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Short communication: material properties

Sensitivity of nanoindentation strain rate in poly(ester-ester-ketone) using atomic force microscopy

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ABSTRACT

The effect of strain rate on poly(ester-ester-ketone) (PEEK) was investigated using an atomic force microscopy (AFM) based nanoindentation technique and applying a wide range of strain rates (0.012 s^{-1} −1 s^{-1}). The test results show that the average hardness and elastic modulus of PEEK follow a linear model with respect to logarithm of strain rate, from 263.9 MPa/1.377 GPa to 323.1 MPa/2.477 GPa. The maximum indentation depth decreased from 287.1 nm to 239.6 nm, indicating an enhanced densification area and shear transform zones under the indentation region. The plasticity index showed a rapid increase at low strain rate and kept stable at ~0.640 until a strain-rate of 0.037 s^{-1}. Moreover, a 'pile-up' phenomenon appeared around the residual indentation area due to more free volume around the cube-corner indenter than a Berkovich indenter during the loading process.

1. Introduction

High performance thermoplastic polymer poly(ester-ester-ketone) (PEEK) has been widely used due to its excellent mechanical properties, chemical stability and wear resistance [1,2]. The overall understanding of the mechanical properties of PEEK is necessary to the structural design in different applications [3,4]. Considering the complex loading conditions such as strain rate in real applications, many attempts have been made to obtain the mechanical properties and viscoelastic behavior of PEEK from nano- to macro- scale [5,6].

Nanoindentation is a useful tool for characterizing the surface hardness and elastic modulus on the nano-scale by calculating the load-displacement curves using mechanical contact models. H. Nakamura et al. [7] studied the indentation hardness of PEEK sheet after ultraviolet exposure. However, the strain rate sensitivity of PEEK under nanoindentation testing is still required for overall understanding. Although some experiment standards, such as ASTM E2456 [8] and ISO 14577 [9], have been published to give a reference for instrumented indentation measurements, many test parameters still need to be considered carefully for polymer samples. L. Malekmotiei et al. [10] explained the yielding and plasticity of poly(methyl methacrylate) (PMMA) under an indenter. D. Tranchida et al. [11] discovered the viscoelastic recovery behavior of semicrystalline poly(ethylene) using an atomic force microscopy (AFM) nanoindentation method. A.-Y. Jee et al. [12] studied the protocol differences between Oliver & Pharr and image analysis for ten different polymers. F. Alisafaei et al. [13] characterized the indentation size effect and indentation depth dependent deformation behavior of epoxy. The previous research reveals that the mechanical behavior under nanoindentation measurements always varies with different loading conditions. However, there is little work about the influence of strain rate in nanomechanical properties of PEEK. In this work, an AFM based nanoindentation technique was used to investigate the effect of strain rate on PEEK nanomechanical properties.

2. Experimental

The poly(ester-ester-ketone) sheets were provided by Changchun Jilin University Special Plastic Engineering Research Co., Ltd. To obtain a smooth surface, the PEEK specimens were cut into small pieces and embedded in acrylic resin matrix (PMMA) for polishing. Samples were ground with 1200, 2500 and 5000 grit silicon carbide paper and polished with 0.04 μm alumina suspension on an automatic polish-grinding machine (Presi Mecatech-234). The surface topology was analyzed by AFM (Bruker Dimension Icon) and the surface roughness was determined to be less than 10 nm.

Nanoindentation tests were carried out with an AFM in an acoustic box at room temperature. Fig. 1a gives the schematic setup of AFM based nanoindentation measurement. The indenter was a

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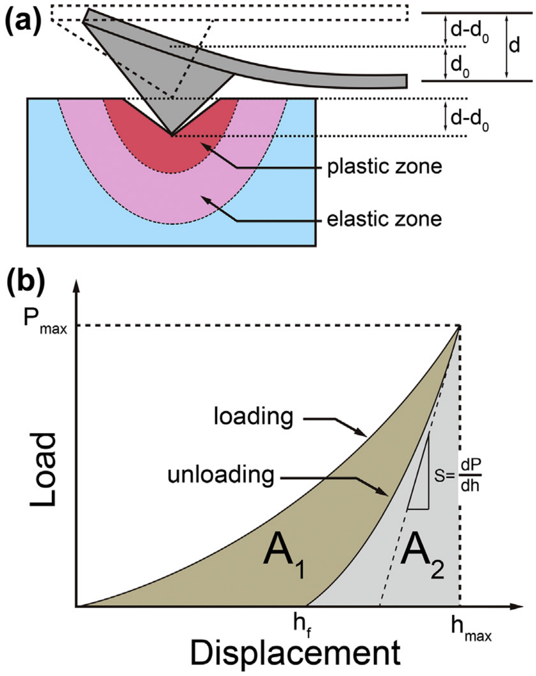

