Indentation properties of the filler and matrix in polymer composites

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The development of techniques for probing the mechanical properties of materials on the submicro scale has been made over the past few years [1, 2]. The advances have made possible the development of instruments that continuously measure force and displacement as an indentation is made [3, 4]. The indentation load-displacement data thus derived can be used to determine the hardness and elastic modulus even when the indentations are too small to be imaged conveniently. The indentation tests were also used to determine the interphase properties by measuring the hardness variation across the interface region [5]. In a commonly used method of indentation, data are obtained from one complete cycle of loading and unloading. According to a model on elastic contact problem, the unloading data can be analyzed and the hardness and elastic modulus of punched materials can be calculated. Owing to the fact that the unloading curves are sometimes nonlinear, an improved technique for determining hardness and elastic modulus has been proposed [6], by which the experimental results obtained with indentation tests were comparable with those obtained by other techniques.

In the case of loading-displacement curves as shown in Fig. 1, the initial gradient of the unloading curves is used to calculate the stiffness of the sample:

$$S = \frac{\mathrm{d}P}{\mathrm{d}h} \tag{1}$$

where h is the depth of penetration called displacement, P the measured load. The stiffness is then used to obtain the reduced elastic modulus [7]:

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

where A is the contact area ($A = 24.5h_c^2$) and $\beta = 1.034$ for a triangular indenter [8], h_c the contact depth of the indent.

The modulus of the indented material is now obtained from the following equation:

$$E_r = \left(\frac{1-v_i^2}{E_i} + \frac{1-v_s^2}{E_s}\right)^{-1} \tag{3}$$

where E_i, v_i are the elastic modulus and Poisson's ratio of the indenter tip (diamond) and E_s, v_s are the equivalent properties of the indented material. The modulus of elasticity for each indent is calculated with Poisson's ratio of the material obtained from the technical literature. The chosen Poisson's ratio and the diamond modulus are presented in Table I.

The hardness of materials calculated from an indent produced by a Berkovich tip can be obtained from the equation below:

$$H = \frac{P}{24.5h_c^2} \tag{4}$$

Glass beads (GB) filled high density polyethylene (HDPE) composites were used in this study. The glass

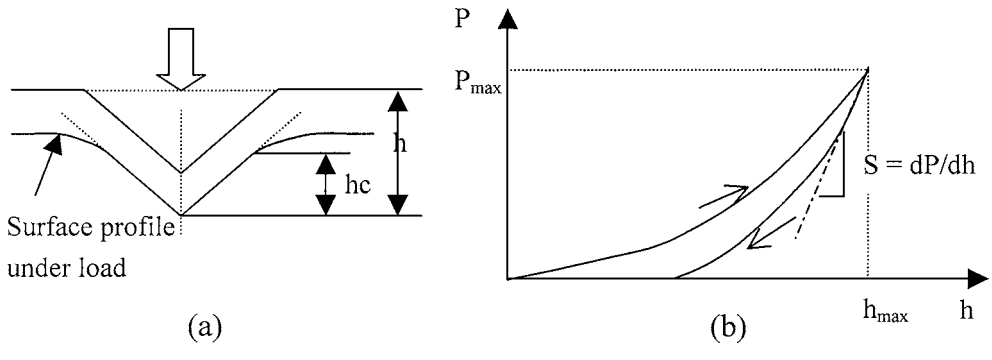

Figure 1 (a) Definition of depth and (b) load P-displacement h relation in indentation tests.

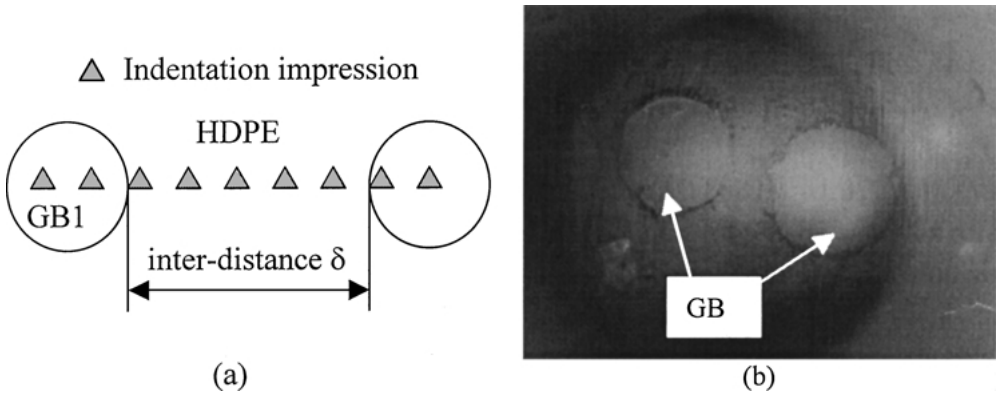

Figure 2 (a) The positions of indentation applied on the samples and (b) micrograph of polished sample.

TABLE I The elastic moduli and hardness measured by indentation tests and chosen Poisson's ratios

	Indenter	HDPE	Glass bead
v	0.07	0.40	0.22
H(GPa)		$0.11^{+45\%}_{-27\%}$	$6.85^{+28\%}_{-35\%}$
E(GPa)	1141	$1.98^{+39\%}_{-27\%}$	$52.01^{+28\%}_{-16\%}$
Contact diameter (nm)		∼110	∼80

beads were first coupled with titanate and then the mixture of GB and HDPE was put into the chamber of a high speed mixer and blended in a twin-screw extruder. The pelleted extrudate was injection molded into tensile samples.The GB volume fraction was 15%. The diameter of 500 glass beads was measured and varied from about 15 μm to 45 μm with maximum percentage at about 30 μm [9].

The monotonic tensile tests were carried out on a MTS810 with strain rates of 8×10^{-3}/s, 8×10^{-4}/s and 3×10^{-5}/s, respectively. The geometry of the tensile samples conformed to standard ASTM D638M. The indentation tests were undertaken with Nano-Indenter II made by Nano Instruments, Inc.. A detailed description of the instrument is available elsewhere [8]. A schematic presentation of the indentation positions on the samples is shown in Fig. 2a. Regions containing two glass beads were chosen to apply the indentation force across the matrix ligament. The inter-distances are 2 μm, 5 μm and 8 μm, respectively. The samples for indentation tests were cut from the tensile specimens and then polished before the tests.

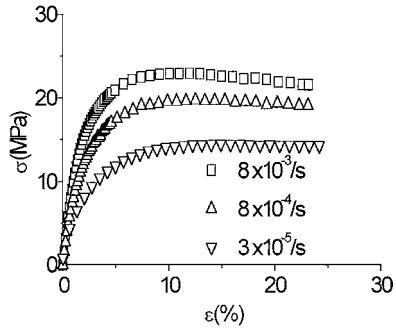

Figure 3 Tensile stress-strain curves under different strain rates.

The tensile σ-ε curves of GB/HDPE composites are given in Fig. 3. The strain softening appears more clearly and earlier for high strain rates. Here, the strain softening means that the tensile stress decreases with the strain, marked by the curve going down with the strain. Both tensile strength and Young's modulus increase with the strain rates.

Representative load-displacement curves of HDPE and GB are shown in Fig. 4. Each curve consists of the loading and unloading portions. The indent in glass shows a better elastic recovery due to its higher elastic modulus than HDPE. In totality, 18 indents were made on glass beads and 13 indents on HDPE. The elastic modulus and hardness were calculated with equations given previously. The average values are given in Table I.

The variation of elastic modulus and hardness with the indentation position is shown in Fig. 5. Because the thickness of the interface is too small to be sampled by the indenter, no evident changes of E and H values are observed across the interface region. Two points with medium E and H values are noted on Fig. 5. This is considered that the indents were applied on the matrix just in the proximity of the interface. The glass bead hinders the plastic deformation of the matrix, which results in the increase of the modulus and hardness compared to the pure matrix. A detailed study on the interface properties between the glass bead and HDPE of such material is presented in [9, 10].

An interesting comparison for elastic moduli of HDPE is made between tensile tests and indentation tests, as shown in Fig. 6, in which the horizontal axis represents two test methods (tension undertaken under three strain rates). It is noted from Fig. 6 that the indentation test gives a higher value of elastic modulus than that by tensile tests. In our opinion, one important factor resulting in the difference of moduli may be the effect of specimen size. The tensile modulus is measured on the available section of specimens. The volume of the section loaded by tension is much greater than the contact zone by indentation tests. Another possible reason is the loading rates. In the case of a tensile test with strain rate of 8×10^{-3}/s, the displacement rate

