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Morphology and properties alterations in cavitating and non-cavitating high density polyethylene

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ABSTRACT

Cavitation phenomenon has been marginalised in the past, although it alters morphology and properties of semicrystalline polymers during their plastic deformation. The formation of cavitational pores are due to the loss of cohesion by the amorphous phase. The research in this paper has been conducted on cavitating and non-cavitating high density polyethylenes with identical microstructure of the crystalline component, however, with modified amorphous phase. The influence of cavitation on selected properties and mechanisms activated during tensile deformation of high density polyethylene has been systematically studied including the alterations of yield stress and yield strain, the strain onset of activation of crystallographic slips and martensitic transformation, the intensity of the lamellae fragmentation, the degree of molecular orientation and the amount of heat generated during deformation.

1. Introduction

The plastic deformation of high density polyethylene is a complex process which requires a cooperative reorganization of the initial structure of the material on its different levels. Due to differences in the structure and properties, different micromechanisms are being activated within the amorphous and crystalline regions. Additionally, these micromechanisms are characterized by different values of the critical stress of activation. This in turn makes them to initiate sequentially – the mechanisms with the lowest critical stress are being activated first. Gradual increase of the stress in the material accompanying the deactivation of the mechanisms with the lowest critical stresses, causes initiating another ones with higher activation thresholds.

The initial stage of deformation of polyethylene takes place mainly in the interlamellar regions. The deformation of the amorphous phase requires much lower stress (usually from 10 to 50 times lower) than needed to activate the mechanisms of the plastic deformation of crystals [1]. Generally, it is believed that the deformation of the amorphous phase in a rubber-like state occurs according to three basic mechanisms: interlamellar slips (shear), interlamellar separation (change of distance between the adjacent lamellae) and rotation of lamellae (rotation of stacks of lamellae). The above mentioned mechanisms are activated in different zones of spherulite, due to a different arrangement of lamellae towards the deformation direction. At the same time, the molecular network of the amorphous component relatively quickly reaches its maximum degree of deformation which results in a gradual increase of the stress cumulated in the material. The further course of tensile deformation requires "activation" of a mechanism of plastic deformation of lamellar crystals and deformation of the amorphous and crystalline component occurs cooperatively.

Plastic deformation of the polyethylene crystals proceeds by crystallographic slip, martensitic transformation and twinning. The mechanism of crystallographic slip is the most important mechanism of deformation of polyethylene crystals, which allow to obtain very high degrees of plastic deformation, much higher than those resulting from two other mechanisms [2]. The studies of the deformation of monocrystals of polyethylene revealed the possibility of appearance of crystallographic slips in any (hk0) plane [3]. Further experimental studies showed particularly high activity of (100)[001] and (010)[001] slips systems [4], for which the critical stresses respectively amounting to 7.2 MPa and 15.6 MPa were estimated [5]. The crystallographic slips are also accompanied by the process of movement and increase of density of dislocations [6].

Martensitic transformation in case of polyethylene results in changing the crystallographic form from orthorhombic into monoclinic. This transformation is usually observed in the lamellae

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oriented parallel to the deformation direction causing relatively small displacement of chains to new positions in the new crystallographic cell in order to accommodate the deformation. The role of both twinning and martensitic transformation, during the plastic deformation of polyethylene, is not so important as the crystallographic slips, however, it causes significant reorientation of the crystal lattice which in turn enables activating the slip systems, which have not been active before.

During the tensile deformation of high density polyethylene the cavitation phenomenon is also observed (this phenomenon is not observed during shearing or compression) [7–10]. The cavitation, as the mechanisms mentioned above, is subject to the rule of the lowest critical stress of activation [11]. In relation to the above findings, the cavitation accompanies the plastic deformation of polyethylene with thick, well-developed crystals (the critical stress of activation of the mechanism of the plastic deformation of crystals is higher than the critical stress of activation of the cavitation – the cavitation is being activated first). However, it is absent during the deformation of polyethylene with small or strongly defective crystallites (the critical stress of activation of the mechanism of the plastic deformation of crystals is lower than the critical stress of activation of the cavitation – the plastic deformation of crystals is being activated first).

