Kinetics and dynamics of two-way shape-memory behavior of crosslinked linear high-density and short-chain branched polyethylenes with regard to crystal orientation

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ABSTRACT

Kinetic and dynamic aspects of the two-way shape-memory effect in covalent networks on the basis of linear high-density and two short-chain branched polyethylenes having appreciably different crystallinity and crystallization/melting temperatures are strongly affected by the crosslink density and applied uniaxial load. The crystallinity of the samples was found to play a key role in the shape-memory performance as it principally determined the capacity to develop the two-way shape-memory effect and the ability of the covalent network to perform mechanical work against the applied external force. Wide-angle X-ray scattering revealed preferred crystal c-axis orientation and its quasi-discrete change with evenly increasing load. The results of modeling the two-way shape-memory behavior of high-density polyethylene under different loads revealed excellent accordance with experimental findings. Theoretical analysis predicted the quasi-discrete change of the orientation of the crystal c-axis as a result of the change of crystal structure.

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1. Introduction

Shape-memory (SM) polymers are intensively studied in the last decades because of a possibility of many potentially interesting and important applications, in particular, as stimuli-responsive sensors and actuators [1–8]. The SM phenomenon in polymers is based on their ability to memorize one or more temporary shapes after application of a quasi-elastic deformation and to recover original shape being exposed to an external stimulus, such as heat, irradiation, moisture, etc. [2–6]. The most attention takes the thermally-induced shape-memory effect (SME) initiated by the thermal transition like melting/crystallization occurring within stable covalent polymer networks or glass transition within physical networks, or, in other words, entanglements. The conventional one-way SME in polymers can be reproduced by the following procedure. At first, a polymer sample is deformed from an initial permanent to a certain temporary shape by applying a load at a temperature above its melting/glass transition temperature ($T > T_m/$

T_g). Secondly, the formation of crystalline structure or vitrification during subsequent cooling in such a deformed state fixes the temporary shape so well that it remains nearly unchanged also after the next step — unloading of the sample at the lowest temperature of experiment ($T < T_c/T_g$). Subsequent heating above the melting/glass transition temperature ($T > T_m/T_g$) induces a recovery of the permanent shape of the sample originated from the release of the stored during programming entropy-elastic and viscoelastic stresses acting as driving force. In order to reproduce such a SM behavior, the programming step is needed again. Therefore, this phenomenon is defined as the one-way SME.

Up to now, only crystallizable covalent networks in addition to the one-way SME enabled the observation of the so-called two-way SME [9–11] discovered for the first time by Mather and coworkers in crosslinked polycyclooctene/trans-polyoctenamer [9]. The principal manifestation of the two-way SME lies in an anomalous elongation of a sample under constant load initiated by non-isothermal crystallization at cooling and in the following contraction triggered by melting of the crystalline phase at heating [9–11]. The two-way SME can be observed iteratively as long as a sample is loaded and the temperature change is sufficient to cause the consecutive crystallization and melting of the ordered phase in the covalent network.

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A novel theoretical approach, which is able to explain and describe the two-way SME in crosslinked semicrystalline polymers, has been recently derived by the authors [12,13]. The theory is based on the three-element mechanical model accounting crystallization/melting of a covalent polymer network and the viscoelastic deformation of entangled slipped macromolecules as the two basic mechanisms involved in the SM performance [12–15]. The developed thermodynamic description of the behavior of a covalent network enables the calculation of the free energy change of a network deformed under constant load and cooled down below the crystallization temperature at a constant cooling rate, i.e. in non-isometric and non-isothermal conditions, respectively. It has been predicted that the anomalous elongation is possible when chains of the crystals formed at cooling are parallel to the direction of load or make a relatively small angle, which depends on crosslink density and a number of crystal folds (stems). The theoretical conclusions were successfully confirmed by fitting the temperature dependent strain obtained during the two-way SME in high-density polyethylene loaded by 1 MPa.

The aim of the work is to test covalent networks on the basis of linear high-density and two short-chain branched low-density polyethylenes characterized by appreciably different crystallinities, crystallization/melting temperatures, and crosslink densities for the two-way SME in order to detect the effect of loading on the kinetics of SM performance and on the orientation of the crystals formed at cooling in the course of the two-way SME. It is aimed to introduce novel empirical parameters, which will enable a proper characterization and deeper understanding of the two-way SME. Based on the recently presented theoretical approach, modeling the two-way SM behavior of high-density polyethylene under different loads as well as the comparison between experimentally obtained crystal orientation and its theoretical prediction will be performed as well.

2. Experimental section

2.1. Materials and processing

Polyethylenes under study have been commercially available products (Dow Chemical, Schkopau, Germany), namely high-density polyethylene (HDPE) and two metallocene-catalyzed homogeneous ethylene-1-octene copolymers (EOCs) with approximately 30 and 60 hexyl branches per 1000C (EOC30 and EOC60, respectively). The peroxide 2,5-bis(t-butylperoxy)-2,5-dimethyl hexane (DHBP) was used as crosslink agent. The films with a thickness of 1 mm were compression molded and crosslinked at a temperature of 190 °C in the press under load as described in Refs. [16,17]. The crosslink density of polyethylenes under study was estimated by tensile tests and swelling procedure on the basis of Flory-Rehner equation [16,17]. The relevant parameters of these materials are given in Table 1.

2.2. SM behavior

SM investigations were carried out in tensile mode using a mechanical spectrometer measuring head Mark III (Rheometric Scientific Inc., New Jersey, USA). The samples of crosslinked HDPE, EOC30, and EOC60 shaped as shouldered test bars with the cross-sectional area of 2×1 mm^2 were tested during the specific thermo-mechanical experiment at an initial clamps distance of 6 mm. The specimens were loaded by different nominal stress σ_{0N}, which is defined as force divided by the initial cross-sectional area, at the highest temperature of SM test T_{high} above the corresponding melting temperature, namely, $T_{high} = 165$ °C in case of HDPE, $T_{high} = 140$ °C and $T_{high} = 120$ °C in case of EOC30 and EOC60,

respectively. Such loading entailed the initial strain ε_{ini}. Subsequent cooling under constant load to the lowest temperature T_{low} of 0 °C at an average rate of 2 °C min^{-1} resulted, at first, in the relatively slight creep of the samples ε_{cr} prior to crystallization and, secondly, in the considerable anomalous elongation of samples by strain increment $\Delta\varepsilon_{inc}$ in the temperature range of crystallization. Afterwards, the loaded specimens were thermally equilibrated for 5 min at T_{low} and then heated to the highest temperature T_{high} at a rate of 2 °C min^{-1}. During melting of the crystalline phase, the specimens considerably contracted by strain decrement $\Delta\varepsilon_{dec}$. After thermal equilibration for 5 min at T_{high}, the thermo-mechanical cycle was repeated. The strain was measured as a function of temperature during the thermo-mechanical experiment.

Because any difference between the measured temperature of a sample and its true value occurs in each cooling/heating tensile experiment using a mechanical spectrometer, a calibration sample of polyamide 6 with embedded conductor of K–type thermocouple (chromel–alumel) was used to determine the true temperature of the specimen during the SM experiment. Another thermocouple was connected to a data logger measuring the electric potential difference and, correspondingly, the real temperature of the sample. The specimen was tested in a mechanical spectrometer under the same thermal conditions of the SM experiment as described in the previous paragraph. The temperature sets from the spectrometer sensor and thermocouple were registered synchronously and their difference was approximated by the polynomial function. Received correction function was used to calculate the true temperature of specimens during the SM investigation.

2.3. Wide-angle X-ray scattering (WAXS)

WAXS patterns of two sets of samples – slowly crystallized undeformed samples and stretched specimens crystallized after cooling under load during two-way SME (see section SM behavior) – were collected in transmission geometry for analysis of the orientation of the crystals. An X-ray flat film camera (Molecular Data Corporation, Cleveland, Ohio, USA) was used equipped with a 0.5 mm pinhole collimation system. The wavelength of the Ni-filtered Cu-K$_\alpha$ radiation was 0.15418 nm, and the sample-to-detector distance was about 30 mm. The photographs were taken with the primary beam being normal to the stretching direction of drawn films as shown in Fig. 1. The results will be discussed below based on the intensity plots $I(q)$ obtained by sector integration of the 2D WAXS patterns over $\pm 5°$ to the orientation on equator.

3. Results and discussion

3.1. Two-way SM behavior

3.1.1. Effect of loading

The strain as a function of temperature shown in Fig. 2(a,c,e) represents the evolution of thermo-mechanical response of HDPE, EOC30, and EOC60 with the highest reached crosslink densities under different nominal stresses during the cyclic two-way SM experiment. As it is seen from Fig. 2(a), only the HDPE sample loaded by nominal stress $\sigma_{0N} = 0.9$ MPa does not reveal typical two-way SM behavior, while the other samples of polyethylenes under study at different loads exhibit the distinct two-way SME. Such a peculiar mechanical behavior of HDPE at 0.9 MPa cannot be explained at this stage, however, it will be specifically discussed on the basis of the results of modeling presented in the next section. The important characteristics of the two-way SM performance like initial strain ε_{ini}, non-isothermal entropy-elastic creep strain ε_{cr}, crystallization-induced strain increment $\Delta\varepsilon_{inc}$, and melting-induced strain decrement $\Delta\varepsilon_{dec}$ mentioned in Section 2.2 are