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Test Procedure

Polishing effect on nanoindentation behavior of nylon 66 and its nanocomposites

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Abstract

The effect of polishing on the near-surface mechanical properties of nylon 66 (PA66) and its clay nanocomposites has been investigated by a nanoindentation technique. The results show that polishing has significantly reduced the uncertainty in determining the surface property when performing nanoindentation experiments. In addition, polishing does not introduce serious strain hardening to a non-filled PA66 system, probably indicating that the polishing effect could be ignored for homogeneous polymer systems. For heterogeneous systems, especially for the injection-molded systems reinforced by nanofiller, polishing tends to expose the inner part of the sample, which may possess slightly different properties from that of the surface layer.

Keywords: Nylon 66; Nanocomposites; Polishing; Nanoindentation

1. Introduction

Recently, the indentation technique has been used extensively to study the mechanical properties of polymers as well as their composite systems [1,2]. This technique can provide the near-surface mechanical properties of the materials, such as elastic modulus and hardness, through the localized deformation on the materials' surface by a hard indenter [3,4]. For example, the indentation technique is useful in interrelating a material's microstructures and its mechanical behavior due to processing-induced inhomogeneous distribution of crystalline morphologies [5]. Most recently, indentation has been successfully employed to investigate the mechanical behavior changes in polymer nanocomposites incorporating nanofillers such as clay [2,6] and multi-walled carbon nanotubes [7,8].

One of the key factors affecting the indentation results is the surface condition of the polymeric material, which can lead to inaccuracy of the measurements of modulus and hardness [9]. Polishing is one of the solutions to eliminate the processing-induced rough surfaces and, hence, to reduce the errors in determination of hardness and modulus. However, it is well known that polymers have prominent strain-hardening behavior, which may be induced by polishing. Hence, the near-surface properties of the materials at the sub-micron level may be affected by the polishing process. In the present study, the polishing effect on the nanoindentation behavior of nylon 66 and its clay nanocomposites has been evaluated and the difference in indentation response between neat resin and the nanocomposites have been comparatively studied.

2. Experimental

2.1. Sample preparation

Nylon 66 (PA66) pellets (EPR32, with relative viscosity of 3.2) used in this study were kindly provided by China

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Shenma Group Co. Ltd. Organoclay, Nanomer® I.34TCN (from Nanocor, Inc., USA), is a surface modified montmorillonite mineral with a mean particle size of 16–22 μm, which is specifically designed for extrusion compounding and is usually used in nylon 6 and nylon 66 systems [10].

PA66 and its nanocomposites with 1, 2 and 5 wt% of clay were prepared by melt-compounding using a Brabender twin-screw extruder at 280 °C with a screw speed of 180 rpm, followed by pelletizing. The pelletized materials were dried and injection molded into rectangular bars with dimension of $12.5\times6.5\times160$ mm^3. The detailed studies on preparation, structure/morphology, thermal and mechanical properties of PA66/clay nanocomposites have been reported elsewhere [11]. The specimens were then cut into small pieces suitable for nanoindentation tests. One set of as-molded specimens were used for nanoindentation testing directly, while the other set of samples were polished using SiC paper in order to remove or eliminate the processing-induced defects or other artifacts (till no discernible scratches were observed under an optical microscope). The polished depth was controlled to be less than 500 μm. All the samples were dried in a vacuum oven at 60 °C for about 24 h before testing and the indentation loading direction was perpendicular to the injection flow direction.

2.2. Nanoindentation measurements

The nanoindentation technique was employed to evaluate the material's mechanical properties including modulus and hardness. The indentation load-hold-unload sequence was performed on a MTS NanoXP® (MTS Cooperation, Nano Instruments Innovation Center, TN, USA) with a continuous stiffness measurement (CSM) technique [5,6,9]. In this technique, an oscillating force with known frequency and amplitude is superimposed onto a nominal applied force. The material, which is in contact with the oscillating force, responds with a displacement phase and amplitude. The material stiffness (S) and damping (ωC) under indentation loading can be calculated using Eqs. (1) and (2), respectively. The hardness and elastic modulus are calculated using stiffness data from Eqs. (3) and (4), respectively. Therefore, the hardness and modulus are determined as a function of indentation depth with a single loading/unloading cycle.

$$S = \left[\frac{1}{\frac{P_{max}}{h(\omega)}\cos\Phi - (K_s - m\omega^2)} - K_f^{-1}\right]^{-1} \tag{1}$$

$$\omega C = \frac{P_0}{h(\omega)}\sin\Phi \tag{2}$$

$$\frac{E}{1-\nu^2} = \frac{\sqrt{\pi}}{2}\frac{1}{\sqrt{A_c}}S \tag{3}$$

$$H = \frac{P_{max}}{A_c} \tag{4}$$

where P_{max} and $h(\omega)$ are driving force and the displacement response of the indenter, respectively; Φ is the phase angle between P_{max} and $h(\omega)$; m is mass of the indenter column; K_s is spring constant in the vertical direction; K_f is frame stiffness. m, K_s and K_f are all constant values for the specified indentation system, ω is angular speed which equals $2\pi f$; f is the driven frequency of the AC signal, ν is Possion's ratio and set to be 0.35 for the present analysis [5], and A_c is the contact area at the moment the material is in contact with the indenter under load P_{max}.

A three-side pyramid (Berkovich) diamond indenter was employed for the indentation experiments. The area function, which is used to calculate contact area A_c from contact depth h_c, was carefully calibrated using a standard sample, fused silica, before the experiments. The nanoindentation tests were carried out in following sequence: firstly, after the indenter made contact with the surface, it was driven into the material with constant strain rate, i.e. 0.05 1/s, to a depth of 5000 nm; secondly, the load was held at maximum value for 60 s; and finally, the indenter was withdrawn from the surface with the same rate as loading until 10% of the maximum load was reached. At least 10 indents were performed on each sample and the separation

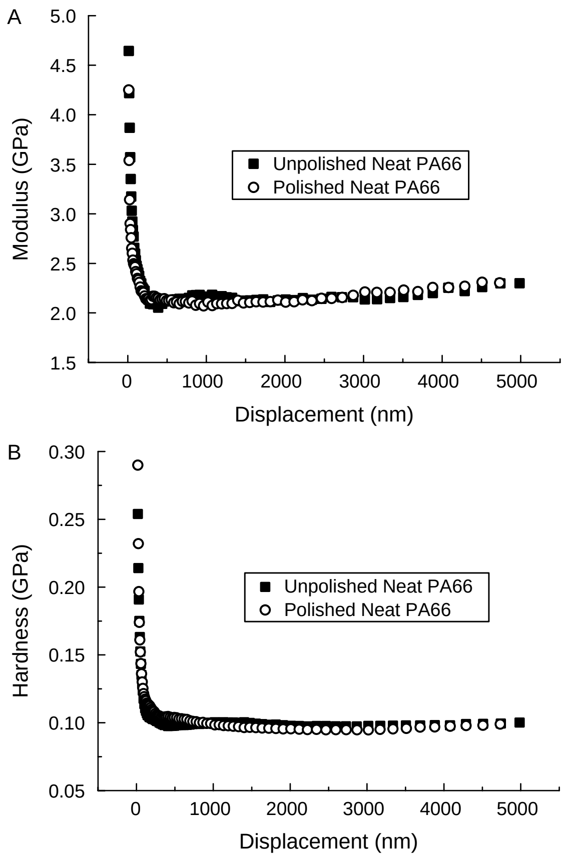

Fig. 1. Modulus (A) and hardness (B) profiles of unfilled PA66. (■) Unpolished samples; (○) polished samples.