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**Achieving polydimethylsiloxane/carbon nanotube (PDMS/CNT) composites with extremely low dielectric loss and adjustable dielectric constant by sandwich structure**

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**Abstract**

Sandwich-structured composites of polydimethylsiloxane/carbon nanotube (PDMS/CNT) bulk between two neat PDMS thin films with different thicknesses are prepared by spin-coating. Taking advantage of CNT's percolation in the matrix, the composite keeps the relatively high dielectric constant ( $\epsilon'=40$ ) at low frequency (at 100 Hz). Meanwhile, due to the existence of PDMS isolated out-layers which can limit the conductivity of the composite and consequently maintain the dielectric loss ( $\tan \delta=0.01$ ) extremely low (at 100 Hz). Moreover, the same matrix of out-layer and bulk can achieve excellent interfacial adhesion and the thickness of the out-layer can be controlled by multi-cycle coating. Then based on the experimental results, the simulation works combining the percolation theory and core-shell model are employed to analyze the thickness effect of the out-layer on  $\epsilon'$  value. Obtained relationship between the  $\epsilon'$  of the composite and the thickness of out-layer can help to optimize sandwich structure in order to obtain the composites with adjustable  $\epsilon'$  and extremely low  $\tan \delta$ .

**Key words:** low dielectric loss, sandwich structure

## 1. Introduction

Polymeric matrix composites with high dielectric constant ( $\epsilon'$ ) and low dielectric loss ( $\tan \delta$ ) are of great interest in energy storage and harvesting devices,<sup>[1, 2]</sup> especially for capacitor's materials in ocean renewable energies. Based on the requirement of the tube-rolled structure of the devices, it requires the material not only with high dielectric performances but also maintains high flexibility in order to adapt the flow of sea waves. Polydimethylsiloxane (PDMS) is one of the candidates due to the excellent flexibility, non-toxicity to the marine environment and low cost.<sup>[3-5]</sup> However, PDMS is a kind of polymer with isolated nature and originally low  $\epsilon'$  (lower than 3) which fails to meet the requirement of dielectric performance.<sup>[6, 7]</sup> Thus, developing PDMS matrix composites can be a promising alternative to solve the problem.

Generally, in light of filler's nature, the composites can be divided into two parts: one is the dielectric-dielectric (D-D) composites incorporated dielectric fillers such as ceramic fillers with high  $\epsilon'$  ( $\text{TiO}_2$ ,<sup>[8, 9]</sup>  $\text{ZrO}_2$ ,<sup>[10, 11]</sup>  $\text{BaTiO}_3$  (BT),<sup>[12, 13]</sup>  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO),<sup>[14]</sup>  $\text{Pb}(\text{ZrTi})\text{O}_3$  (PZT),<sup>[15, 16]</sup> etc). The other is the dielectric-conductive (D-C) composites incorporated conductive fillers as metal particles<sup>[17, 18]</sup> or carbon family materials (carbon black,<sup>[19, 20]</sup> carbon nanotube (CNT),<sup>[21, 22]</sup> graphene,<sup>[23, 24]</sup> etc). D-D composites usually need high filler contents (the volume fraction usually over 50%) for pursuing high  $\epsilon'$ . But a high content of fillers unavoidably decreases the flexibility of polymeric matrix. D-C composites can achieve high  $\epsilon'$  only with much lower filler's volume fraction based on the classic percolation theory,<sup>[25]</sup> which can maintain the flexibility of the matrix. However, the dielectric loss ( $\tan \delta$ ) near percolation threshold ( $f_c$ ) is extremely large caused by the strong interfacial polarization. Hence, a D-C composite with low  $\tan \delta$  ( $<0.05$  at 100 Hz) and adjustable  $\epsilon'$  ( $>35$  at 100 Hz) will be very interesting and attractive for different applications.