Over the years, the cavitation phenomenon has been marginalised, due to the common belief that it does not have any significant influence on the behaviour/properties of semicrystalline polymers during its plastic deformation. Recent experimental studies were related mainly with the influence of morphological (crystal thickness, degree of crystallinity, orientation of crystallites, molecular weight, morphology of amorphous phase (free volume, entanglements, tie molecules)) [7,12–20] and experimental (temperature, deformation rate) [7,21–23] factors on the intensity of the cavitation. The cavitation phenomenon was also taken into account during studies of tensile deformation of semicrystalline polymers with the use of molecular dynamics simulations [24–28]. However, only a few papers describe the impact of cavitation phenomenon on the properties and mechanisms activated during plastic deformation of semicrystalline polymers [29–31]. Only in our latest paper we have thoroughly analyzed the influence of the cavitation phenomenon on the properties and the process of plastic deformation of polypropylene [32]. We have corroborated the non-negligible influence of the cavitation phenomenon on the yield strain value, the intensity of the lamellae fragmentation process, the reorientation dynamics of the crystalline and amorphous component and the degree of crystals orientation at selected stages of deformation.

Consequently, in this paper, we have systematically analyzed the influence of the cavitation phenomenon on the value of yield stress/strain, the strain onset of activation of crystallographic slips and martensitic transformation, the intensity of the lamellae fragmentation process, the deformation-induced degree of molecular orientation and the amount of heat generated during plastic deformation of high density polyethylene. The research has been conducted for cavitating/non-cavitating model systems with an identical microstructure of the crystalline component during their tensile deformation.

2. Experimental

2.1. Materials

High density polyethylene Hostalen GC 7260 (HDPE) of melt flow index MFI = 8 g/10min (at 190 °C, 2.16 kg according to ISO 1133), by Lyondell Basell was used. A paraffin wax (m.p. 58 °C), by Loba Chemie and n-nonadecane 99% (m.p. 30–34 °C, b.p. 330 °C, d = 0.786 g/mL), by Sigma-Aldrich were used as low molecular weight modifiers.

2.2. Modification

Modification in solid state (SS). The process of modification was performed by immersion of polyethylene samples (obtained by compression moulding and cooled between metal plates) in a modifier bath placed in an oven at 70 °C for 7 days in order to obtain full penetration of the amorphous phase of the material with a low molecular weight modifier (polyethylene/n-nonadecane (SSn) or wax (SSw)). The content of modifiers has been estimated basing on samples weight increase after completion of the modification process. The reference samples had the same thermal history. *Modification in the molten state (MS)*. The process of modification was melt blending using Brabender batch mixer (Duisburg, Germany) operating at 190 °C for 5 min at 60 rpm. The content of modifiers has been estimated basing on TGA measurements. Neat HDPE was also processed under the same conditions to obtain a reference material. The samples for proper measurements were cut out from 1 mm thick polymer films, obtained by compression moulding and cooled between metal plates.

2.3. Thermogravimetry (TGA)

The content of modifiers in samples was estimated by means of thermogravimetry (TGA). A thermogravimetric analyzer Hi-Res TGA 2950 by TA Instruments was used with the heating rate of 10K/min in an air environment.

2.4. Supercritical CO_2 extraction

The extraction was performed in a batch manner. The samples were loaded into the 50-ml extraction vessel of supercritical fluid extractor (SFT-110, Supercritical Fluid Technologies, Inc., Newark, DE, USA). The extraction was conducted by continuously flowing CO_2 through the extraction vessel at a rate of 12 ml/min, at temperature 70 °C and pressure 4000Psi for 8 h. The extract was separately accumulated.

2.5. Mechanical testing

Mechanical properties of the materials examined in the paper were assessed using a tensile testing machine (Instron 5582) of load range 0–2 kN. The shape of tensile samples was according to ISO 527-2 standard, with 1 mm thickness and 5 mm width. The gauge length was 25 mm. Tests were performed at room temperature at the rate $3.3 \times 10^{-3}\ s^{-1}$ and $3.3 \times 10^{-2}\ s^{-1}$ (strain rate jump experiment).

The actual shape of a sample during deformation was recorded using Nikon D50 digital camera. In order to determine the local strain (LS), dot markers of sputter coated gold forming a rectangular grid located in the entire gauge of a sample. Similar measuring technique was used by us and others in the papers [17,33]. Local strain (LS) was calculated as a change in distance between the dot markers according to a relation: $(l-l_0)/l_0$, where l_0 is a distance between markers for the undeformed sample and l is a distance between markers for the deformed sample.

Volume strain for local strains was determined using the following relation: $(V-V_0)/V_0$, where V_0 denotes the volume of the undeformed sample. The volume of the sample between markers was determined on the basis of a distance between markers and the thickness of the photographed sample.