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Static and dynamic mechanical properties of polydimethylsiloxane/carbon nanotube nanocomposites

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ABSTRACT

The purpose of this study is to investigate the static and dynamic mechanical properties of polydimethylsiloxane (PDMS) and the mixture of PDMS and carbon nanotubes. The PDMS/CNT nanocomposites were stirred by an ultrasonic instrument to prevent agglomerations. The tested specimens of nanocomposites were manufactured by using the thermoforming method at 150 °C for 15 min. A micro tensile tester was adopted in this testing system with a maximum load of 500 mN and a crosshead extension of 150 mm. The static elastic modulus can be calculated by means of a tensile test and the average elastic modulus of pure PDMS is 1.65 MPa. In addition, the Nano Bionix tensile tester was also used to perform the dynamic mechanical analysis. Its dynamic frequency range is from 0.1 Hz to 2.5 KHz. The dynamic properties of PDMS/CNT nanocomposites such as storage and loss modulus can be obtained by this system. The storage modulus increased with the CNT content and also with the higher frequencies. Finally, the nanoindentation measurement system was employed to characterize the mechanical properties of PDMS and PDMS/CNTs. The measurement results of elastic modulus by a nanoindentation test have the similar trend with the results obtained by the tensile test method.

1. Introduction

Polydimethylsiloxane (PDMS) silicon-based organic polymer is composed of a repeating $[SiO(CH_3)_2]$ unit. It is in the rubber state at room temperature because it has a glass transition temperature of less than −120 °C. In addition, it possesses hydrophobic, non-conductive and bio-compatible properties and is applied in casting molds and micro-fluidic devices [1,2]. As is well known, carbon nanotubes (CNTs) were found by Iijima in 1991 [3]. CNTs exhibit excellent mechanical and electrical properties such as light weight, high stiffness, premium thermal conduction and electric conductivity. By micro-Raman spectroscopy, Lourie et al. [4] found that the Young's moduli of single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) were 3.58 TPa and 2.24 TPa, respectively when the temperature gradient was −122 K. In 1999, Salvetat et al. [5] showed that the Young's modulus of single-walled carbon nanotube was 1 TPa by using the transmission electron microscopy (TEM) technique.

In the meantime, many researchers [6–8] have also found that adding proper CNTs into polymers or epoxy resins can enhance the strength and elastic modulus of polymers. Allaoui et al. [7] added one weight percentage of MWCNTs to an epoxy resin and found that the Young's modulus and yield strength of nanocomposites had been doubled and tripled respectively, compared to the pure epoxy resin. In 2006, Yeh et al. [8] found that the tensile strength and Young's modulus of MWCNTs/phenolic composites increased with the addition of MWCNTs.

It was also found that the elastic modulus and strength of the PDMS/CNT nanocomposites were enhanced by adding MWCNTs [9]. However, there are fewer investigations of the dynamic behavior of PDMS/CNT nanocomposites. To comprehend the static and dynamic properties of these composites, the Nano Bionix universal testing system (MTS Systems Corp., Oak Ridge, TN, USA) was employed to analyze the elastic modulus, storage and loss modulus of PDMS/CNT nanocomposites. The testing system possesses the ability of continuous dynamic analysis (CDA) which is different from the traditional dynamic mechanical analysis (DMA). In addition, the nanoindentation technique [10,11] has been widely used to measure the mechanical properties of thin films in recent years. As a comparison, the elastic modulus of PDMS/CNTs polymeric nanocomposites can be determined by a commercial Nano Indenter. The TriboIndenter (Hysitron Inc., MN, USA) was adopted to characterize the mechanical properties of PDMS and nanocomposites.

2. Elastic, storage and loss modulus

The static elastic modulus (E) is the ratio of stress (σ) to strain (ε) within the range of elastic limit. The value can be obtained by

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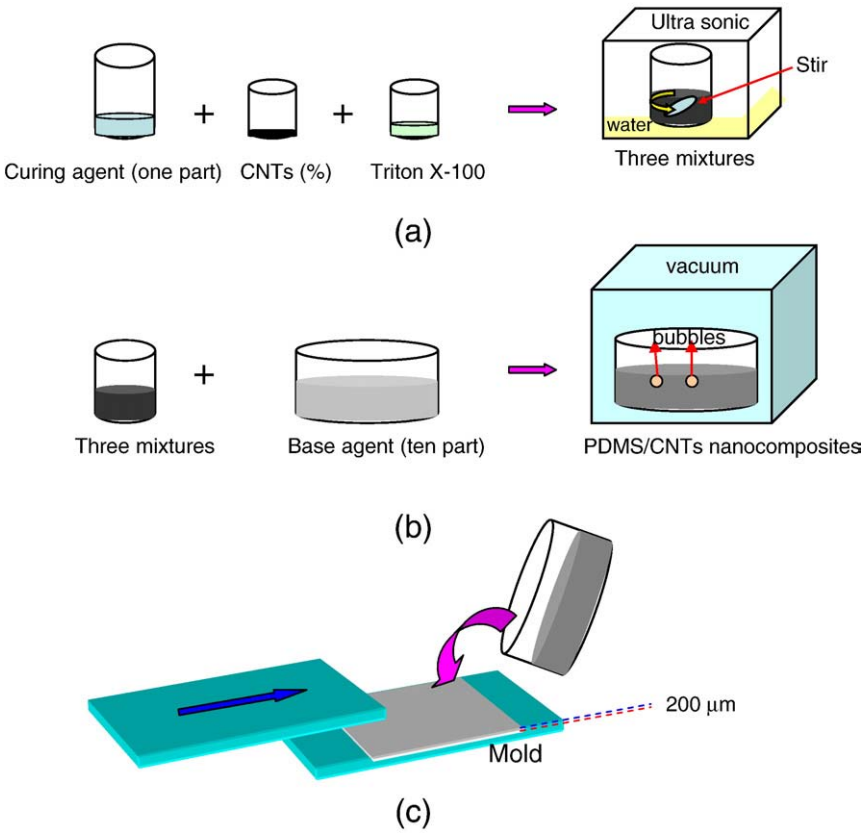

Fig. 1. Manufacturing procedure of the PDMS/CNT nanocomposites.

calculating the slope of the stress–strain curve resulting from the tensile test. For simplification, the engineering stress and strain was adopted to determine the elastic modulus in this study.

On the other hand, the dynamic behavior of PDMS/CNT nanocomposites was tested on the CDA option of Nano UTM by using a frequency sweep method. The complex modulus of the nanocomposites can be calculated from applying harmonic force and oscillation amplitude. If a linearly viscoelastic material is subjected to an oscillatory strain (input), then the dynamic strain (ε_d) is expressed as follows.

$$\varepsilon_d = \varepsilon_0 e^{i\omega t} \tag{1}$$

where ε_0 is the dynamic strain amplitude, ω is the frequency, and t is time.

Then dynamic stress (output) can be expressed as,

$$\sigma_d = \sigma^* e^{i\omega t} \tag{2}$$

where $\sigma^* = \sigma_0(\cos\delta + i\sin\delta) = \sigma_0 e^{i\delta}$, σ_0 is the dynamic stress amplitude, δ is the phase lag angle between strain and stress at the same frequency.

Substituting (1) and (2) into the general constitutive equation of the viscoleastic material,

$$[p_0 + p_1\partial_t + \ldots]\sigma_d = [q_0 + q_1\partial_t + \ldots]\varepsilon_d \tag{3}$$

In which p_0, p_1..., q_0, q_1 ... are material constants.

Then the ratio of the stress (σ^*) to strain (ε_0) can be defined as complex relaxation modulus $G^*(\omega)$ as follows,

$$G^*(\omega) = \frac{\sigma^*}{\varepsilon_0} = \frac{\left[q_0 + (i\omega)q_1 + (i\omega)^2 q_2 + \ldots\right]}{\left[p_0 + (i\omega)p_1 + (i\omega)^2 p_2 + \ldots\right]} \tag{4}$$

$$G^*(\omega) = \frac{\sigma^*}{\varepsilon_0} = \frac{\sigma_0}{\varepsilon_0}(\cos\delta + i\sin\delta) = G' + iG'' \tag{5}$$

Therefore, the real part of the complex relaxation modulus is called storage modulus $G' = \frac{\sigma_0}{\varepsilon_0}(\cos\delta)$ and the image part is called loss modulus $G'' = \frac{\sigma_0}{\varepsilon_0}(\sin\delta)$.

In addition, the ratio of storage to loss modulus can be defined as the loss tangent ($\tan\delta$),

$$\tan\delta = \frac{G''}{G'} \tag{6}$$

The storage modulus represents the elastic portion of stored energy and the loss modulus illustrates the dissipated energy of a material (i.e. viscous portion). The loss tangent is the ratio of elastic to viscous portion and would change with the storage and loss modulus.

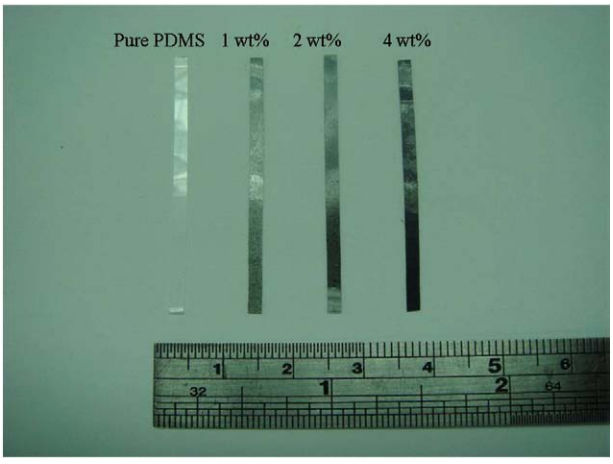

Fig. 2. The specimen of pure PDMS, 1.0 wt.%, 2.0 wt.% and 4.0 wt.% CNT nanocomposites.

3. Specimen manufacture and experiment instruments

3.1. Specimen manufacture

In this research, multi-walled carbon nanotubes (MWCNTs) with external diameters less than 10 nm and lengths of 1–2 μm were mixed with pure PDMS (Dow Corning Sylgard 184) consisting of a base and a curing agent. First, the curing agent was mixed with the CNTs and the surfactant Triton X-100, and then three mixtures were dispersed by magnetic stirring for 1 h and oscillated by ultrasonic waves for half an hour as shown in Fig. 1(a). Secondly, the base and curing agent were mixed with a 10:1 weight ratio, stirred in for 1.5 h, and then put into a vacuum state to remove the bubbles as shown in Fig. 1(b). Furthermore, a casting mold was used to define the thickness of the specimens. The thickness can be controlled in 200 μm scale. Shear force was applied to scrape the redundant materials on the mold and then a stable temperature was used on this mold in the vacuum system. The curing temperature was set at l50 °C for 15 min. The recipe was based on the finding that the higher curing temperature process resulted in better mechanical properties for PDMS/CNT nanocomposites [9]. Finally, the specimens were cut into pieces that were 2 mm wide and 200 μm thickness. The gauge length was 20 mm. There were four different kinds of specimens including pure PDMS, 1.0 wt.%, 2.0 wt.% and 4.0 wt.% CNT nanocomposites as shown in Fig. 2. It can be observed that the transparency of the specimens decreases with the content of the CNTs.

3.2. Experiment set-up and instrument calibration

The Nano Bionix UTM consists of a loading frame, moving crosshead, and a nanomechanical actuating transducer (NMAT) as shown in Fig. 3. It is performed with an extension range of 0 to 150 mm and a load range of 0 to 500 mN. To investigate the uncertainty of this machine, the standard weights and electronic balance were used to calibrate the force of Nano UTM. The standard weights can be traced back to International Prototype Kilogram (IPK). The precise electronic balance (WZ 215-CW, Sartorius) was used to calibrate the force of Nano UTM system. The relative expanded uncertainty of force measurement within the range of 0.1 to 200 mN is 5.0×10^{-3} with error of ~5%. The displacement measurement was calibrated by an optical interferometer system. The expanded uncertainty of displacement measurement within the range of 0 to 88 mm is 14 μm with similar accuracy [12]. The quasi-static tensile strength tests were conducted at a strain rate of 0.01 mm/mm/s for all specimens and the different dynamic frequencies were adopted in this research.

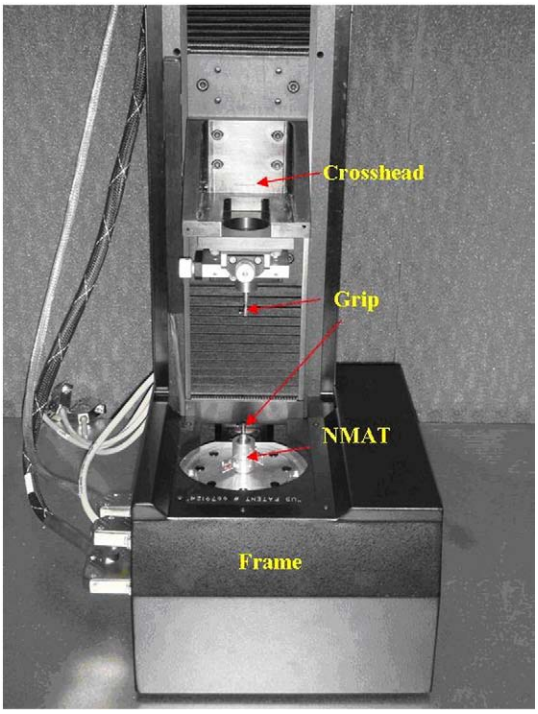

Fig. 3. The Nano Bionix® universal testing system.

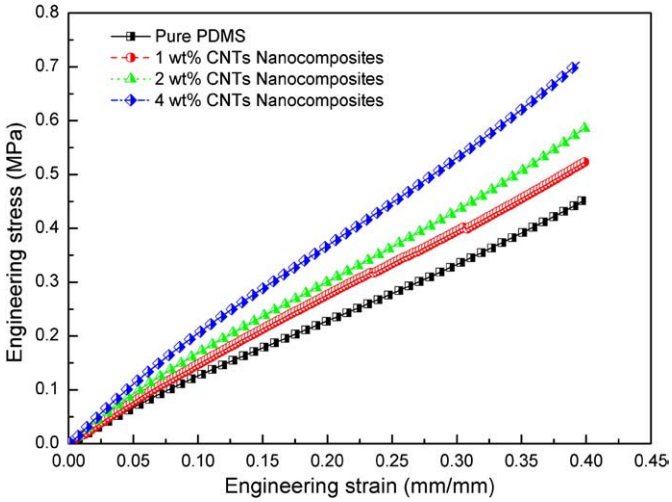

Fig. 4. The engineering stress–strain curves of pure PDMS and PDMS/CNT nanocomposites.

The TriboIndenter has a force resolution of 1 nN and a displacement resolution of less than 0.04 nm in out-of-plane direction. A traceable electronic balance and an optical interferometric system were also used to calibrate the forces and displacements of nanoindentation measurement system, respectively. A diamond tip of the Berkovich type was employed for the indentation test.

4. Results and discussion

4.1. Static results

For each kind of nanocomposite, the experiments were tested on at least five specimens. The elastic modulus of pure PDMS was calculated within the range of 0 to 0.05 mm/mm of strain and the average value was 1.65 MPa. Comparing with four types of specimens as shown in Fig. 4, it is found that the increase of elastic modulus is obvious after adding the CNTs in the PDMS matrix. The nanocomposites with high content of CNTs have better tensile strength when compared at the same strain. The average elastic modulus of 1.0 wt.%, 2.0 wt.% and 4.0 wt.% CNT contents were 1.71 MPa, 1.91 MPa and 2.34 MPa, respectively. In general, the elastic modulus of PDMS/CNT nanocomposites improved as the weight percentage of CNTs increased.

To analyze the fracture behavior of PDMS and PDMS/CNT nanocomposites, the specimens were also tested by the tensile tester (Instron 8848) at the same strain rate until failure. Compared with four different cases of SEM photo, the fracture surface of pure PDMS was very smooth as shown in Fig. 5(a). From Fig. 5(b), there was the defect on the fracture surfaces of 1 wt.% CNT nanocomposites because of CNT agglomeration. The fracture surfaces of 2.0 wt.% CNT nanocomposites were much rougher than PDMS and there were few voids and agglomerations of CNTs on the surfaces as shown in Fig. 5(c). The voids were caused as the agglomerations of CNTs were pulled-out. From Fig. 5(d), the single MWCNT on the fracture surface can be clearly observed as the content of CNTs reached four weight percentage. Although the voids and agglomerations increased with the content of CNTs, the good bonding between PDMS and CNTs as shown in Fig. 5(e) helped to improve the elastic modulus of PDMS.

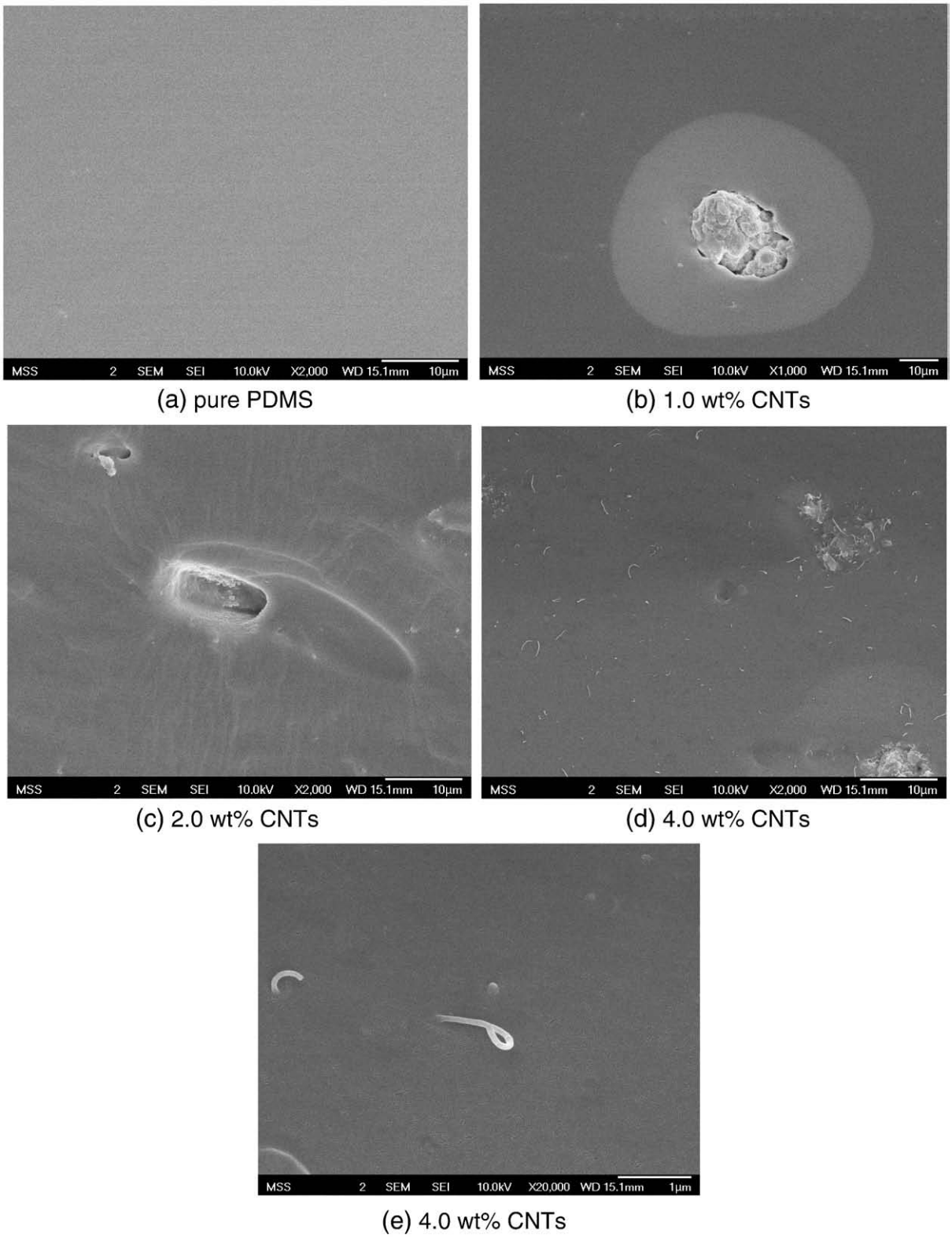

Fig. 5. Observations of the fracture surfaces of PDMS and nanocomposites with different CNT contents by scanning electron microscope. (a) The fracture surface of pure PDMS. (b) The fracture surface of 1.0 wt.% PDMS/CNT nanocomposites. (c) The fracture surface of 2.0 wt.% PDMS/CNT nanocomposites. (d) The fracture surface of 4.0 wt.% PDMS/CNT nanocomposites. (e) SEM image shows the good bonding between CNTs and PDMS matrix.

4.2. Dynamic results

The pure PDMS was tested by a constant force amplitude 4.5 mN and tension trigger of 1000 μN with different frequencies. The dynamic tests were conducted at a strain rate of 0.01 mm/mm per second. The frequencies of 10, 20 and 40 Hz were used in this study. Fig. 6 shows the results of storage modulus, loss modulus and loss tangent, respectively. Since the tests were performed on a continuous dynamic analysis under high frequency, the peak at about 1% strain was caused by environmental noise in the case of

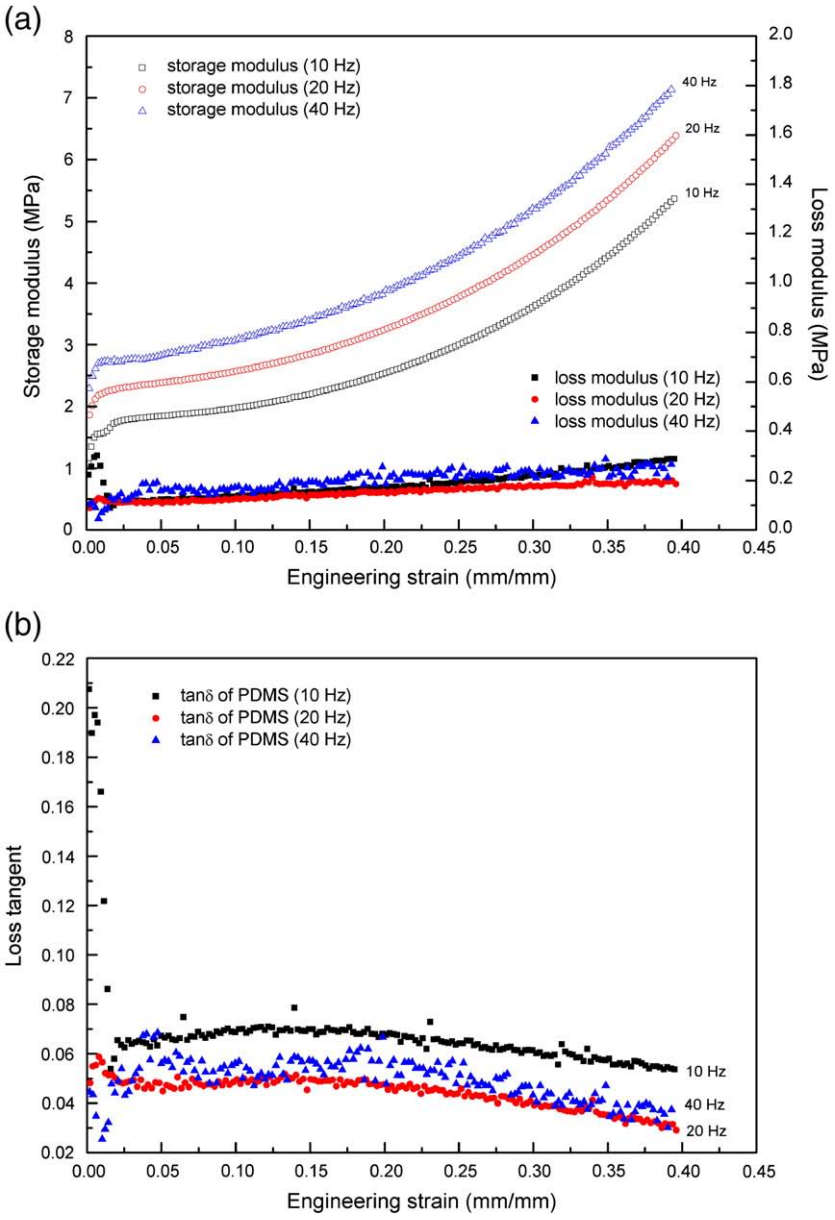

Fig. 6. The storage modulus, loss modulus and loss tangent of pure PDMS subjected to different loading frequencies. (a) The storage and loss modulus varied with engineering strain. (b) The loss tangent varied with engineering strain.

10 Hz. As shown in Fig. 6(a), it is clear that the storage modulus increased with the frequency, and the loss modulus showed no significant change. In addition, the loss tangent of pure PDMS decreased at a high frequency as shown in Fig. 6(b).

Comparing the four different specimens at the test condition of 40 Hz, the storage modulus of PDMS/CNT nanocomposites increased with the content of CNTs as shown in Fig. 7(a). From the results of loss tangent as shown in Fig. 7(b), the variance of loss tangent in pure PDMS and PDMS/CNT nanocomposites is small when considering the error of loss modulus. The addition of CNTs into the PDMS matrix showed no apparent effect on the viscoelastic behaviour of PDMS.

