

IR Spectroscopic Study of the Structure of Isotactic Polypropylene Deformed by the Crazing Mechanism

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Abstract—The deformation of isotropic isotactic polypropylene with a spherulitic initial structure has been studied. Fourier transform IR spectra of polypropylene deformed to various stretch ratios in air and in a physically active medium have been recorded. From the spectroscopy data, the dichroic ratios and orientation functions have been calculated for the amorphous and crystalline polypropylene phases. It turned out that the orientations of macromolecules in the amorphous and crystalline polypropylene phases change identically while stretching in a physically active (water–ethanol) medium. However, the deformation in air leads to a more pronounced orientation of macromolecules in the crystalline phase as compared with the orientation in the amorphous phase. The maximum values of the orientation function in the deformation in air coincide with the stretch ratio at the yield point. This is how a physically active medium acts in crazing in comparison with shear deformation in air.

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Crazing is one of the types of plastic deformation and can be performed while stretching amorphous glassy and crystalline polymers in physically active media. A characteristic sign of deformation of amorphous polymers by the crazing mechanism is the development of a specific fibrous porous structure in polymer on the nanometer level with sizes of pores and fibrils of no more than several tens of nanometers [1–3]. Deformation of crystalline polymers in air can also be accompanied by the development of cavities and pores in the interlamellar space [4]. However, significant porosity can be reached only in crystalline polymers the structure of which is determined by special forming conditions and consists of ordered lamellas oriented perpendicular to the stretching axis. Such materials were called hard elastic [5]. Stretching of crystalline polymers in physically active media results in much higher porosity and, equally importantly, does not require the preliminary creation of the specific structure inherent in hard elastic polymers. Nevertheless, although crazing of crystalline polymers was studied in numerous works, the question remains open as to how the nature of the medium affects the deformation mechanism and the formation of the specific fibrous porous structure in polymer. The purpose of this work was to study the structure of isotactic polypropylene deformed in air and in a physically active medium.

EXPERIMENTAL

In this work, we studied polypropylene with an isotropic structure with α -spherulites 1.5–4 μm . Films of extruded isotactic polypropylene ($M_w = 200\,000$, $M_w/M_n = 3.5$) were preannealed for 3 h at 140°C to increase the degree of crystallinity of polypropylene. According to the DSC data, the degree of crystallinity of polypropylene was 57%. Specimens 40 × 20 mm in size were deformed at room temperature at a stretching rate of 5.4 mm/min in air and in a physically active medium (1 : 7 water–ethanol solution). The mechanical properties were studied with an Instron 4301 universal testing machine while stretching 90- μm -thick polypropylene films in air and in the physically active medium. The thermophysical properties of 30- μm -thick polypropylene films were investigated with a Mettler TA 4000 thermal analysis system with a DSC-30 low-temperature cell. The heating rate was 10 K/min. The specimen weight was 0.5–2 mg. The degree of crystallinity was calculated using the heat of melting of a perfect crystal of polypropylene (190 J/g). The IR spectra were recorded on a Fourier transform IR spectrophotometer (number of scans, 30; resolution, 2 cm^{-1}). The measurements were made with an IR film polarizer placed in the cell compartment parallel and perpendicular to the polymer stretching direction. The FT IR spectroscopic studies were conducted on 30- μm -thick polypropylene films that were deformed to a certain stretch ratio in air or in the physically active medium after mounting on circular frames to prevent them from shrinking in the course of relaxation and removal of the medium.

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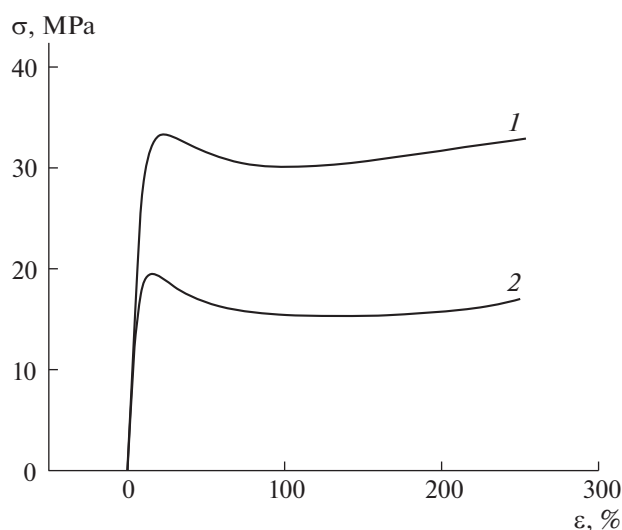


Fig. 1. Engineering stress–strain curves of polypropylene while stretching in (1) air and (2) a water–ethanol medium at a stretching rate of 5.4 mm/min.

