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Micromechanical analysis of molecular orientation in high-temperature creep of polycarbonate

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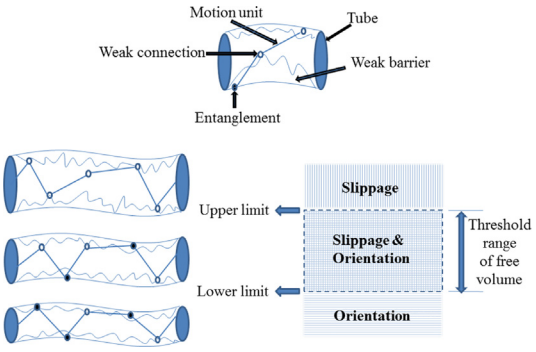
HIGHLIGHTS

- High-temperature creep and orientation were analyzed using four element viscoelastic model.
- A threshold range of free volume was proposed to understand the change of retardation time and delayed elastic modulus.
- The micro-mechanism of non-affine deformation was interpreted by the threshold range assumption.

GRAPHICAL ABSTRACT



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ABSTRACT

The molecular orientation of bisphenol-A polycarbonate (PC) was determined by the in-situ wide-angle X-ray diffraction (WAXD) measurement during high-temperature creep. The resulting creep and WAXD data were used to analyze the coupled deformation of macro-continuum and micro-structure. A four elements viscoelastic model was introduced to fit the creep results and describe the time-dependent orientation in creep. The delayed elastic stress was regarded as an assessment of molecular orientation, and two dashpots in the model were used to analyze the physical meanings of retardation time, which helped to understand the mechanism of molecular orientation and the role of free volume and stress on the viscoelastic parameters. A threshold range of free volume was proposed to interpret the change regularity of retardation time, delayed elastic modulus and coefficient C. The delayed elastic stress can be successfully used in assessing the orientation. Our work provides a deeper insight into the evolution of molecular orientation induced by high-temperature creep.

1. Introduction

The temperature and external forces lead to macromolecular directional movement, which contributes to the anisotropy and nonlinear viscoelastic behavior [1–4]. Hence, it is significant to do the research on the molecular orientation in the process of macro deformation for understanding the mechanisms of polymer creep. The creep retardation of polymer becomes more severe near the glass transition temperature. Meanwhile, the thermal-induced residual stresses can be removed through increasing the temperature. Therefore, the high-temperature creep is often used in place of long-term creep measurement [5–9]. Besides that, the average orientation is easy to be determined in high-temperature creep, because the multi-scale deformation was

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approximately uniform according to rubbery elastic theory [10–13]. Therefore, using the high-temperature creep to research the long-term properties and the mechanisms of nonlinear multi-scale deformation is reasonable and efficient.

A great deal of research on molecular orientation has been carried out by creep. The effects of temperature, drawing rate and molecular weight on orientation were experimentally observed. The orientation dependence of surface contact creep, recovery and the stretch strain hardening were studied. The relationship between molecular orientation and the decreased retardation time during creep was analyzed. The creep was also used to analyze the molecular orientation in a steady flow analogically [14–20]. The time-temperature-stress superposition principle (TTS) was used to give an explanation for creep of polymers [21–24]. However, it is difficult to give a complete and microstructural interpretation for the creep of amorphous polymers. The affine deformation assumption may be failed for uni-axial drawing, because the change of entanglement density with orientation was unclear [25]. The entropic stress was difficult to reveal the relationship between creep and orientation below the glass transition temperature [26]. During the hot drawing, the combined effects of temperature and stress hided the real mechanism of multi-structure change, which made the free volume theory difficult to interpret the nonlinear deformation and molecular orientation in creep [27].

In this study, in order to better understand the molecular mechanism of creep and give a more reasonable interpretation on the deformation at macro and micron levels, the high-temperature creep test was coupled with the in-situ WAXD measurement to determine the deformation in multi-scale experimentally. A linear four elements viscoelastic model was introduced to analyze the nonlinear multi-scale behavior through comparing the fitting parameters of different samples. The creep results were fitted with the model. The resulting fitting parameters were used to calculate the time dependent delayed elastic stress, which was regarded as the assessment of orientation. The linear relationship between Hermans' factor and delayed elastic stress was assumed according to the research of Priss [28]. The relevant coefficient was obtained by adjusting the curve of calculated orientation close to the curve of Hermans' factor. Through comparing the parameters under different stresses and pressures, the influence of free volume and stress on molecular orientation was proposed. A threshold range of volume assumption was proposed to reveal the microstructural mechanism of macro viscoelastic parameters change.