4.3. Nanoindentation results

The experiment was tested in the displacement control and the maximum depth of indentation was 1 μ m. The elastic modulus of the specimen, E, can be determined from the reduced modulus, E_r. The reduced modulus (E_r) was defined as,

$$E_r = \frac{\sqrt{\pi}S}{2\beta\sqrt{A}} \tag{7}$$

where β is a constant that depends on the geometry of the indenter, the elastic contact stiffness S and the projected area A.

The elastic modulus of the specimen, E, can be determined from the reduced modulus, E_r,

$$\frac{1}{E_r} = \frac{\left(1-\nu^2\right)}{E} + \frac{\left(1-\nu_i^2\right)}{E_i} \tag{8}$$

where ν is the Poisson's ratio for the testing material. E_i and ν_i are the elastic modulus and the Poisson's ratio of the material of indenter,

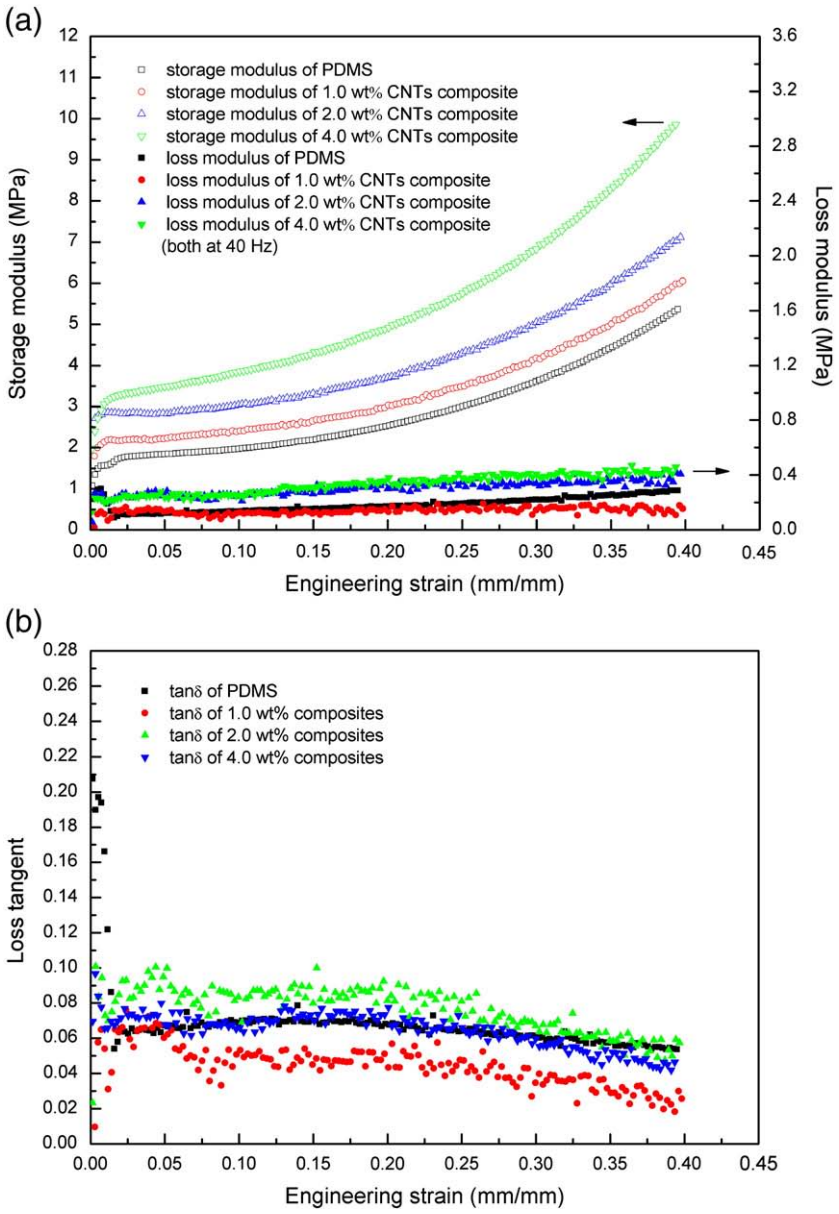

Fig. 7. The storage modulus, loss modulus and loss tangent of PDMS and nanocomposites with different CNT weight percentages at a constant loading frequency of 40 Hz. (a) The storage and loss modulus varied with engineering strain. (b) The loss tangent varied with engineering strain.

respectively. In the experiments of this study, $E_i = 1141$ GPa and $\nu_i = 0.07$ are used for the diamond tip.

