Synthesis and Characterization of Dielectric Elastomer Nanocomposites Filled With Multiwalled Carbon Nanotubes

Dielectric elastomers (DEs) have been attracting great attention in the field of electromechanical actuation and sensing. In this paper, we develop a new type of silicone-based DEs by incorporating multiwalled carbon nanotubes (MWNTs) to the DEs as fillers. The dispersion of MWNTs during the material processing plays a significant role in deciding the final properties of the nanocomposites. In this work, acetone and ultrasonication along with characterization tools such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are utilized to examine the MWNT dispersion quality within DE nanocomposites. Furthermore, microstructural MWNT dispersion and filler–matrix interfacial bonding as well as the overall dynamic mechanical responses are investigated to reveal the correlation between them. It is concluded that the processing of DE nanocomposites strongly affects the dynamic mechanical properties, which can inversely provide with microstructural information for the nanocomposites.

Keywords: nanocomposites, carbon nanotubes, processing, dynamic mechanical analysis

1 Introduction

Polymeric composites filled with carbon nanotubes (CNTs) are promising materials demonstrating excellent thermal, mechanical, and electrical functionalities due to the unique properties such as high aspect ratio and high conductivity of CNTs. Traditionally, many research efforts have been conducted to utilize CNTs as fillers to reinforce the mechanical properties and increase the electrical conductivity of the polymeric composites [1–6].

Within the family of electro-active polymers (EAPs), DEs have been attracting great attention in the field of energy harvesting materials [7,8] as well as actuating materials for potential applications such as artificial muscles, capacitors, sensors, and even generators due to their high electromechanical efficiency, durability, stability, lightweight, low cost, and easy processing [8–12]. Pelrine et al. first demonstrated the potential of DEs [9,13,14] and developed models to describe the behavior of silicone-based DEs to seek the possibility to be used as actuators. They numerically showed how the Maxwell stress correlated with the electromechanical response of DE materials. An electromechanical response is the physical response of a mechanical system to electrical stimulation and vice versa. Despite the advantages of DEs, technical challenges must be resolved for wider applications. A high electric field of at least 10–30 V/μm is required for DEs to actuate, which hinders the practical applications especially in biomedical fields [8,15].

For wider applications, the required electric fields need to be reduced. In this paper, it is proposed to utilize CNTs as fillers to further improve performance of DEs [16–20] by enhancing the dielectric response of DEs. Among CNTs, MWNTs are commercially the cheapest and easiest to obtain in the market. Specifically, we aim to develop a new generation of silicone-based DEs by incorporating MWNTs to the DEs as fillers at low cost. The idea comes from that only a small amount of conductive CNT fillers can drastically increase the dielectric constant [21–23] while avoiding the unwanted increase of materials rigidity [23]. There have been efforts to implement ceramic powder DEs with high dielectric constants such as TiO$_2$ particles [24], BaTiO$_3$ nanoparticles [25–27], and PbTiO$_3$ [28,29]. However, high loading of these particles up to 20–30 vol. % are required for meaningful increase, at which the ceramic powders-filled composites can lose its flexibility, leading to limited improvement of the electromechanical response. Higher dielectric constant of nanocomposites brings more charges on the electrodes, resulting in larger deformation under the application of the electric fields. It is known that MWNTs in a polymer matrix can increase the dielectric constant, especially, around the electrical percolation threshold [21,30]. Charge accumulation occurs at the interface of DE matrix and MWNTs with different charge carrier relaxation time (Maxwell–Wagner effect) [31,32].

The critical challenge to enable DE nanocomposites filled with MWNTs, however, is the dispersion control of MWNTs inside polymer matrix. CNTs can easily form aggregates and bundles due to van der Waals force. Aggregation of CNTs can easily be the sites of electrical conduction paths and a source of cracks [33]. Moreover, these aggregates work as stress concentration and initiator of cracks. In the practical application, the thickness of the DEs is in the range of 50–200 μm [11,33]. The size of the MWNT aggregates, as we will see in Sec. 3.1, is in the similar range as the thickness of the DEs, which causes the DEs to fail. Thus, the dispersion of MWNT is the critical issue that needs attention for DE applications.