Fig. 1. (a) Schematic setup of AFM based nanoindentation. (b) Typical load vs. displacement curve of nanoindentation.

diamond cube-corner tip with a steel cantilever (PDNISP probe). The spring constant and the resonance frequency of the cantilever are 285 N m^{-1} and 40 kHz respectively. To determine the relationship between the cantilever deformation and the tip force, the cantilever deflection sensitivity was calibrated with several ramps on sapphire. As depicted in Fig. 1a, d is the piezo distance, d_0 is cantilever deflection, d-d_0 is the indentation depth on samples. During each indentation test, the load-displacement curve was automatically captured, as shown in Fig. 1b. Each group contains 9 repeats of the indentation test. The results were analyzed by the Oliver and Pharr method [14]. The hardness of the material is defined as:

$$H = \frac{P_{\max}}{A} \tag{1}$$

where $P_{\max}$ is the applied load. The contact area A depends on the type of indenter and the contact depth h_c. The function of contact area was calibrated by several indentation tests on a standard fused silica sample. The reduced modulus E_r can be calculated by using the unloading curve with the following equation:

$$E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A}} \tag{2}$$

where β is a constant for indenter shape and S is the initial slope of the unloading curve, defined by:

$$S = \frac{dP}{dh} \tag{3}$$

Then, the elastic modulus E of the specimen can be calculated by reduced modulus E_r and indenter modulus E_i, while ν and ν_i are the Poisson's ratios of specimen and indenter, respectively.

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \tag{4}$$

To characterize the changes in the ratio of the plastic indentation work to the total indentation work from the unrecoverable deformation, the plasticity index is defined using the formula [15]:

$$\eta_p = \frac{A_1}{A_1 + A_2} \tag{5}$$

Here, A_1 is the surface area between the loading and unloading curves and A_2 is the area under the unloading curve, representing the plastic work and elastic work, respectively (see Fig. 1b). Similarly, the elasticity index is defined as:

$$\eta_e = 1 - \eta_p \tag{6}$$

Load on the PEEK surface layers was 50 μN, with a ramp rate varying from 0.0025 Hz to 0.2 Hz Table 1 reports the ramp rates used in this study, and the nominal strain rate is the reciprocal of the loading time. The in situ AFM images were obtained with the same probe using tapping mode at 0.8 Hz scan rate.

3. Results and discussion

Fig. 2a shows the indentation hardness and elastic modulus of PEEK as a function of the nominal strain rate. The average hardness increased from 263.9 MPa to 323.1 MPa, and the average elastic modulus increased from 1.377 GPa to 2.477 GPa. Both the hardness and elastic modulus values show linear increments with respect to the logarithm of nominal strain rate. This trend indicates that the variance of surface mechanical properties in nanoindentation of PEEK is sensitive at low strain rates (<0.1 s^{-1}). According to the Oliver & Pharr method, the indentation hardness and elastic modulus is sensitive to the maximum indentation depth $h_{\max}$ and unloading stiffness S. Both $h_{\max}$ and S are directly related to the deformation behavior in nanoindentation. As shown in Fig. 2b, the maximum indentation depth reduces from 287.1 nm to 239.6 nm, indicating an enhanced densification area and shear transform zones (STZs) under the indentation region. An ascending trend of the unloading stiffness appears with increase of nominal strain rate from 1086 N m^{-1} to 1763 N m^{-1}, which represents the reductions of elastic deformation in the high strain rate loading process.

To illustrate the influence of energy dissipation at the different nanoindentation strain rates, areas under the loading and unloading curves were integrated to determine the work of plastic and elastic deformation. Fig. 3 shows the plasticity indices and elasticity indices for PEEK at different indentation strain rates, using Eqs. (5) and (6). All the plasticity indices and elasticity indices range from 0 to 1, demonstrating the typical elastic-plastic characteristic. The plasticity index rapidly increased from 0.553 to 0.640 at low strain rate (<0.037 s^{-1}) and kept stable at the following strain rate. The elasticity index shows the opposite trend, indicating a growth of plastic deformation ratio in the loading process. These results demonstrate that low strain rate in nanoindentation tests can cause less plastic deformation and energy dissipation under the indentation region, and influence the hardness and modulus values significantly. The possible reasons may be as follows: (i) low strain rate of the loading process provides the polymer enough time to transfer and release the stress from the initial contact area to a deeper and wider region under the indenter; (ii) some time-dependent behavior, such as stress relaxation, exists and decreases the inhomogeneous shear flow stress.

Fig. 4a and 4b show the profiles obtained from the residual indentation morphologies through the horizontal and vertical directions, with nanoindentations performed at 0.25 s^{-1} nominal strain rate. Here, the width and height of 'pile-up' in Fig. 4a is around 300 nm and 35 nm, respectively, narrower but higher than the similar area showed in Fig. 4b. This can be attributed to the x