MECHANICAL PROPERTIES AND POROSITY OF POLYPROPYLENE WHILE DEFORMING IN AIR AND A PHYSICALLY ACTIVE MEDIUM

Characteristic signs of deformation of polymers in liquid media by the crazing mechanism are a decrease in the tensile stress and an increase in the polymer volume in comparison with the respective quantities while stretching in air [1]. Figure 1 presents the engineering dynamometric stress–strain curves of polypropylene while stretching in air (curve 1) and in a physically active medium (curve 2). In comparison with the stretching in air, the polypropylene deformation in the water–ethanol solution occurs at lower stress.

An important characteristic of polymer deformation in physically active media is porosity data, which suggest the stretching mechanism and the crazing efficiency. Figure 2 presents the bulk porosity of specimens versus polypropylene stretch ratio. It is seen that the deformation in air (curve 1) does not lead to an increase in the volume of the deformed polymer, which is characteristic of shear deformation. By contrast, the polypropylene stretching in a physically active medium (curve 2) is accompanied by an intense increase in the volume of the deformed specimen, which suggests the polymer deformation by the crazing mechanism.

Thus, the polypropylene deformation in air occurs by the shear mechanism, whereas the stretching in a physically active medium develops by the crazing mechanism and is accompanied by the development of porosity.

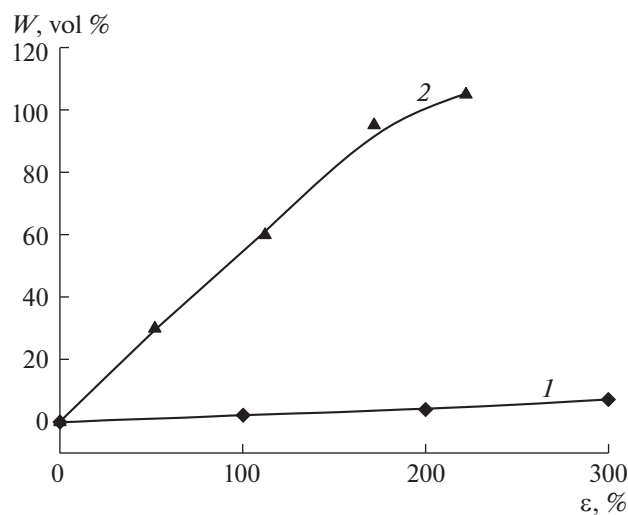


Fig. 2. Bulk porosity W versus polypropylene stretch ratio ε in (1) air and (2) a physically active medium.

IR SPECTROSCOPIC STUDY OF THE STRUCTURE OF POLYPROPYLENE DEFORMED IN AIR AND IN A PHYSICALLY ACTIVE MEDIUM

To study the evolution of the structure of crystalline polymers, including polypropylene, while deforming, various investigation methods are used, such as atomic force and electron microscopy, X-ray diffraction analysis, IR and Raman spectroscopy, DSC, etc. The most informative of them are in situ studies, which enable one to observe the change in the polymer structure directly in the course of deformation. However, matching a stretching device with an investigation method involves experimental difficulties and is not always possible. As an alternative to in situ studies of the structure of polymers deformed in air and a physically active medium, a simpler technique was proposed to preserve the sizes of deformed specimens by mounting them on circular frames for preventing them from shrinking in the course of relaxation and removal of the medium. Frame-mounted specimens are easier to match with a polymer structure investigation method. For example, this technique was used when the structure of high-density polyethylene deformed in a physically active medium was subjected to direct investigation in liquid [2, 3].

Crystalline polymers are two-phase system comprising a crystalline phase and an amorphous phase. Therefore, in studying their structure and its evolution in the course of deformation, of special interest are methods that can simultaneously characterize the structure of both phases. One of such methods is polarized IR spectroscopy, which can evaluate the orientation of macromolecules in both the crystalline and the amorphous phases. This method is widely used for characterizing the structure of polymers, in particular,