2. Experimental

2.1. Material and sample preparation

The optical grade PC (PC110) with a density of 1.2 g/cm^3 and melt flow rate (MFR) of 10 g/10 min (300 °C/1.2 kg, ASTM D1238) from Chi-Mei Co., Taiwan was used. Before hot pressing and creep measurement, the PC pellets and dumbbell-shaped samples were annealed at 120 °C for 6 h. The PC dumbbell-shaped samples with 1 mm thickness were hot pressed by self-designed and assembled hot-pressing machine (Fig. 1). The PC pellets were filled into the frame and heated up to 285 °C, then kept that temperature for 15 min, where the time for loading pressure was 5 min, the pressure was set for 0.61 MPa, 0.89 MPa and 1.16 MPa. The hot pressing machine was cooled down to 60 °C by water after unload the pressure. All the samples were stored in the sealed plastic bags for preventing absorbing water. The hot-pressed dumbbell-shaped samples were further cut into rectangular samples with a nominal width of 5 mm and a length of 28 mm for creep measurement (Fig. 1a).

2.2. Characterization

The creep measurements were performed on a Linkam temperature-controlled stage (TST350, Linkam Scientific Instruments, USA). The drawing direction was parallel to the long direction of tensile samples. The constant uni-axial stresses, 4 MPa, 6 MPa, 8 MPa, 10 MPa and 12 MPa, were applied during the high-temperature creep test respectively. Before stretching, the samples of PC having a Tg of about 147 °C (from DSC at 10 °C/min, in Fig. S1 of Supplement information) were heated from 40 to 140 °C at 10 °C/min. Then the temperature kept constant for 5 min. After that, the samples start to be stretched under the constant uniaxial stress. The loading time was controlled from 200 to 1300 s to ensure that the yield deformation did not occur. The fluctuant results in the initial period were removed. In order to determine the frozen orientation in the PC injection molded samples and the time–dependent orientation, the WAXD was carried out on a Bruker Nanostar system. The CuKα radiation source (λ = 0.154 nm) was selected with a point focusing monochromator. The distance of sample to detector was 8.5 cm and the generator settings were 45 kV and 0.67 mA. The WAXD patterns were recorded using a Hi-STAR two-dimensional area detector. Take use of Hermans' factor (Eq. (1)), the

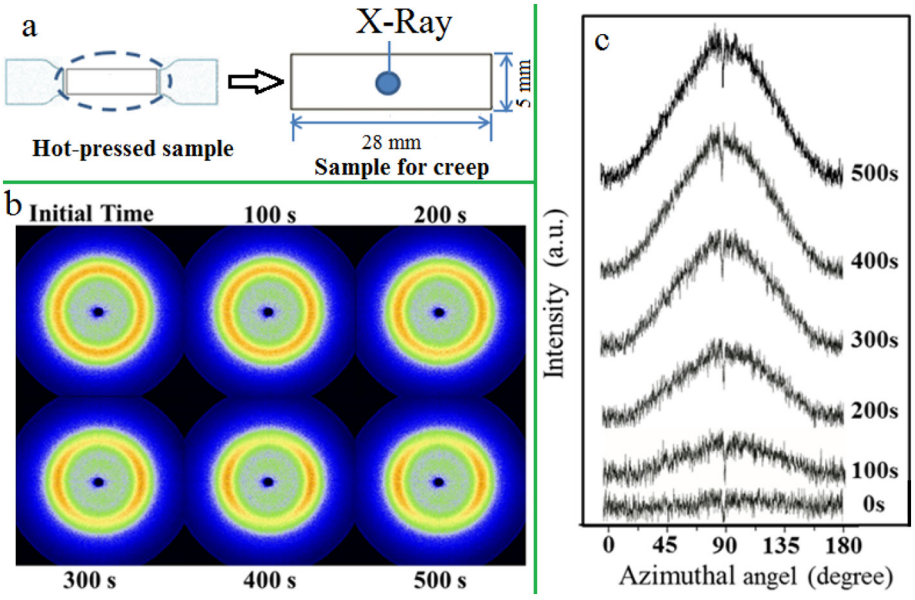

Fig. 1. The typical time-dependent 2D-WAXD patterns and the related intensity-azimuthal angle curves of PC sample under a uni-axial stress of 8 MPa and hot press pressure of 0.61 MPa. The drawing direction is vertical.