For the past decade, dispersion of CNTs has been under extensive investigations. CNTs surface functionalization [34–40] and the utilization of solvent [41–48] such as acetone and ketone have been attempted to improve the dispersion in polymer matrix as well. The selection of solvent has a significant influence on the dispersion of CNTs in elastomer matrix. Acetone is a simple polar organic solvent and a common chemical commodity. Acetone is...
utilized as a solvent to dilute the pure elastomer and reduce the viscosity during the fabrication process [47].

In this paper, synthesis and characterization of DE nanocomposites filled with MWNTs are studied. The techniques to disperse MWNTs are discussed. Furthermore, the damage to MWNTs due to the processing techniques is investigated. The correlation between the dispersion of MWNTs and properties of DE nanocomposites is revealed.

2 Materials and Method
Alumilite HS III RTV high-strength mold-making silicone rubber is chosen as the DE matrix. Acetone, from Fisher Scientific, is used as a solvent to help CNTs disperse in elastomers. MWNTs, purchased from Cheap Tubes,[2] are used as fillers in DEs. MWNTs have outer diameter 20–30 nm, inside diameter 5–10 nm, length 10–30 μm, and specific surface area 110 m²/g according to Cheap Tubes.

Figure 1 shows the flowchart of the DE nanocomposite processing steps. The fabrication process consists of the following seven steps: (1) grinding the pristine MWNT aggregates with a mortar and pestle, (2) stirring MWNTs in acetone solution by ultrasonic processor (Sonics & Materials, Inc., Newtown, CT, VCX 130) for hours, (3) pouring the elastomer matrix into the solution, (4) adding the curing agent once acetone evaporates and mixing the solution, and (5) vacuum degassing the mixture for minutes using MZ2C+2AK oil-free vacuum pump, (6) spin coating the materials to obtain thin film specimens with controlled thickness, and (7) pouring the materials to the mold. The curing process takes approximately 72 h.

Uniform dispersion of MWNTs in elastomer matrix can be a common challenge. Therefore, based on our previous development [49], grinding and solution mixing with ultrasonication are applied to break the van der Waals forces between MWNTs to minimize the formation of MWNT aggregates. Vacuum degassing is utilized to eliminate air voids in the cured material. DE Nanocomposite samples for mechanical testing are prepared by using the molding as shown in Fig. 1. The mold is in cylinder shape with diameter 9.5 mm and height 9.5 mm following ASTM Standard D 5992-96.

Next, spin coating technique is utilized to prepare nanocomposite films for electromechanical and dielectric property
measurement. The thickness of the films for DEs and DE nanocomposites is controlled to be about 150 μm by adjusting the revolution per minute (RPM) of the spin coater (Laurell Photoresist Spinner). The spin coating time is 40 s. Then the thickness of the film is measured by Digital Instruments Dektak 3 surface profiler.

After fabrication, each sample is observed by FEI Quanta three-dimensional FEG SEM. FEI/Philips CM-20 TEM is utilized to investigate the damage to MWNTs after the processing. Furthermore, mechanical properties of DE matrix and DE nanocomposites are characterized by dynamic mechanical analysis (DMA) to investigate the correlation with MWNTs dispersion. All the mechanical testing is carried out at room temperature of 24°C by BOSE ElectroForce 3200.

3 Results and Discussion

3.1 Minimizing the Size of MWNT Aggregates. The DE Nanocomposites with 0.3 wt.% MWNTs are examined to investigate the acetone effect. The pristine MWNTs are shown in Fig. 2. Due to the van der Waals forces, MWNTs naturally tend to form aggregates as shown in Fig. 2.

The nanocomposites processed with and without acetones are compared. Figure 3 shows SEM images of MWNT aggregates found in the nanocomposite processed without acetone. Various sizes of MWNT clusters are observed. The typical size of the observed aggregates is in the range of 10–50 μm. For application, the DE films are typically 50–200 μm in thickness; thus, aggregates with 10–50 μm in size could easily be the sites of electrical conduction paths and a source of cracks [33], causing the DEs to fail. Figure 4 shows SEM images of DE nanocomposites processed with acetone. The typical size of the MWNT aggregates is found to be 5–20 μm, which is smaller than that of aggregates
observed in the DE nanocomposites processed without acetone as shown in Fig. 3. This shows that the acetone is playing a crucial role in improving the dispersion of MWNTs. Acetone dilutes the elastomer and reduces the viscosity during the fabrication process, which enables easier mixing between the elastomer matrix and each MWNT. As a result, smaller size of MWNT aggregates is obtained.