Many efforts and attempts have been made to address this issue and developing conductive fillers with the core-shell structure is a popular and effective method to decrease  $\tan \delta$  of the composite.<sup>[26]</sup> Due to the existence of shell structures, it enhances the interfacial adhesion between fillers and matrix as well as impedes the leakage current in the interfacial polarization of percolation. However, fillers with core-shell structures are not easy to prepare and well control in large amounts which limits the further applications and it is still necessary to find other simple ways. Recently, designing the dielectric composite with a special structure has aroused lots of

interest and attention. Among them, the sandwich structure is the most useful one,<sup>[27-31]</sup> but a potential problem among them should be the strength of the interfacial adhesion between two heterogeneous materials. Furthermore, the thickness of the out-layer is hard to control which makes difficult to evaluate the influence of out-layer's thickness. Therefore, in this study, we present a sandwich-structured PDMS matrix composite with controlled out-layer thickness. The conductive filler used is CNT due to its excellent electrical conductivity and well compatibility with PDMS which can lower  $f_c$  of the composite.<sup>[1, 35, 36]</sup> Then the composite with high  $\epsilon'$  and high  $\tan \delta$  is selected to be coated by thin films of PDMS respectively on sample's double surface. Due to the same matrix, the interfacial adhesion between the bulk part and out-layer is excellent after curing and the thickness of out-layer can be controlled by spin coating's condition. By adjusting the out-layer's thickness, its influence on the dielectric performance of the composite can be investigated not only by the experimental results but also by the simulation.

## **2. Experimental**

### **2.1 Materials:**

Liquid two-component PDMS (RT625) was provided by Wacker Chemie. The weight ratio of the siloxane based oligomer and the curing agent was 9:1. Multi-walled CNT (the commercial name: TNSM-5) was purchased from Timesnano Co. Chengdu, China. The out diameter of CNT is from 20 to 30 nm and the length is from 0.5 to 2  $\mu\text{m}$ . Its electrical conductivity is over 100 S/cm and the purity is over 98% (weight fraction).

### **2.2 Fabrication of PDMS/CNT composite:**

The preparation of the composites was as follows: first, CNT with calculated weight fraction was mixed into the siloxane base oligomers by the three-roll mill for 20 min at room temperature (25  $^{\circ}\text{C}$ ). Then the curing agent was dropped into the slurry and mixed manually. After 30 min degassing in the vacuum, the slurry was removed from molds for shaping and curing by hot press at 110  $^{\circ}\text{C}$  for 1 h.

### **Fabrication of the composite with multi-coating PDMS layers:**

The coating process for the selected sample was as follows: the mixture of the siloxane base oligomers and the curing agent was applied on one surface of the selected sample with the size of 10 mm  $\times$  10 mm. Then the coated sample was removed to a spin-coating machine to form a

thin film on sample's surface at the speed of 7000 r/min for 2 min. The further curing of PDMS was conducted in the oven under 110 °C for 30 min. When the sample cooled to room temperature, another PDMS film was coated on the other face by the same method. After coating on double surfaces respectively, the sample was concerned to have one cycle's coating. The multi-cycle coating would be done for one sample in order to obtain the PDMS layer with different thickness. The whole process procedure is presented in Figure 1.

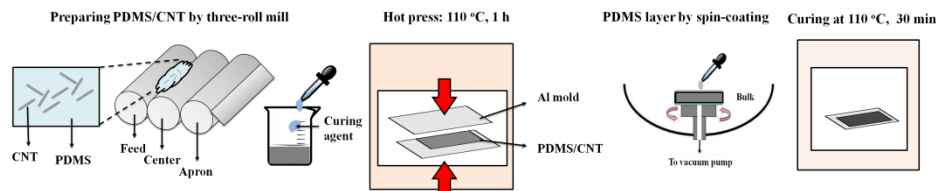


Figure 1 Schematic figure for preparation the PDMS/CNT composite with sandwich structure

### 2.3 Characterization:

The sample was tested by thickness gauge way on the iron plate (Surfix Pro, PHYNIX) to obtain different thicknesses after each coating's cycle and each time five points were tested on one plane for the average result. The dielectric properties of composites were characterized as a function of frequency by an impedance analyzer (Solartron 1260) at room temperature from 1 Hz to  $10^7$  Hz. After each cycle coating, the dielectric properties would be measured. Before the measurement, silver pastes were applied on both faces of the sample for reducing contacting resistance.

### 3. Results and discussions

At first, dielectric properties of samples with different CNT volume fractions are presented in Figure 2 (a) and (b), respectively. It can be found that as the volume fraction of CNT increasing, the values of  $\epsilon'$  and  $\tan \delta$  increase simultaneously which can be explained by the percolated behavior of forming micro-capacitors.<sup>[1, 25]</sup> The sample with 3.7% CNT volume fraction is selected for the studied sample since its highest  $\epsilon'$  and  $\tan \delta$  among other samples. The thicknesses of the sample before and after multi-cycle coating measured by the thickness gauge way are listed in Table 1 and the increased thickness is calculated by subtracting with the one before coating.

Averagely, the thickness of the layer on one face after each cycle by spin-coating is about  $41.83 \pm 12.96 \mu\text{m}$ .

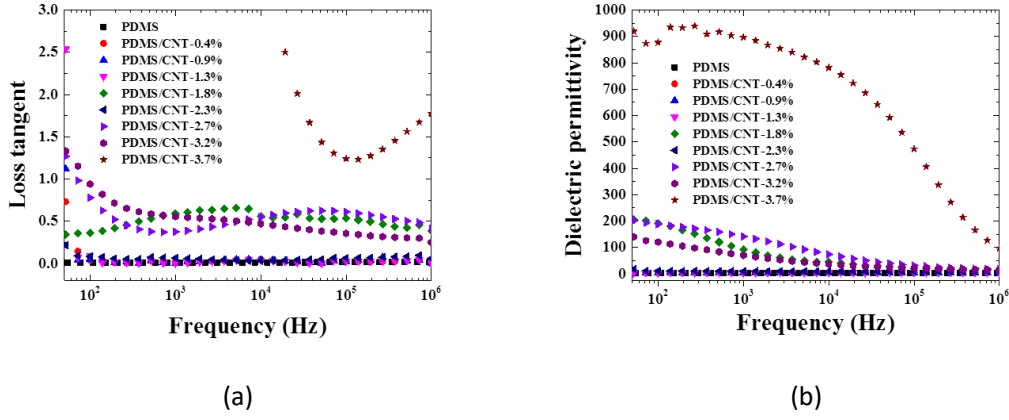


Figure 2 (a) Frequency dependence of dielectric properties with different  $f_{\text{CNT}}$  in the wide frequency range from 50 Hz to  $10^6$  Hz. (a) is for  $\tan \delta$ . (b) is for  $\epsilon'$ .

Table 1 Thickness of the sample before and after multi-cycle coating

PDMS/CNT-3.7%	Thickness of the sample (d) ( $\mu\text{m}$ )	Increasing thickness ( $\mu\text{m}$ )
Without coating	$687.5 \pm 38.9$	
1 <sup>st</sup> coating	$800.5 \pm 48.8$	$113 \pm 9.9$
2 <sup>nd</sup> coating	$875 \pm 40$	$187.5 \pm 17.7$
3 <sup>rd</sup> coating	$938.5 \pm 96.9$	$251 \pm 58$

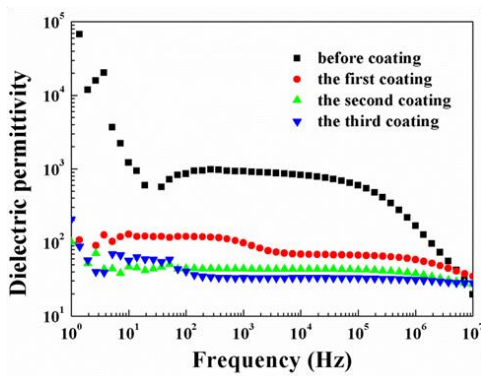
The frequency dependence of  $\epsilon'$  and  $\tan \delta$  of PDMS/CNT-3.7% before and after multi-cycle coating are presented in Figure 3 (a) and (b), respectively. Meanwhile, the values of  $\epsilon'$  and  $\tan \delta$  at 100 Hz and  $10^6$  Hz are listed in Table 2. It can be found that after multi-coating on double face of the sample, not only  $\epsilon'$  but also  $\tan \delta$  decreases significantly and the values become stable to the frequency gradually. This interesting phenomenon is attributed to the existence of the isolated PDMS layer which directly reduces the electrical conductivity ( $\sigma$ ) of the sample. For a sample approaching to  $f_c$ ,  $\tan \delta$  mainly results from the conduction loss and the polarization loss of space charges, and the conduction loss contributes much more. According to the free electric theory, at low frequency,  $\tan \delta$  can be expressed in Equation (1)<sup>[30]</sup>:

$$\tan \delta \approx \frac{\sigma'}{\omega \epsilon_0 \epsilon'} \quad (1)$$

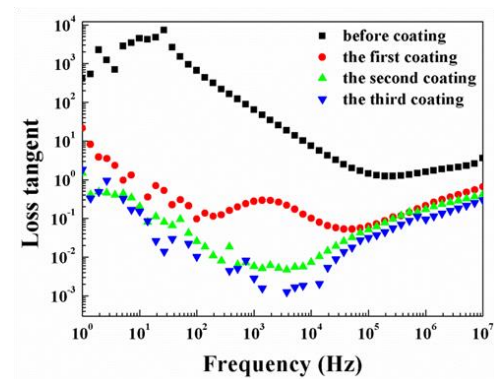
Where  $\sigma'$  is the conductivity of the composite. The frequency dependence of AC conductivity for PDMS/CNT-3.7% before and after multi-coating is presented in Figure 3 (c). The decrease of the conductivity for the sample after multi-cycle coating infers that coating isolated PDMS layer on sample's surface can reduce the electrical conductivity remarkably in the out-of-plane direction. Furthermore, the more the thickness increases, the more the conductivity decreases and until to a stable value. Thus, experimental results demonstrate that  $\epsilon'$  and especially  $\tan \delta$  of the composite can be controlled and reduced by multi-cycle coating isolated layer.

Table 2  $\epsilon'$  and  $\tan \delta$  for PDMS/CNT-3.7% at 100 Hz and  $10^6$  Hz before and after multi-cycle coating

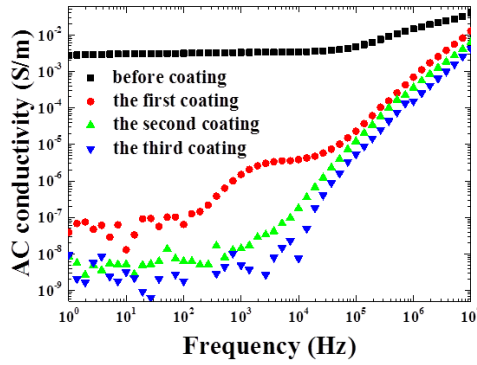
PDMS/CNT-3.7%	At 100 Hz		At $10^6$ Hz	
	$\epsilon'$	$\tan \delta$	$\epsilon'$	$\tan \delta$
Without coating	$866 \pm 14$	$501 \pm 226$	$112 \pm 21$	$1.74 \pm 1.74$
1 <sup>st</sup> coating	$129 \pm 11$	$0.08 \pm 0.03$	$49 \pm 14$	$0.29 \pm 0.11$
2 <sup>nd</sup> coating	$43 \pm 2.3$	$0.04 \pm 0.03$	$37 \pm 1.3$	$0.16 \pm 0.02$
3 <sup>rd</sup> coating	$40 \pm 13$	$0.01 \pm 0.004$	$28 \pm 2.2$	$0.08 \pm 0.02$



(a)



(b)



(c)

Figure 3 Frequency dependence of dielectric properties including  $\epsilon'$ ,  $\tan \delta$  and AC conductivity for PDMS/CNT-3.7% before and after multi-cycle coating are shown in (a), (b) and (c), respectively

With the regard that coating PDMS out-layer with different thicknesses can effectively adjust  $\epsilon'$ , it will be interesting to investigate the influence of different thickness on dielectric properties for the composite by simulation. A schematic figure is presented in Figure 4 (a) to illustrate the basic structure including the dimension of the bulk material in the blue part and the thickness of the out-layer on double faces in the gray part of the sample. Meanwhile, in Figure 4 (a), the thicknesses of the out-layer by multi-coating are also presented which are 57  $\mu\text{m}$  after the first cycle, 94  $\mu\text{m}$  after the second cycle and 126  $\mu\text{m}$  after the third cycle, respectively. The simulation will be made based on these experimental results in the following parts.

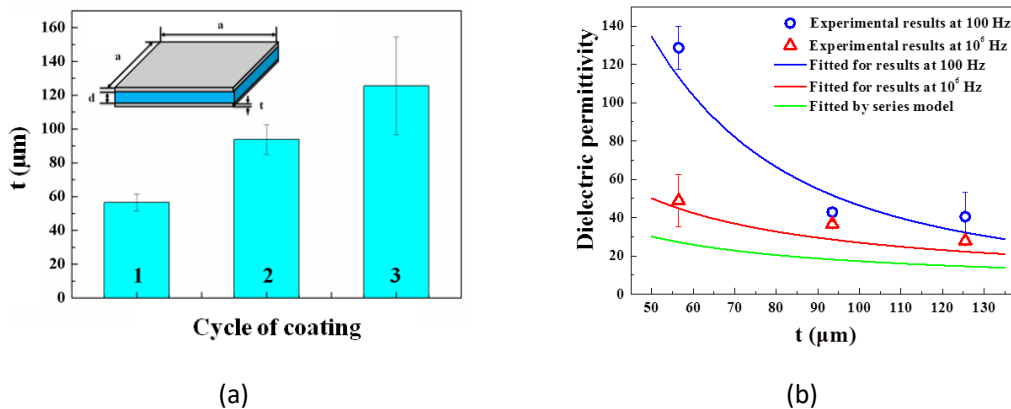


Figure 4 (a) Schematic figure of sample's structure:  $d$  is the original thickness before coating;  $a$  is the length and width of the sample and  $t$  is the thickness of the out-layer by coating. (b)  $\epsilon'$  of PDMS/CNT-3.7% with different  $t$  fitted by three methods



Aforementioned, the sandwich-structured composite of the bulk part between two out-layers can be viewed as a kind of series model. Thus, the series model will be firstly used to analyze the influence of  $t$  on  $\epsilon'$ . The equation is presented in (2)<sup>[29]</sup> where  $\epsilon_{\text{composite}}$  is the dielectric constant of the sandwich-structured composite;  $\epsilon_{\text{PDMS}}$  is the one of PDMS (2.94 is used in the calculation);  $\epsilon_{\text{bulk}}$  is the one of PDMS/CNT-3.7% before coating shown in Table 2. The fitting result is shown in the green line of Figure 4 (b):

$$\epsilon_{\text{composite}} = \left( \frac{2t}{(d+2t)\epsilon_{\text{PDMS}}} + \frac{d}{(d+2t)\epsilon_{\text{bulk}}} \right)^{-1} \quad (2)$$

As shown in Figure 4 (b), it can be found that the results calculated by the series model are much lower than the experimental ones, which infers that the percolation still influences  $\epsilon_{\text{composite}}$  of the composite and the influence cannot be ignored. Hence, it is necessary to retrospect the percolation theory on the dielectric response.

On the one hand, based on the polarization mechanism, the dielectric response is dependent on frequency ( $f$ ). For a composite with conductive fillers like CNT, the interfacial polarization is the main contribution for  $\epsilon_{\text{composite}}$  at low frequency (100 Hz).<sup>[1, 25]</sup> To estimate the effect of interfacial polarization, the relationship between  $\epsilon_{\text{composite}}$  and  $f$  in Equation (3)<sup>[32]</sup> is used according to percolation theory:

$$\epsilon_{\text{composite}} \propto (2\pi f)^{\mu-1} \quad (3)$$

where  $f$  is 100 Hz and  $\mu$  is a critical exponent. But considering the influence of  $t$ ,  $\mu$  may be expressed as the function of  $t$ . In fact, the sample with the sandwich structure as shown in the schematic figure can be roughly viewed as an enlarged filler with partial core-shell structure. Meanwhile, considering that the interface volume fraction of the core-shell model can be expressed by (4)<sup>[1, 33]</sup>:

$$v = 3 \frac{2t}{d} \left[ 1 - \frac{2t}{d} + \frac{1}{3} \left( \frac{2t}{d} \right)^2 \right] \quad (4)$$

and the coating layer does not thoroughly cover the whole sample, thus a modified interface volume fraction can be expressed by (5):

$$\mu = m \cdot v \quad (5)$$

where  $m$  is defined as the relationship between  $t$  and  $a$  as expressed in (6):

$$m = \frac{a}{a+2(d+2t)} \quad (6)$$

Hence, based on these equations,  $\epsilon'$  at 100 Hz of the composite can be estimated by (7)

$$\epsilon_{\text{composite}} = \epsilon_{\text{bulk}} \cdot (2\pi f)^{\mu-1} \quad (7)$$

