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Dynamic mechanical analysis of silicone rubber reinforced with multi-walled carbon nanotubes

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Abstract. The dynamic mechanical behavior of silicone rubber reinforced with multi-walled carbon nanotubes (MWCNTs) has been investigated in this study. The MWCNT-reinforced nanocomposites are tested in compression mode through dynamic mechanical analysis (DMA). Multiple effects including MWCNT loading, testing frequency, dynamic strain amplitude, and pre-strain level are taken into consideration. Results show that, by adding 5 wt% of MWCNTs, the dynamic stiffness and damping coefficient of the silicone rubber are significantly enhanced. It is further observed that the dynamic mechanical properties of the nanocomposites are sensitive to dynamic strain amplitude but only slightly affected by pre-strains.

Keywords: nanocomposites; carbon nanotubes; mechanical behavior; damping.

1. Introduction

Due to their extremely high stiffness and aspect ratio with low density, carbon nanotubes (CNTs) as mechanically reinforcing fillers for polymers are extensively studied in the last decade (Thostensen *et al.* 2001, Odegard *et al.* 2002, McNally *et al.* 2005, Moniruzzaman and Winey 2006, Hussain *et al.* 2006, Coleman *et al.* 2006a, 2006b, Sato and Shima 2009, Spitalsky *et al.* 2010). Compared with matrix polymers, CNT-reinforced composites have shown dramatic improvement in stiffness, strength, and damping properties, although the strain at failure is usually decreased. It is believed that the small size and high aspect ratio of CNTs leads to dramatic increase in surface area, hence a significant volume fraction of strong interfacial region, which renders the polymer nanocomposites great enhancement in modulus and strength even with tiny amount of nanofillers (Bansal *et al.* 2005, Ramanathan *et al.* 2005, Schadler *et al.* 2007). Meanwhile, the widely accepted explanation of increased damping is the energy dissipation due to interfacial debonding and sliding between CNTs and polymer matrix (Zhou *et al.* 2004, Suhr *et al.* 2005, Suhr and Koratkar 2008). Good dispersion and functionalization of CNTs in polymer matrix are challenging tasks and critical to reinforcing effects, and the processing methods are summarized by Xie *et al.* (2005).

However, most researches on polymer nanocomposites focus on stiff polymer matrix such as epoxy and thermoplastics, while only a few are dealing with CNT-reinforced elastomers (Frogley *et al.* 2003, Bokobza and Kolodziej 2006, Kim *et al.* 2006, Bokobza and Belin 2007, Cantournet *et al.*

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2007, Park *et al.* 2007, Blighe *et al.* 2008, Das *et al.* 2008, Unnikrishnan *et al.* 2008, Guo and Sluys 2008, Bokobza 2009, Perez *et al.* 2009, Cataldo *et al.* 2009). Filled rubber and elastomers are often associated with large deformation and always of great industrial importance. The reinforcing mechanisms with conventional fillers such as carbon blacks and silica are well learned (Wang 1999, Heinrich and Kluppel 2002, Heinrich *et al.* 2002). Among the limited studies on elastomer-based nanocomposites, it is mostly observed through dynamic mechanical analysis (DMA) that the addition of a small amount of CNTs greatly improves the dynamic mechanical properties of the matrix elastomers, and by tensile tests increased strength accompanied by reduced ductility is found. The strain sensitivity of dynamic properties, or Payne effect, is also discovered as in the conventional filled elastomers. However, Park *et al.* (2007) find the storage modulus of silicone rubber is substantially reduced at very low multi-walled CNT (MWCNT) loadings up to 0.7 wt%. Cantournet *et al.* (2007) find that the failure strain for MWCNT-reinforced elastomers in greatly increased by over 40% at the MWCNT loading range from 2.6 wt% to 12.2 wt%. Furthermore, Blighe *et al.* (2008) studied the reinforcing effects of very high SWNT loadings up to 75 wt% and drastic stiffness increase and ductility loss are observed together with moderate increase in strength.

In this paper, the less focused dynamic compression testing mode and pre-strain effect on MWCNT-reinforced silicone rubber are studied, in addition to the effects of frequency and dynamic strain amplitude at various MWCNT loadings. The good dispersion of MWCNTs in the silicone rubber matrix is achieved via a solution mixing method. DMA results are evaluated and the underlying mechanisms are discussed.