Hence, the results of pure PDMS and 4.0 wt.% are shown in Table 1 and Fig. 8. From Fig. 8, it is obvious that the slope of the unloading curve from a nanoindentation of a nanocomposite is higher than pure PDMS. After adding the 4.0 wt.% CNTs into polymer matrix, the reduced modulus (E_r) and hardness of PDMS/CNT nanocomposites are higher than pure modulus. The average reduced modulus of pure

Table 1
The results of reduced modulus and hardness of pure PDMS and 4.0 wt.% CNT nanocomposites.

Specimens	Reduced modulus E_r (MPa) (PDMS)	Hardness H (MPa) (PDMS)	Reduced modulus E_r (MPa) (PDMS/CNTs)	Hardness H (MPa) (PDMS/CNTs)
Test-1	7.883	1.539	8.36	2.834
Test-2	6.709	2.11	8.677	2.736
Test-3	6.155	2.051	8.722	2.996
Test-4	6.428	2.929	8.829	2.617
Test-5	5.691	1.775	9.124	2.832
Test-6	5.868	1.911	8.508	2.68
Test-7	6.24	1.65	9.045	2.525
Test-8	5.784	1.855	8.755	2.844
Test-9	6.319	2.17	8.373	2.937
Test-10	9.594	3.689	10.716	2.607
Average	6.667	2.168	8.911	2.761
STDEV	1.204	0.658	0.683	0.153

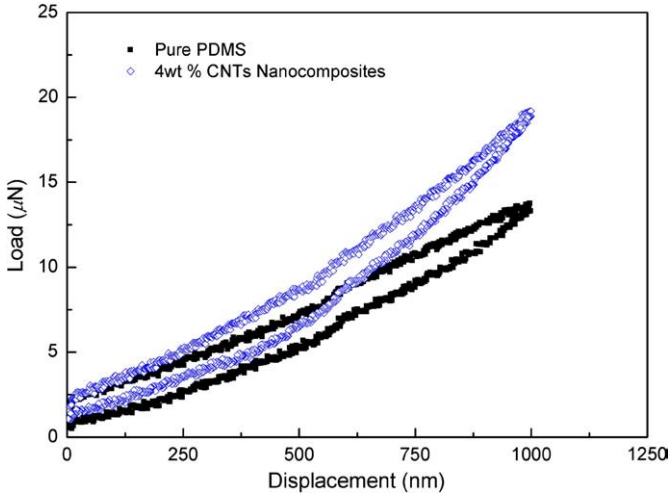

Fig. 8. Load–displacement curves of indentations made at a maximum depth of 1 μm on pure PDMS and 4 wt.% CNT nanocomposite.

PDMS and 4.0 wt.% CNT nanocomposites were 6.67 MPa and 8.91 MPa, respectively. The average hardness of pure PDMS and 4.0 wt.% CNT nanocomposites were respectively 2.17 MPa and 2.76 MPa. The increase of hardness was 21.38% after adding 4.0 wt.% CNTs. From reference [13], it was found that the Young's modulus and hardness values by using Oliver–Pharr method would be overestimated because of material pile-up, substrate effect and so on. The similar results were presented in this study. Compared with the pure PDMS and 4.0 wt.% PDMS/CNT nanocomposites, the increase in elastic modulus of pure PDMS after adding 4.0 wt.% CNTs is 29.49% by tensile test. By using nanoindentation test, the increase is 25.15%. The variations of increase are similar for both of these methods.

5. Conclusions

The static and dynamic mechanical properties of PDMS and PDMS/CNT nanocomposites were studied experimentally by Nano UTM. It can be concluded that the elastic modulus of PDMS/CNT nanocomposites increased obviously when 2.0 wt.% CNTs were added into the PDMS matrix. The storage modulus increased with the CNT content and also with the higher frequencies. Transformation of the viscoelastic behaviour of PDMS by adding the CNTs into the polymer matrix was not observed. The specimens of 4.0 wt.% PDMS/CNTs possess the higher hardness than pure PDMS. The measurement results of elastic modulus by nanoindentation test have the similar trend with the results obtained by the tensile test method.

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