Next, in order to further improve the dispersion of DE nanocomposites filled with MWNTs, ultrasonication is utilized. Ultrasonication is a technique to utilize high-intensity acoustic energy to mix and disperse materials [33]. Figures 5–7 show the dispersion of MWNTs before and after 0.5 h or 4.0 h ultrasonication. It is observed that aggregates of MWNTs still exist even with 0.5 h ultrasonication. However, as observed in Fig. 5, the typical size of MWNT aggregates is 3–8 μm, which is smaller than those observed in DE nanocomposites filled with 0.3 wt.% MWNTs processed without ultrasonication in Fig. 4. Figure 7 shows the typical DE nanocomposites after 4.0 h ultrasonication. As shown in Fig. 7, the aggregates are rarely observed in the DE nanocomposite processed with 4.0 h ultrasonication process, and uniformly dispersed individual MWNTs are observed.

It is also observed that the viscosity of DE matrix is significantly increased for the nanocomposites with 4.0 h ultrasonication than ones with 0.5 h ultrasonication [34]. This is due to the DE matrix–MWNT interaction, making the viscosity of DE nanocomposites higher than pure DE matrix. This is another indication that the dispersion of MWNTs is improved by longer ultrasonication technique.

Although ultrasonication significantly improves the dispersion of MWNTs in DE matrix, the damage is caused to MWNTs [33,50–53] because of the energy introduced by ultrasonication. It is reported that the aspect ratio strongly depends on the material processing, and 420, 80, and 8 are reported as MWNT average aspect ratio under different treatments even for the same type of MWNTs [52].

Here, TEM is utilized to investigate the aspect ratio of MWNTs after the processing. Figure 8 shows three typical images obtained from TEM. Based on images obtained from TEM as shown in Fig. 8, the typical length of MWNTs after 4.0 h ultrasonication ranges from 400 nm to 1 μm. This is significantly shorter than the pristine MWNTs with 20–30 nm in diameter, and 10–30 μm in length. This is most likely due to the lengthy time of ultrasonication, resulting in the breakage of MWNTs. Table 1 shows the calculated approximate aspect ratio of MWNTs. After the 4.0 h ultrasonication, the aspect ratio significantly dropped. Ultrasonication introduces shearing along the axis, causing failure between MWNTs at stresses much below the intrinsic properties of a single nanotube [54]. As a result, ends of each MWNT, for instance, are damaged and opened, leading to higher reactivity of MWNTs. Figure 8(b) shows an example of the probable damage to MWNTs.

3.2 Relationship Between the MWNT Dispersion and Mechanical Properties of Nanocomposites. Silicone-based DEs are viscoelastic in nature. Thus, dynamic mechanical analysis is
used to investigate the responses of DE nanocomposites with MWNT dispersions. The response of viscoelastic materials to a sinusoidal loading is usually represented by storage modulus, loss modulus, and \( \tan \delta \). Storage modulus represents the elastic portion and loss modulus represents the viscous portion. The value of \( \tan \delta \) represents the ratio of the dissipated energy over the stored energy, showing the damping capacity of the materials.

**Fig. 8** TEM images of MWNTs processed with acetone and 4.0 h ultrasonication treatment. (a)–(c) show different MWNTs.

**Table 1** Aspect ratio of MWNTs before and after processing

<table>
<thead>
<tr>
<th>Material</th>
<th>Diameter</th>
<th>Typical length</th>
<th>Typical aspect ratio</th>
</tr>
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<tbody>
<tr>
<td>Pristine MWNTs(^a)</td>
<td>20–30 nm</td>
<td>10–30 ( \mu )m</td>
<td>500</td>
</tr>
<tr>
<td>MWNTs after processing</td>
<td>20–30 nm</td>
<td>400 nm–1 ( \mu )m</td>
<td>20 (4.0 h)</td>
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\(^a\)Specifications provided by CheapTubes.com

**Fig. 9** Dynamic strain sweeps of DE nanocomposites filled with 0.3 wt.% MWNTs processed with acetone and ultrasonication: (a) storage moduli, (b) loss moduli, and (c) loss factors under compression loading. The test frequency is 10 Hz.

Figure 9 shows the dynamic mechanical analysis results of nanocomposites with 0.3 wt.% MWNTs at 10 Hz. The introduction of 0.3 wt.% MWNTs in elastomer matrix enhances the storage modulus of the DE nanocomposites. The specimen with 4.0 h
ultrasonication improves the storage modulus by about 25% at all the dynamic strain amplitude range while the specimen with 0.5 h ultrasonication also improves the modulus by around 11% at all the dynamic strain amplitude. This demonstrates that more load transfer under compression is enabled after longer ultrasonication. This is made possible by improved MWNT dispersion together with the higher reactivity due to the damages to MWNTs as discussed earlier, leading to the larger interaction area between DE matrix and MWNTs. As a result, higher storage modulus is obtained. It is worth pointing out that the well dispersed MWNTs significantly improve the storage modulus compared to poorly dispersed MWNTs due to the increased interaction between DEs and MWNTs. While MWNTs with lower aspect ratio decrease the storage modulus of nanocomposites compared with MWNTs with higher aspect ratio, there should be a competition between these two mechanisms of aspect ratio and dispersion of MWNTs. It is believed that uniform MWNT dispersion can play a leading role with respect to the increasing mechanical properties of nanocomposites.

It is also shown that the loss modulus and loss factor are increased with the longer ultrasonication. The 0.5 h ultrasonication increases the loss modulus up to 9% while the 4.0 h ultrasonication increases the loss modulus by 40%. Moreover, the 0.5 h ultrasonication increases the loss factor up to 15% while the 4.0 h ultrasonication increases loss factor by 20–25%. One possible reason behind this is related to the nature of bonding between DE matrix and MWNTs. Although improved dispersion enables the larger interaction area between DE matrix and MWNTs, the bonding between them is partially weak. As a result, energy loss by interfacial frictions between the MWNTs and elastomer matrix under dynamic mechanical loading becomes more significant as the interfacial area between MWNTs elastomers increases [55]. This phenomenon is not prominent for samples with 0.5 h ultrasonication compared to those with 4.0 h ultrasonication as the existence of aggregates significantly reduces the effective interfacial areas between the elastomer matrix and MWNTs. However, the DE nanocomposites processed with 4.0 h ultrasonication show the significant energy loss. Figure 10 shows the two-dimensional schematic image of the MWNTs and MWNT aggregates within DE nanocomposites. For simplicity, complex geometric features such as waviness [56,57] are not included. Dash lines in the figure show the interfacial area between DE matrix and MWNT aggregates. As the MWNT dispersion improves, interfacial area between DE matrix and MWNT aggregates is replaced by that between DE matrix and individual MWNTs, resulting in significantly more interfacial sliding and energy loss under dynamic mechanical loading. As a result, DE nanocomposites processed with 4.0 h ultrasonication shows larger loss modulus and loss factor.

In summary, dynamic mechanical analysis is a simple material characterization tool to study the dispersion of filler in DE nanocomposites. Along with characterization techniques such as SEM and TEM, DMA can be utilized to investigate the quality of DE nanocomposites and processing procedures.

4 Conclusions

Acetone and ultrasonication are demonstrated to be an effective approach to disperse MWNTs in DE matrix for dielectric elastomer nanocomposites. Acetone reduces the size of the aggregates and the viscosity of elastomer, resulting in improved mixing of DEs and MWNTs. Ultrasonication further improves the dispersion of MWNTs by adding energy to break the van der Waals force between each MWNT. Another important outcome of ultrasonication is the damage to MWNTs as mentioned earlier, resulting in shortened aspect ratio. Under dynamic mechanical loading, higher load transfer and larger energy dissipation are observed from the DE nanocomposites filled with MWNTs as a result of improved MWNTs in DE matrix. Dynamic mechanical properties of DE nanocomposites have been proven to be closely correlated with the dispersion of MWNTs. The increase of the storage modulus is associated with the enhanced elastic properties of DE nanocomposites due to the MWNT dispersion improvement. As the dispersion improves, more elastomer–MWNT interaction is enabled. As a result, more dynamic load can be carried due to the extended interfacial area between elastomer and MWNTs. The loss modulus and loss factor are associated with the nature of the bonding between elastomer and MWNTs. As the dispersion improves, more elastomer–MWNT interaction is enabled. Although interfacial
area elastomer and pristine MWNs increases, the weak bonding between two phases enables sliding. As a result, the friction is generated at the weak bonding sites when dynamic mechanical loading is applied.

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References


