of 1.17  $\text{g}/\text{cm}^3$ , and effective molecule diameter of 2–5 nm) and hyperbranched polymethylsilsesquioxane (HPMSS) ( $M_w = 0.5$ –1 kD) were used. The organosilicon compounds were synthesized according to the procedure [22] developed in the Laboratory of the Synthesis of Organoelement Polymers of Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences.

PLA samples were subjected to stress-strain tests in air and liquid media using an Instron 4301 instrument at a stretching rate of 25%/min under room conditions (temperature of about 20–25  $^{\circ}\text{C}$  and relative humidity of nearly 50%) until break. For this purpose, dumbbell-shaped samples with gage size of 6  $\times$  20  $\text{mm}^2$  were cut from the films. For each medium, 5–10 tests were performed depending on the reproducibility of the results. Dependences of stress  $\sigma$ , MPa, on tensile strain  $\epsilon$ , %, were plotted and used to determine the basic mechanical parameters of the polymer, including yield point value  $\sigma_y$ , MPa; the flow stress at the plateau  $\sigma_f$ , MPa; the slope of the initial region of the stress-strain curve, which correlates with elasticity modulus  $E$ , GPa; and breaking strain,  $\epsilon_{br}$ , %. The average value and the root-mean-square deviation were determined for each value.

The appearance and development of crazes on the surfaces of PLA film samples were studied using a Carl Zeiss optical microscope (Jena). For this purpose, the drawing procedure was performed with a manual tensile tool directly under the eyepiece of the microscope. The strain value was determined by the following equation:

$$\epsilon = \frac{l - l_0}{l_0} \cdot 100,$$

where  $l_0$  is the initial sample length and  $l$  is its final length.

## 3. Results and discussion

Fig. 1 is presented the stress-strain curves resulting from testing a PLA film in air and different liquid media. Table 1 is listed the average values of the basic mechanical parameters determined for the polymer from the experimental stress-strain curves. Being uniaxially stretched in air, PLA exhibits a very brittle behavior; the average value of the breaking strain is about 15%. In this case,

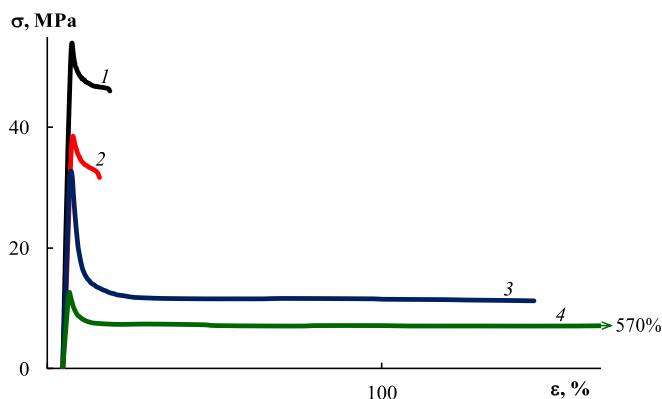


Fig. 1. Stress-strain curves obtained for amorphous PLA film in (1) air, (2) water, (3) HPEOS, and (4) *n*-pentanol.

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