



# Noncovalently functionalized multi-walled carbon nanotube with core-dualshell nanostructure for improved piezoresistive sensitivity of poly(dimethyl siloxane) nanocomposites



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## ABSTRACT

Poor sensitivity in low pressure regimes (<100 kPa) of pressure-sensitive rubbers (PSRs) is one of their major disadvantages compare to other piezoresistive materials. The reasons induced the poor sensitivity include bad dispersion and week interface of multi-walled carbon nanotubes (MWCNTs) applied in poly(dimethyl siloxane) (PDMS). A novel vinyl-terminated poly(dimethyl siloxane)-poly(phenylmethyl siloxane)-multi-walled carbon nanotubes (V-P-MWCNTs) with core-dualshell nanostructure is fabricated by noncovalently functionalized method. The V-P-MWCNTs as conductive fillers exhibits homogenous dispersion as well as good interfacial interaction in PDMS matrix. Slightly above the percolation threshold (0.19 vol.%), the PDMS-based nanocomposites with 0.2 vol.% of V-P-MWCNTs shows high piezoresistive sensitivity ( $22.16 \times 10^{-3} \text{ kPa}^{-1}$ ), high electrical conductivity ( $5.43 \times 10^{-3} \text{ S/m}$ ) and low Young's modulus (288.83 kPa). These results demonstrate that the V-P-MWCNTs are of great potential as the conductive fillers for improved piezoresistive sensitivity of PDMS nanocomposites, which can be potentially applied in the flexible touch sensors.

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## 1. Introduction

Pressure-sensitive rubbers (PSRs) are one of the most promising classes of piezoresistive materials that exhibit excellent performance such as flexibility, low cost, nontoxicity, durability, as well as easiness of producing [1,2]. By composing conductive fillers into flexible elastomer matrix as nanocomposites, a piezoresistive material of PSRs is obtained. It has emerged as a highly active field due to promising applications in various tactile devices, such as artificial electronic skin [3,4], artificial intelligence systems [5,6] and wearable health care devices [7,8]. However, a key limitation for the practical application of conventional PSRs is the poor sensitivity in low pressure regimes (<100 kPa) [9]. Such pressure regimes are very important for approximating gentle touch and object manipulation, which largely limit its wide application. Therefore, the preparation of PSRs with high sensitivity among pressure regimes (0–100 kPa) is the biggest challenge for PSRs.

According to the well-known piezoresistive theory, the ultra-high piezoresistive sensitivity ( $S$ ) is generally observed at the fillers content slightly above the percolation threshold ( $\varphi_c$ ) [10]. At the

percolation threshold, the conductive network is just formed and electrical conductivity ( $\sigma$ ) increases significantly. If the PSRs is applied pressure, breakage of conductive network occurs and a drastic change in resistance can be observed. To obtain a PSRs with high  $S$ , a low  $\varphi_c$  is required [11,12]. Most PSRs, such as poly(dimethyl siloxane) (PDMS) with low Young's modulus ( $E < 1 \text{ MPa}$ ), transparency and flexibility, always exhibit electrical insulating [13,14]. One common method to obtain a PSRs with a low  $\varphi_c$  is to introduce sphere metallic particles with high intrinsic  $\sigma$  into the polymer [15]. This strategy usually requires high loading fraction, and thus produces the large increase in elastic modulus, resulting in destroying of the flexibility, largely limiting the wide-spread application of PSRs. Another method is to add conductive fillers such as multi-walled carbon nanotubes (MWCNTs) into the polymer to improve the  $S$ . Because of the high  $\sigma$  ( $>100 \text{ S/cm}$ ) and large aspect ratio ( $>1000$ ) [16,17], even quite a low content of MWCNTs could lead to the formation of conductive network, and thus leading to the large decrease in  $\varphi_c$ . However, in this case, a poor dispersion of MWCNTs applied in polymer is also obtained because of the aggregation and entanglement caused by the Van-der Waals force [18]. Moreover, MWCNTs also have a week interfacial interaction applied in polymer, including compatibility and chemical bonding for polymer [19]. Consequently, the added

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amount of MWCNTs will be largely increased and thus also result in high  $\varphi_c$ , which in turn leads to the decrease of  $S$ . In addition, the high cost of MWCNTs is not good for the industrial application of PSRs materials.

Previous studies of the control dispersion of MWCNTs in polymer as well as the interfacial interaction between them have promoted interest in surface functionalization [20–23]. The functionalized layers that on the surface of conductive fillers, which not only enhance the dispersion capability of MWCNTs and their good compatibility in the polymer matrix but also form strong bonding with polymer during the curing process, thus improving the  $S$  of nanocomposites. In contrast with covalently functionalized MWCNTs, which locally disrupted  $sp^2$  hybridization or defect creation of MWCNTs, noncovalently functionalized MWCNTs, including either  $\pi$ - $\pi$  stacking onto or wrapping the MWCNTs, are advantageous in that they conserve  $sp^2$ -conjugated structures and preserve the intrinsic  $\sigma$  of MWCNTs [24]. Noncovalently functionalized MWCNTs using the polyaromatic molecule with hydrophobic groups poly(phenylmethyl siloxane) (PPMS) has been reported [25]. However, the enhanced homogenous dispersion does not meet the critical requirement of MWCNTs/PDMS nanocomposites, because both the homogenous dispersion and good interfacial interaction are all required. Considering the fact that functional groups that are structurally similar to the polymer may have good interfacial interaction, it is promising to fabricate noncovalently functionalized MWCNTs with excellent interfacial interaction through wrapping vinyl-terminated poly(dimethyl siloxane) (Vi-PDMS) onto MWCNTs surface.

Herein, we first designed a noncovalently functionalized method to modify MWCNTs through the stacking PPMS onto pristine MWCNTs surface (P-MWCNTs) and subsequently wrapping of Vi-PDMS (V-P-MWCNTs). The V-P-MWCNTs with unique core-shell nanostructure could be used as conductive fillers for PSRs with significantly improved piezoresistive sensitivity at low pressure regimes (0–100 kPa). The PDMS nanocomposites with different loading of the pristine MWCNTs, P-MWCNTs and V-P-MWCNTs were prepared and comparatively investigated. The V-P-MWCNTs/PDMS nanocomposites with excellent piezoresistive sensitivity could be potential applications as flexible touch sensors.

## 2. Experimental

### 2.1. Materials

Multi-walled carbon nanotubes (MWCNTs, diameter 10–20 nm, length 10–30  $\mu$ m, purity 95 wt.%, Hengqiu Graphene Technology (Suzhou) Co. Ltd.) was used as conductive fillers materials, which was grown using the CVD technique. The poly(phenylmethyl siloxane) (PPMS, Molecular weight ( $M_w$ )  $\approx$  2500–2700 g/mol) was purchased from Alfa Aesar, and vinyl-terminated poly(dimethyl siloxane) (Vi-PDMS, Molecular weight ( $M_w$ )  $\approx$  300,000 g/mol) was bought from Guiyou new technology (Shanghai) Co.,Ltd. Chloroform (>99.5 wt.%) was obtained from Sinopharm Chemical Reagent Co.,Ltd. The silicone rubber used was poly(dimethyl siloxane) (PDMS, Guiyou new technology (Shanghai) Co., Ltd.). The PDMS was supplied in liquid form which consisted of Part-A (base: siloxane oligomers terminated with vinyl groups (Molecular weight ( $M_w$ )  $\approx$  50,000 g/mol) and Part-B (curing agent: platinum-based catalyst and cross-linking siloxane oligomers which each contains at least three silicon-hydride bonds).

### 2.2. Preparation and functionalization of MWCNTs

According to the noncovalently functionalized method [26], MWCNTs were prepared by two steps: low molecular PPMS  $\pi$ - $\pi$

stacked on the surfaces of MWCNTs and then wrapped by high molecular Vi-PDMS, as shown in Fig. 1: (1) A mixture containing 1 g of MWCNTs and 2 g of PPMS in 50 ml of chloroform was ultrasonicated for 10 min at 25 °C. The resulting PPMS-functionalized MWCNTs (P-MWCNTs) were then dried under vacuum at 120 °C for 1 h. (2) 1 g of P-MWCNTs and 0.8 g of Vi-PDMS were then added in 50 ml of chloroform via ultrasonication for 2 min at 25 °C. The resulting Vi-PDMS-functionalized P-MWCNTs (V-P-MWCNTs) were then dried under vacuum at 120 °C for 1 h.

### 2.3. Preparation of noncovalently functionalized MWCNTs/PDMS nanocomposites

Preparation of noncovalently functionalized MWCNTs/PDMS nanocomposites were given as follows: (1) Weighted amount of pristine MWCNTs, P-MWCNTs and V-P-MWCNTs were dispersed in 50 ml chloroform separately and sonicated in an ultrasonic bath for 10 min achieve uniform dispersion. (2) The noncovalently functionalized MWCNTs/chloroform suspension were added into the PDMS (Part-A: Base) and mechanically stirred for 10 min at 80 °C to completely evaporate the chloroform. (3) After the mixture was cooled to room temperature, the PDMS (Part-B: Curing agent) was added in the mixture: cross-link agent ratio of 10:1 (Part-A: Part-A) in mass and the mixture was again stirred for 10 min at room temperature (4) After degassing under vacuum for 10 min, those viscous mixtures were molded onto the flexible polyamide (PI) substrates on which were painted with parallel silver paste as electrodes, and then cured at 120 °C for 30 min to form a thin film with a size of 20  $\times$  10  $\times$  4 mm.

### 2.4. Characterization

The surface properties and nanostructure of noncovalently functionalized MWCNTs were examined by Fourier transform infrared (FTIR, Bruker, VERTEX-70), Energy dispersion spectroscopy (EDS, Ametek, EDAX-GENESIS 2000), Transmission electron microscopy (TEM, FEI, Tecnai-G2 20). The dispersion state and morphology of noncovalently functionalized MWCNTs in the PDMS matrix were analyzed using optical transmission microscope (TOM, RaxVision, TK-C921EG) and field emission scanning electron microscope (FE-SEM, FEI, Sirion-200). The electrical properties of the nanocomposites were measured using a multimeter agilent 34401a by four-wire (Europe, Kelvin) measurement [27]. The electrical conductivity ( $\sigma$ ) was then computed use the equation:

$$\sigma = \frac{1}{\rho} = \frac{L}{R \times A} \quad (1)$$

where  $\sigma$  is electrical conductivity (S/m),  $\rho$  is resistivity ( $\Omega$ ·mm),  $A$  is cross-sectional area ( $\text{mm}^2$ ) and  $L$  is length (mm). Mechanical and electromechanical measurements were performed to determine uniaxial compression utilizing an electronic universal testing machine (MTS Exceed 40.SANS.China) with a constant rate of 0.2 mm/min in order to obtain steady and accurate test results [28,13].

## 3. Results and discussion

### 3.1. Characterization and nanostructure of noncovalently functionalized MWCNTs

#### 3.1.1. FT-IR analysis of noncovalently functionalized MWCNTs

Fig. 2 shows the FT-IR spectra of the pristine MWCNTs, the P-MWCNTs, and the V-P-MWCNTs. Obviously, in contrast to the pristine MWCNTs (Fig. 2(a)), both the P-MWCNTs (Fig. 2(b)) and V-P-MWCNTs (Fig. 2(c)) show C–H stretching vibration peaks in

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