2. Experimental methods

2.1 Materials

The matrix material used in this study is Silastic® T-2 silicone moldmaking rubber (Dow Corning Corporation). This is a pourable translucent two-component material consisting of a base and a curing agent. The low viscosity helps uniformly distribute MWCNTs and avoid cavities in the specimens effectively. The MWCNTs are 95 wt% in purity, and have the diameter range of 20-40 nm and length range 10-30 μm (Cheap Tubes Inc.).

2.2 Specimen preparation

Nanocomposite specimens are fabricated with different MWCNT loadings: 0 wt% (pure silicone rubber), 1 wt%, 2 wt%, 3.5 wt%, and 5 wt%. The geometry of cylindrical specimens is 10 mm in diameter and 9.5 mm in height, following ASTM Standard D 5992-96 on dynamic testing of vulcanized rubber and rubber-like materials using vibratory methods.

To fabricate the nanocomposites, appropriate amount of MWCNTs are first mixed in acetone by a VCX 130 ultrasonic distributor (Sonics & Materials, Inc.) for 4 hours to disentangle MWCNT bundles. Silicone rubber base is then added in the suspension of MWCNTs and acetone, followed by another 2 hours of sonication. After that the mixture was heated using a hotplate to accelerate the evaporation of acetone. When no acetone remains in the mixture, silicone rubber agent is added into it followed by 30 minutes of mechanical stirring. Finally the composite melts are vacuumed to remove cavities and poured into molds to cure. The nanocomposite specimens are fully cured in one

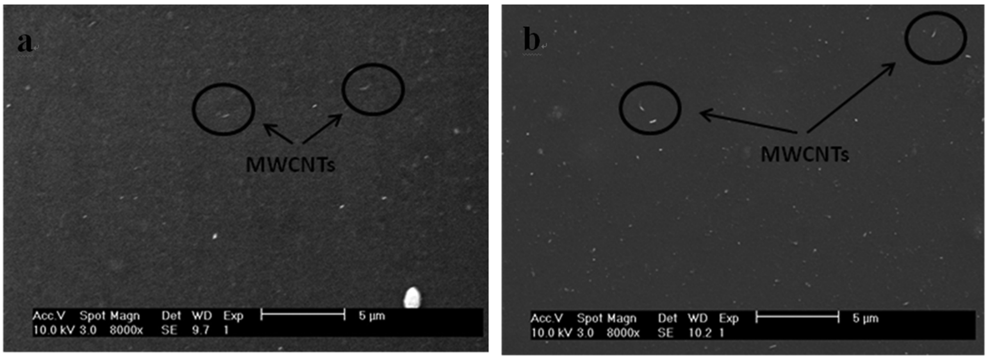


Fig. 1 Scanning electron micrographs of MWCNT-reinforced silicone rubber with MWCNT loadings of: (a) 1 wt% and (b) 3.5 wt%

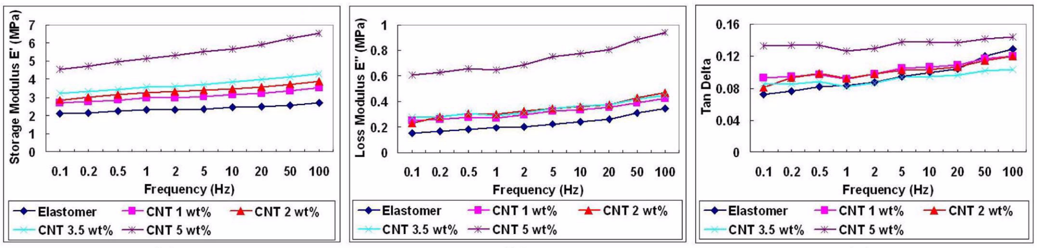
day. Scanning electron microscope (SEM) is used to evaluate the microstructures of the nanocomposites, and good dispersion of MWCNTs in the silicone rubber matrix is achieved as shown in Fig. 1.

2.3 Dynamic mechanical characterization

The dynamic mechanical analysis of nanocomposite specimens is implemented on ElectroForce® 3200 test system (Bose Corporation) at room temperature. The testing mode is dynamic compression with sinusoidal strain input. Both top and bottom surfaces of the specimen are lubricated so that lateral restriction is kept as minimum during the test, which would otherwise give wrongly higher modulus. The range of testing frequency is from 0.1 Hz to 100 Hz. To observe the effects of dynamic strain amplitude and pre-strain level on dynamic mechanical properties, strain sweep from 0.1% up to 10% is performed at 10 Hz and three different pre-strain levels: 2%, 5%, and 8%. Storage and loss Young's moduli and tan delta (loss factor) of specimens are then obtained.

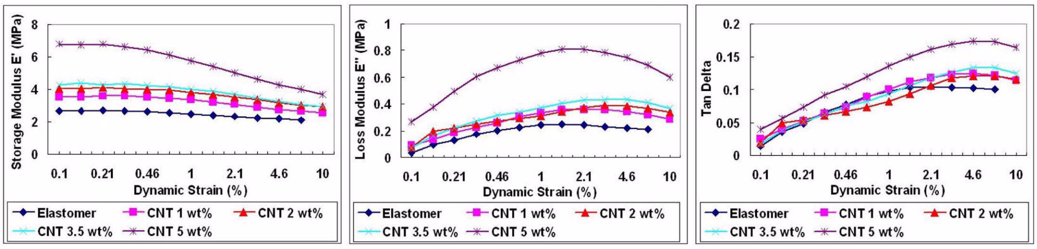
3. Results and discussion

The results of frequency sweep for all specimens from 0.1 Hz to 100 Hz are shown in Fig. 2. The dynamic strain amplitude and pre-strain level are 1% and 5%, respectively. The storage moduli (E'), loss moduli (E''), and tan delta of all specimens show upward trends when frequency increases, and continuing increasing frequency is expected to lead to further increasing storage moduli and decreasing loss moduli and tan delta past their peaks, which is the viscoelastic nature of silicone rubber and the nanocomposites. Although at MWCNT loadings below 3.5 wt% the reinforcements in all three dynamic mechanical properties are only moderate, there are great jumps when the MWCNT loading reaches 5 wt%. In addition to the well known interphase theory, which highlights the "bonus" interphase volume brought by the extremely small size and high aspect ratio of CNTs, the jump in dynamic stiffness may also be attributed to the filler networks formed by the MWCNTs and the entrapped silicone rubber. Especially at high loading, MWCNTs are more likely to form large three dimensional filler structures or so-called filler networks even well dispersed, due to their high aspect ratio and waviness. The entrapped silicone rubber is restrained from deforming hence



(a) (b) (c)

Fig. 2 DMA results of (a) storage modulus, (b) loss modulus, and (c) tan delta of all specimens in a frequency sweep from 0.1 Hz to 100Hz at 5% pre-strain and 1% dynamic strain amplitude



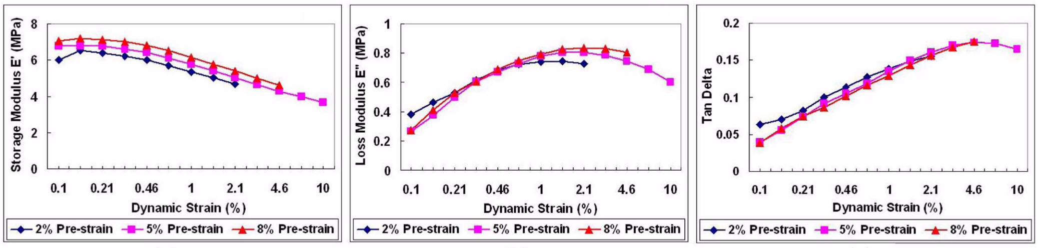
(a) (b) (c)

Fig. 3 DMA results of (a) storage modulus, (b) loss modulus, and (c) tan delta of all specimens in a dynamic strain sweep from 0.1% to 10% at 5% pre-strain and frequency of 10 Hz

further increases the effect volume of MWCNTs. Meanwhile, the additional energy dissipation due to breakdown and reformation of the filler networks during cyclic dynamic strain also leads to the jump in damping, asides from the interfacial sliding between individual MWCNTs and the matrix silicone rubber. Future tests will not be limited at room temperature and the master curves over a much wider frequency range will be obtained by repeating the frequency sweep above at different temperatures, based on the time-temperature superposition principle (Ferry 1980).