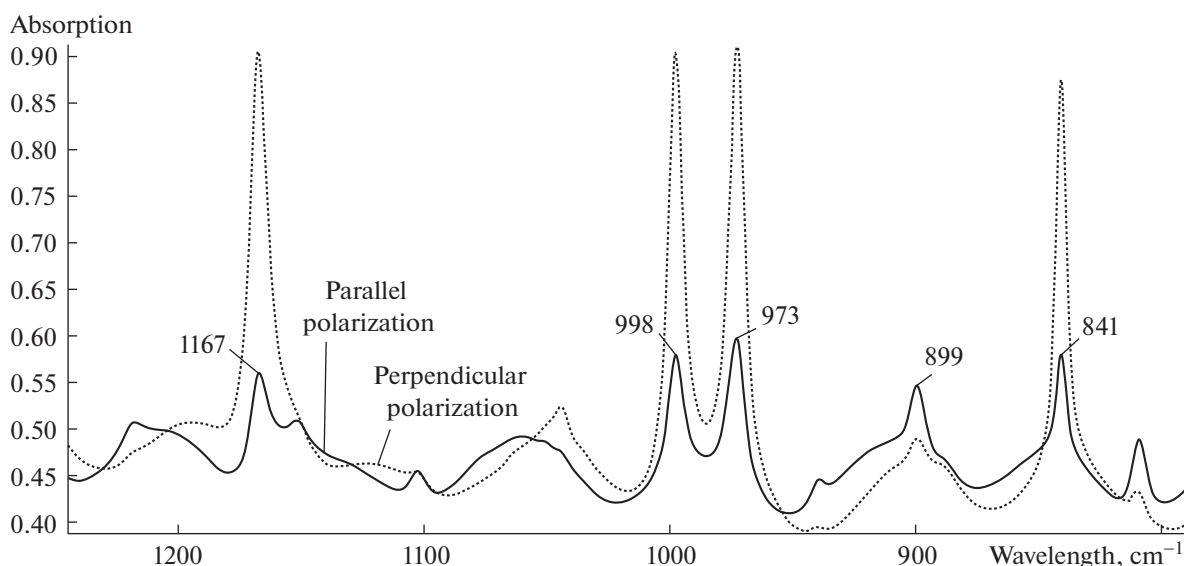


Fig. 3. IR spectrum of polypropylene deformed by 100% in air.

polypropylene, while deforming in air by the shear mechanism [6–11]. However, we failed to find the results of using this method for investigating the evolution of the structure of crystalline polymers deformed by the crazing mechanism in physically active media.

Studied in this work, the region (800–1300 cm^{-1}) of the IR absorption spectrum of polypropylene deformed by 100% in air using a polarizer placed parallel and perpendicular to the polymer stretching direction is shown in Fig. 3.

As the presented data show, a change in the IR radiation polarization direction causes significant changes in the polypropylene spectrum. To characterize the orientation of macromolecules of the crystalline phase of polypropylene while deforming, the absorption band 998 cm^{-1} was chosen. The complex vibration at 998 cm^{-1} includes the wagging vibrations of CH_2 - and CH_3 - groups, the stretching vibration of C–C bonds, the bending vibration of CH, and the out-of-plane torsional-bending vibration of CH_2 in the crystalline phase [10]. To characterize the molecular orientation in the amorphous phase, the band at 973 cm^{-1} was selected, which is assigned to the rocking vibration of CH_3 group and the axial and equatorial stretching vibrations of C–C bonds in the amorphous and crystalline phases.

To evaluate the degree of orientation of polypropylene macromolecules in the amorphous and crystalline phases, the dichroic ratios $R = A_{\parallel}/A_{\perp}$ were determined, and the orientation functions of the crystalline phase were calculated from the corresponding absorption bands according to a published procedure [10] as

$$f_{cr} = \frac{R - 1}{R + 1} \frac{R_0 + 2}{R_0 - 1},$$

where $R_0 = 2\cot^2\Psi$ and the angle Ψ between the polymer chain axis and the transition moment for the bands at 998 and 973 cm^{-1} is 18°.

The orientation function of polypropylene chains in the amorphous phase was also calculated by a described procedure [10] as

$$f_{am} = (f_{av} - X_{cr}f_{cr})/(1 - X_{cr}),$$

where f_{av} is the chain orientation function of the amorphous and crystalline phases (for the band 973 cm^{-1}), and X_{cr} is the fraction of the crystalline phase, which was found from the differential scanning calorimetry data and was 0.57.

The polypropylene deformation at room temperature is accompanied by the formation of a neck, and, as was shown previously [10, 12], it is in this region that the degree of polymer orientation is maximum, whereas, at the boundary of the forming neck, the degree of orientation is lower. In this work, we tested the deformation of specimens mounted on circular frames and studied the central part of a specimen, i.e., the zone of the maximum orientation of the polymer. Figure 4 presents the data on the orientation functions of the amorphous and crystalline phases of polypropylene deformed in air and in a physically active medium.

