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Hierarchical microstructure changes and the molecular mechanism of polypropylene under a critical failure strain during creep

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ABSTRACT

The hierarchical microstructure evolution of polypropylene during creep was explored via various methods, such as differential scanning calorimetry (DSC), scanning electron microscope (SEM), two-dimensional small-angle X-ray scattering (2D-SAXS), two-dimensional wide angle X-ray diffraction (2D-WAXD) and positron annihilation lifetime spectroscopy (PALS). The results revealed a correlation among the changes of micron-scale spherulites, nano-scale lamellae, crystalline blocks, atomic scale free volume and the deformation of polypropylene during creep. The elongation of micron-scale spherulites along the creep direction, accompanying with the increase of nano-scale lamellar long spacing, as well as the enlargement and amalgamation of atomic scale free volume were observed at ε below 17%; the imperfect fibrillar crystallites with polymer chains preferentially oriented along the creep direction, formed in the stress-induced crystalline block disaggregation–recrystallization process, were proved by SEM and 2D-SAXS results when ε was between 17% and 55%; the further orientation of polypropylene chains led to a higher degree of orientation and crystallinity. The molecular deformation mechanism of polypropylene during creep included three stages: the intralamellar slipping of crystalline blocks, accompanying with the enlargement and amalgamation of free volume, was activated at small strain ($\varepsilon \leq 17\%$); whereas the stress-induced crystalline block disaggregation–recrystallization process as well as the rearrangement and orientation of chains were proceeded at medium strain ($17\% < \varepsilon \leq 55\%$); at last, orientation-induced crystallization occurred at larger strain ($\varepsilon > 55\%$).

1. Introduction

Polymer materials are used in a wide range of applications in daily life and engineering field. It is impossible to avoid suffering force for materials during service. Evaluation of lifetime of polymer materials is a significant issue in their service design for security reasons [1]. Creep test in laboratory serves as an effective method for assessment of lifetime under time-independent force. At relatively high force (sub-yield), creep curves obtained from creep tests may be split into four intervals [2]: (i) primary creep – at the beginning, within sufficiently small times, strain grows sharply with time, (ii) transition region - the dependence $\varepsilon(t)$ is convex, (iii) secondary creep – strain increases linearly with time, (iv) tertiary creep – the last stage, strain grows nonlinearly with time, and the dependence $\varepsilon(t)$ exhibits concave first and then turns to be convex. The four stages, occupying different proportions of the whole lifetime of polymer materials, attract attention of the researchers to the mechanical property changes of polymer materials during creep. Li et al. [3] have successfully used Burgers' model to explain the reinforcing effect of the liquid crystalline (LC) phase in creep experiment. Cheng et al. [4] applied the creep experiment to get structural failures on reasonable time scales to better show the mechanical and structural responses of polycarbonate (PC) glass at different temperature. Dai et al. [5] employed Burger' model and Weibull distribution function to understand the reinforcing mechanisms of creep-resistant behavior of MWCNT – polycarbonate spun nanocomposite fibers at elevated temperature. Braunsmann et al. [6] gave maps of the instant glassy modulus, the equilibrium rubbery modulus, and the retardation time by

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quantifying the local creep compliance of the sample in terms of the standard linear solid model.

Although considerable researches have been devoted to the macroscopical engineering mechanics of the polymer materials during creep, rather less attention has been paid to the root reasons caused by microstructure changes. While the microstructure changes during the creep are ignored, the deformation of polymer under uniaxial tensile has been well documented, such as the deformation of spherulites under cold drawing [7,8], intralamellar slipping of crystalline blocks and stress-induced crystalline block disaggregation–recrystallization process at critical strain [9,10], free volume changes during deformation at room temperature [11]. Brown et al. [12,13] have shown measurements of crystalline lattice strain development during deformation of polytetrafluoroethylene (PTFE) utilizing neutron diffraction measurements. The results revealed that the vast majority of deformation in PTFE was taken up by the amorphous phase. On the basis of the similarity between uniaxial tensile and creep, it is reasonable to draw lessons from uniaxial tensile to research the creep behavior of polymer materials.

In the previous study, we found that the transition from secondary to tertiary creep in polypropylene (PP) occurred when the strain reached certain critical value, ε_{cr} [14,15], which was invariant against variations in the temperature (room temperature and above), force, whether heat treatment or exposed to UV light [16]. However, the reason and mechanism of phenomena involved in the creep process has not been completely understood yet [17–22]. Since the mechanical properties of PP depend on its microstructure and morphology, it is essential to probe into the hierarchical microstructure changes, which occur during creep of the material, to gain further insight into the molecular deformation mechanisms of PP and to provide possible routes for properties improvement and service lifetime prediction of the material.