As shown in the blue line of Figure 3 (b), the simulation by modified percolation with core-shell model can well fit the experimental results of  $\epsilon'$  at 100 Hz. It infers that although the conductivity resulting from the interfacial polarization of bulk part can be largely suppressed by coating isolated out-layer,  $\epsilon_{\text{composite}}$  is still influenced by interfacial polarization at low frequency. Moreover,  $\epsilon_{\text{bulk}}$  and  $t$  will simultaneously affect the  $\epsilon_{\text{composite}}$ . Combining these factors together, the relationship among  $\epsilon_{\text{bulk}}$ ,  $t$  and  $\epsilon_{\text{composite}}$  at 100 Hz can be obtained in Figure 5 and from the graph, we may optimize sandwich structure for designing the composite with adjustable  $\epsilon'$  as well as extremely low  $\tan \delta$ .

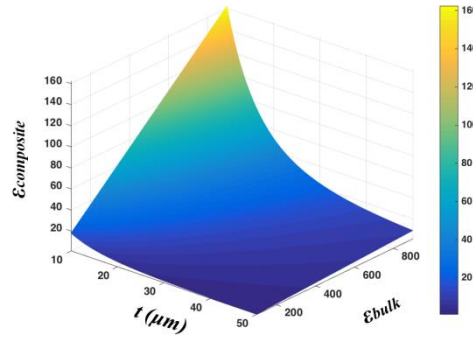


Figure 4 The relationship among  $t$ ,  $\epsilon_{\text{bulk}}$  and  $\epsilon_{\text{composite}}$ .

On the other hand, the polarization of  $\epsilon_{\text{composite}}$  at high frequency ( $10^6$  Hz) is more associated with sample's structure while the interfacial polarization affects much less. Thus, for fitting  $\epsilon_{\text{composite}}$  at  $10^6$  Hz, the core-shell model in the Equation (8)<sup>[34]</sup> may be employed directly:

$$\epsilon = \epsilon_{\text{PDMS}} \left( 1 + \frac{d}{t \cdot m} \right) \quad (8)$$

The fitting result is presented in the red line of Figure 4 (b). Core-shell model can fit better than the series model which infers that the analogy for the sandwich-structured composite to

enlarged core-shell structure is reasonable which can be explained the effect of  $t$  on  $\epsilon_{\text{composite}}$ . Therefore, the modified percolation with core-shell model can be well-fitted  $\epsilon_{\text{composite}}$  at 100 Hz and  $10^6$  Hz. In the case of 100 Hz,  $\epsilon_{\text{composite}}$  is still contributed to the interfacial polarization but PDMS out-layer can largely shield the leak current of interfacial polarization and then well control  $\epsilon_{\text{composite}}$ . Such shielding effect greatly depends on  $t$  and  $\epsilon_{\text{composite}}$  can be adjusted by optimizing sandwich structure with different  $t$ . In the case of  $10^6$  Hz, the interfacial polarization influences much less on  $\epsilon_{\text{composite}}$  much less and then  $\epsilon_{\text{composite}}$  can be well fitted by core-shell model directly.

#### 4. Conclusion

The existence of isolated PDMS out-layers on double faces of the PDMS/CNT composite approaching  $f_c$  can largely decreases  $\tan \delta$  by reducing the conductivity of the composite. Meanwhile, due to the percolation of CNT in the bulk part,  $\epsilon'$  of the composite can be effectively adjusted and less frequency-dependent. Furthermore, the experimental results indicate that the thickness of the out-layer is essential to the dielectric properties. By the simulation combining percolation and core-shell model, the relationship between the thickness of out-layer and  $\epsilon'$  of the composite can be obtained that helps to design the composite with required  $\epsilon'$ . Besides, this type of sandwich composite structure is easy to prepare for the practical applications.

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