The initial polypropylene films were characterized by insignificant molecular orientation along the extrusion axis, which was caused by their forming conditions. With increasing polypropylene stretch ratio in air (Fig. 4, curve 1), the chain orientation in the crystalline phase increases. The most abrupt increase in the degree of orientation is observed at 50% strain, a

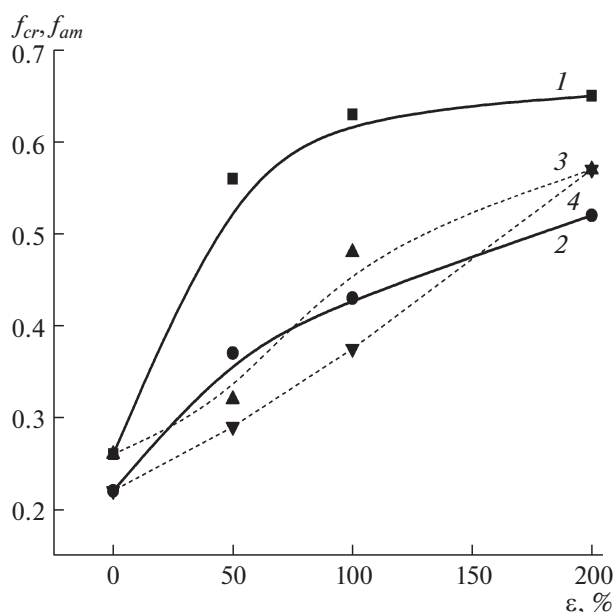


Fig. 4. Orientation functions of the (1, 3) crystalline and (2, 4) amorphous phases of polypropylene versus its stretch ratio in air (solid lines) and a physically active medium (dashed lines).

value close to the yield region of polypropylene in the stress–strain curve (Fig. 1), in which the necking begins. At higher strains, the orientation function changes insignificantly.

The orientation function of the amorphous phase of polypropylene deformed in air is lower than that of the crystalline phase and gradually increases with increasing strain (Fig. 4, curve 2). The amorphous phase of the semicrystalline polymer is constituted by tie chains linking neighboring lamellas, loops and cilia formed by macromolecules packed in one of the lamellas, and also free chains. The main contribution to the orientation of the amorphous phase while stretching crystalline polymers is made by tie chains acting as stress transmitters.

For polypropylene deformed in a physically active medium by the crazing mechanism, the orientation functions of the crystalline and amorphous phases also increase with increasing stretch ratio and are close to each other. The orientation function of the crystalline and amorphous phases of polypropylene deformed in a physically active medium is also close to the orientation function of the amorphous phase of polypropylene deformed in air (Fig. 4, curve 2). Thus, the results of our studies suggest that the stretching both in air and in a physically active medium deforms the amorphous phase of polypropylene virtually identically in the course of the emergence and gradual development of the orientation of polypropylene chains.

It is known that a liquid physically active medium decreases the surface energy of polymer and, under the

action of stress, exerts a plasticizing effect on polymer, changing the deformation mechanism from shear to crazing [1]. Obviously, the surface energy decrease and the polymer plasticization facilitate structural rearrangements in the crystalline phase: the expansion, fragmentation, shear, and orientation of fragments of lamellas occur at lower stress together with the rearrangement and orientation of chains in the amorphous phase. On the level of the molecular orientation while deforming in a physically active medium, the polymer material is deformed with no clear difference between the crystalline and amorphous phases (Fig. 4, curves 3, 4). Indeed, previous X-ray diffraction studies showed that the deformation by the crazing mechanism up to 400% is accompanied by a very little change in the main reflections of the crystalline phase of polypropylene, whereas the deformation in air results in a significant orientation of crystallites [13].

In the absence of a medium, the deformation occurs by the shear mechanism, which leads to an abrupt increase in the orientation function of the crystalline phase within the necking strain range (Fig. 4, curve 1; Fig. 1). The obtained result agrees with the literature data, according to which [11, 14, 15], within the necking strain range, there is local melting of lamellas, or interlamellar shear, accompanied by the orientation of chains along the stretching axis. While further stretching, the structure of fibrils is perfected. At this stage (at high stretch ratios), spectroscopy can detect only insignificant orientation changes, what we observed in this work (Fig. 4, curve 1).

Thus, we determined that the molecular orientation of polypropylene in the amorphous and crystalline phases increases with increasing stretch ratio while deforming polymer by a mechanism of both shear in air, and crazing in a physically active medium. The orientation of macromolecules of the crystalline phase of polypropylene deformed in air by the shear mechanism is higher than the orientation of macromolecules of the crystalline phase of polypropylene deformed in a physically active medium by the crazing mechanism. In a physically active medium, the orientations of macromolecules of the crystalline and amorphous phases virtually coincide. The obtained data allowed one to determine the difference on the molecular level between the polypropylene deformations by the shear and crazing mechanisms for the crystalline and amorphous phases of polypropylene.

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