The dependence on dynamic strain amplitude of dynamic mechanical properties is investigated and the results are shown in Fig. 3. The dynamic strain sweep is from 0.1% to 10% at fixed pre-strain of 5% and frequency of 10 Hz. The storage modulus of nanocomposites decreases with increasing dynamic strain amplitude, while it exhibits little change for silicone rubber, as can be seen in Fig. 3(a). This effect is more pronounced at high MWCNT loading, showing a non-linear behavior. This phenomenon is referred to as Payne effect (Payne 1962), which has been extensively studied since 1950s especially for fillers of carbon blacks and silica (Lion 1996, Maier and Goritz 1996, Wang 1999, Heinrich and Kluppel 2002, Sternstein and Zhu 2002). The main reason for the Payne effect is that as dynamic strain increases, the breakdown of filler networks tends to release more formerly entrapped elastomer, resulting in decreased dynamic stiffness. This explanation is also applicable to CNT-filled elastomers since CNTs are easily to form filler networks. In rubber industry the Guth model (Guth and Gold 1938) and its derivations (Medalia 1972, Wolff and Donnet 1990) are commonly used for predicting reinforcement in elastomer stiffness by fillers, however they do not consider deformation amplitude and therefore are limited to small strain level. Phenomenological models are used to describe Payne effect, of which Kraus model (Kraus 1984) is the first and well known attempt.

Both the loss modulus and tan delta show increase and then decrease past their own peaks upon



(a) (b) (c)

Fig. 4 DMA of (a) storage modulus, (b) loss modulus, and (c) tan delta of MWCNT-reinforced silicone rubber with 5 wt% MWCNT loading in a dynamic strain sweep from 0.1% to 10% at frequency of 10 Hz and three different pre-strain levels

increasing dynamic strain amplitude, as shown in Figs. 3(b) and 3(c). This phenomenon is in accordance with the test results with carbon blacks as fillers, while different from those with silica fillers (Wang 1999, Sternstein and Zhu 2002), which is conceivable due to the chemical similarity between CNTs and carbon blacks. When dynamic strain increases starting from very low amplitude, the breakdown and reformation of filler networks are gradually initiated, causing growing energy dissipation. However, when dynamic strain continues increasing, a growing portion of filler networks are destroyed and lose the ability to reform. When the speed of the destruction is over the initiation of filler networks, the loss modulus starts to drop. Since the storage modulus decreases monotonically, as the ratio of loss modulus to storage modulus, tan delta first increases more rapidly and then starts to decrease at a higher dynamic strain level compared with loss modulus. It is noticed that pure silicone rubber also exhibit similar trend, which is probably due to the non-uniformly cross-linked microstructure.

Fig. 4 shows the effect of pre-strain level on the dynamic mechanical properties of the nanocomposites. Dynamic strain sweeps with frequency of 10 Hz are conducted at three pre-strain levels: 2%, 5% and 8%. Busfield *et al*. (2000) observed that the storage modulus, loss modulus and tan delta of carbon black filled natural rubber are not dependent on the pre-strain, based on tension tests. Similarly, in this study loss modulus and tan delta are also found not clearly dependent on the pre-strain level. However, it seems that higher pre-strain level leads to slightly higher storage modulus for each nanocomposite specimen over the entire dynamic strain sweep. The example shown in Fig. 4 is results of nanocomposite specimen with MWCNT loading of 5 wt%, while the results of the others show alike trends. This phenomenon may be accounted for by two possible reasons. One is the gradually increased tangent modulus within the test range from the non-linear stress-strain curve behavior of both silicone rubber and nanocomposites in compression. The other is that the modulus is calculated based on engineering stress, which is higher than the true stress in case of rubber compression with lubricated contact surfaces. An accurate explanation on the pre-strain effect is to be given upon further experimental studies with more considerations.

4. Conclusions

MWCNT-reinforced silicone rubber is investigated in this paper in compression mode through DMA. Dynamic strain amplitude has a significant effect on the dynamic mechanical behavior of the nanocomposites, which is similar compared with the observations from tension tests. Pre-strain level seems to affect the dynamic stiffness while the true reason is to be discovered. Results also show that the addition of 5 wt% of MWCNTs notably improves the dynamic stiffness and damping of the silicone rubber. It is suggested that the theory of filler networks in filled-elastomers well explains the dynamic mechanical behavior of CNT-reinforced elastomers at finite deformation, therefore is an important complement other than addressing distinct interphase and interfacial sliding in stiff polymer based nanocomposites.

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