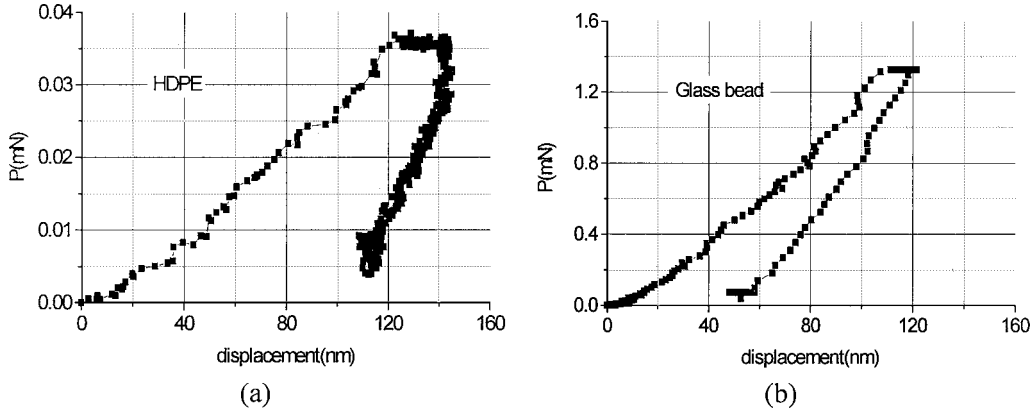

Figure 4 Load-displacement curves of (a) HDPE and (b) GB in indentation tests.

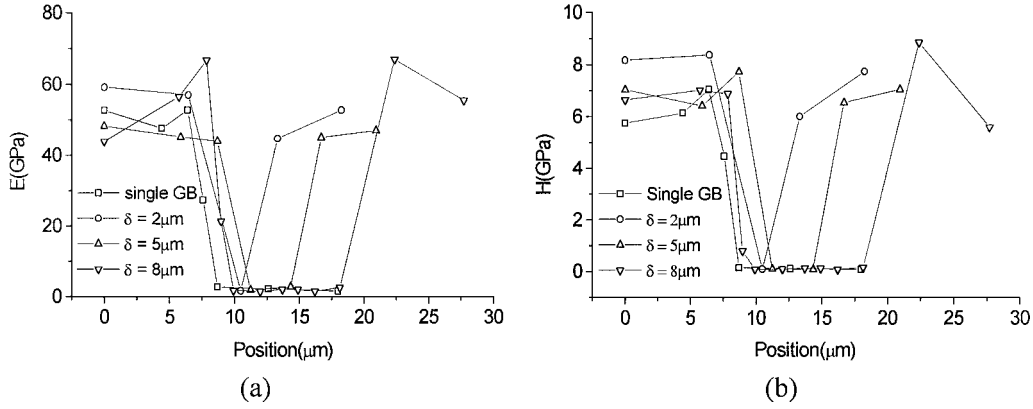

Figure 5 (a) Elastic modulus and (b) hardness variation with indentation position.

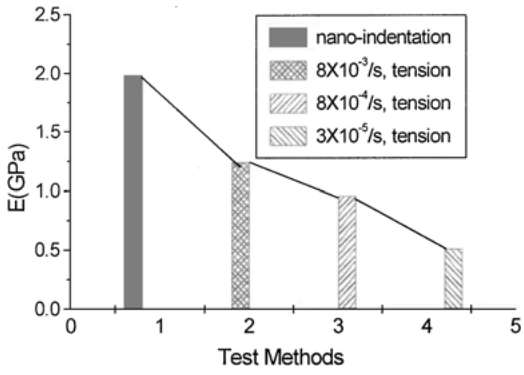

Figure 6 Comparison of elastic moduli of HDPE between tensile and indentation tests.

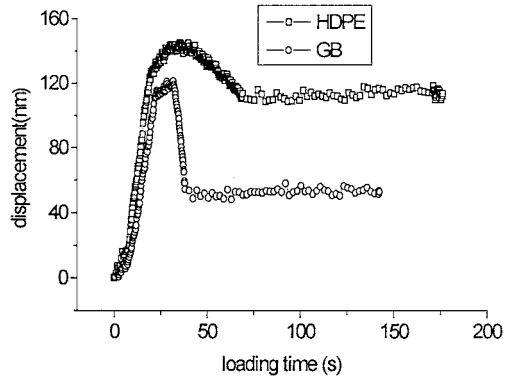

Figure 7 Time-displacement dependence of HDPE in indentation test.

is about 8×10^{-6}nm/s (5 mm/min). While for the indentation test, the indenter displacement rate is about 8 nm/s calculated from the initial loading stage of time-displacement curves shown in Fig. 7. Even though the rate of indenter displacement is not that of the material tested, the material around the indenter is probably loaded with greater loading rate than that by tensile tests. The specimen is extended under tensile tests, while the material around the indenter is compressed by indentation tests. This difference of deformation mechanisms may be the third reason for the different moduli.

From the study, the mechanical properties of the materials by nano-indentation should be well explained because they represent the properties in micro scale.

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