For these purposes, our main objective is to investigate the hierarchical microstructure changes of PP during the creep by means of a nondestructive, powerful and sensitive microanalytical technique, positron annihilation lifetime spectroscopy (PALS), which could provide the information about the crystalline packing, defects of the crystalline regions, and size and number of free volume, combining with differential scanning calorimeter (DSC), scanning electron microscopy (SEM), two-dimensional small-angle X-ray scattering (2D-SAXS) and two-dimensional wide angle X-ray diffraction (2D-WAXD). The explanations for molecular deformation mechanisms at critical strains were given according to these experiment measurements.

2. Experimental

2.1. Materials and sample preparation

The PP used in this study is supplied by Lanzhou Petrochemical Company, China. The molecular weights are $M_w = 3.27 \times 10^5$ g/mol and $M_n = 8.72 \times 10^4$ g/mol. Dumbbell-shaped samples with a total length of 120 mm and gauge dimensions $45 \times 20 \times 2.5$ mm^3 were compression molded at 180 °C for 15 min. After being held in its molten state for 5 min to erase the residual stress and local orientation, the samples were slowly cooled down to room temperature.

2.2. Creep test

To avoid strain-whitening caused by cavitation in the samples during creep test, each one was prepared at 100 °C with constant force $F = 375$ N, using a multifunction stress aging testing machine. Under a constant force, the stress acting on the sample continuously increases as a result of decrease in cross-section area. Samples with different final strains were prepared on the same condition. Once reaching the strain needed, the samples were rapidly quenched by a liquid nitrogen gun, and a pair of metal frames was applied to preserve the deformation by fixing the sample.

2.3. Differential scanning calorimetry (DSC)

Measurements were carried out on a TA Instruments DSC-Q20 fitted with a nitrogen purge chamber, applying heating and cooling rates of 10 and 20 K/min in a temperature range between 40 and 200 °C. The heating and cooling cycle included: first heat, first cool, second heat. For clarity only the measurements during the first heat were shown in a restricted temperature range.

The crystallinity is estimated from equation:

$$\chi_c = \Delta H_m / \Delta H_m^0 \qquad (1)$$

where ΔH_m is the fusion enthalpy measured by DSC and ΔH_m^0 is the fusion enthalpy for the completely crystalline PP, $\Delta H_m^0 = 209$ J/g [23].

2.4. Scanning electron microscope (SEM)

The morphologies of the crystalline region in PP samples were studied via SEM. The test samples were etched by 2% solution of potassium permanganate in a mixture of sulfuric acid, 85% orthophosphoric acid. After covered with a thin layer of gold, the etched surface was observed by an SEM instrument (model JSM-5900LV) operating at 20 kV.

2.5. Two-dimensional small-angle X-ray scattering (2D-SAXS)

SAXS experiments were carried out on a modified Xeuss system of Xenocs France equipped with a semiconductor detector (Pilatus 100 K, DECTRIS, Swiss) attached to a multilayer focused CuK$_\alpha$ X-ray source (GeniX^{3D} Cu ULD, Xenocs SA, France), generated at 50 kV and 0.6 mA on page 7, line 3. The experiments were carried out in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. Because the samples were not measured at one time, two conditions were applied. 1060 mm for sample-to-detector distance and 60 min for exposure time were applied for samples with $\varepsilon = 0$, 5, 15, 17, 20, 25, 30, 110% as the final strains, while 1753 mm for sample-to-detector distance and 20 min for explosion time were applied for samples with $\varepsilon = 10$, 40, 55, 70, 90, 135, 160% as the final strains. The scattering intensity distributions were not affected by these two conditions, while the affected intensities were not compared together. The long spacing results could be compared unambiguously when the background of intensity distributions corrected and normalized using the standard procedure.

2.6. Two-dimensional wide angle X-ray diffraction (2D-WAXD)

The 2D-WXRD experiments were carried out using a Bruker D8-DISCOVER diffractometer. The generator was set up at 40 kV and 40 mA. The wavelength of the monochromated X-ray from CuK$_\alpha$ radiation was 0.154 nm and the transmission mode was used. The sample to detector distance was fixed at 9 cm. All the 2D-WAXD patterns given in this paper have extracted the background, so a qualitative comparison between the various samples was allowed. The orientation parameter f, of various samples could be obtained by the following formulas [11]: