

## Mechanically enhanced electrical conductivity of polydimethylsiloxane-based composites by a hot embossing process

Xiaolong Gao,<sup>a</sup> Yao Huang,<sup>b</sup> Xiaoxiang He,<sup>a\*</sup> Xiaojing Fan,<sup>a</sup> Ying Liu,<sup>a,b</sup> Hong Xu,<sup>a</sup> Daming Wu,<sup>a,b\*</sup>,  
Chaoying Wan<sup>c\*</sup>

<sup>a</sup> College of Mechanical and Electrical Engineering,

Beijing University of Chemical Technology, Beijing 100029, China

<sup>b</sup> State Key Laboratory of Organic-Inorganic Composites,

Beijing University of Chemical Technology, Beijing 100029, China

<sup>c</sup> International Institute for Nanocomposites Manufacturing (IINM), WMG,

University of Warwick, UK, CV4 7AL

\*Correspondence: XX He, [heshosha@163.com](mailto:heshosha@163.com) (X.H.); DM Wu, [wudaming@vip.163.com](mailto:wudaming@vip.163.com) (D. W.); C Wan, [Chaoying.wan@warwick.ac.uk](mailto:Chaoying.wan@warwick.ac.uk)

### Abstract

Electrically conductive polymer composites are in high demand for modern technologies, however, the intrinsic brittleness of conducting conjugated polymers and the moderate electrical conductivity of engineering polymer/carbon composites have highly constrained their applications. In this work, super high electrical conductive polymer composites were produced by a novel hot embossing design. The polydimethylsiloxane (PDMS) composites containing short carbon fiber (SCF) exhibited an electrical percolation threshold at 0.45 wt%, and reached a saturated electrical conductivity of 49 S/m at 8 wt% of SCF. When reduced the sample thickness from 1.0 mm to 0.1 mm by the hot embossing process, a compression-induced percolation threshold occurred at 0.3 wt%, while the electrical conductivity was further enhanced to 378 S/m at 8 wt% SCF. Furthermore, the additional of a second nanofiller of 1 wt%,

such as carbon nanotube or conducting carbon black further increased the electrical conductivity of the PDMS/SCF (8 wt%) composites to 909 S/m and 657 S/m, respectively. The synergy of the densified conducting filler network by the mechanical compression and the hierarchical micro-/nanoscale filler approach has realized super high electrical conductive yet mechanical flexible polymer composites for modern flexible electronics applications.

**Keywords:** electrical conducting network, forced assembly, compression-induced percolation threshold, hybrid filler, synergy

## 1. Introduction

The development and popularity of smart electronics have attracted increasing demands for high performance and mechanically flexible electrically conducting polymer composites. Intrinsic electrical conducting polymers such as polypyrrole, polyaniline, polyacetylene and polythiophene have the constraints of unstable conductivity, insolubility, difficulty of processing, small-scale and high cost. Electrically conducting polymer composites can be prepared by incorporating conductive fillers into an insulating polymer matrix, and provides the advantages of ease of processing and an ability to tailor the electrical properties based on composite architecture [1-6]. The electrical conductivity of polymer composites rely on the nature of the conductive fillers and the formation of a continuous and percolated conducting pathway in the insulating polymeric matrix [7-11]. The dispersion of conducting fillers such as carbon nanotubes (CNTs), carbon fibers, graphene and carbon black, in a polymer matrix have been improved by using in situ polymerization [12] or forming segregated microstructures under specific processing conditions[13]. It has been reported that multi-walled CNTs formed a segregated and percolated conductive network structure in poly(phenylene sulfide) matrix by using solid-mixing and subsequent melt-compression. A percolation threshold as low as 0.33 wt% of CNTs was obtained, and the electrical conductivity of the composites was increased from  $\sim 10^{-10}$  S/cm to  $\sim 0.11$  S/cm with the use of CNT contents up to 10 wt%.

The electrical percolation threshold and electric conductivity of polymer composites are highly

dependent on the properties of the conducting fillers, their dispersion and interfacial interactions between the filler particles and the polymer matrix [14-18]. A good dispersion of graphene oxide (GO) was achieved in polyamide-6 (PA6) composites by in-situ polymerization, which facilitated the formation of an electrically conductive network and resulted in a significantly improved electrical conductivity of the composite [12]. A PA6/polypropylene(PP)/CNT (20/80/4) composite exhibited a high electrical conductivity in comparison with the PA6/PP/CNTs (50/50/4) composite due to the selectively localized CNT in the PA6 phase to forming a compact conductive network[19]. In addition a synergistic effect between graphene and CNTs in a thermoplastic polyurethane matrix led to a reduced percolation threshold, where the graphene acted as a 'spacer' to separate the entangled CNTs from each other and the CNT bridged the gap between individual graphene sheets. Such an effect was beneficial for the dispersion of the CNTs and the formation of effective conductive paths, leading to improved electrical conductivity at a lower conductive filler content[20].

The electrical conductivity of filled polymer composites generally reaches saturation and becomes independent of filler loading once the filler loading level is above the percolation threshold. As a result, the enhancement of electrical conductivity of polymer composites is very limited[21-24]. To promote the maximum electrical conductivity of polymer composites, we proposed a Spatial Confining Forced Network Assembly (SCFNA) method to increase the packing density of the conducting network in the composites by mechanical compression [8, 25-26], which reduced the separation distance between the fillers by excluding insulting polymer phase out of the network. This mechanical compression approach effectively enhanced the electrical conductivity of polypropylene/short carbon fiber (SCF) composites by 2-4 orders of magnitude [25] and thermal conductivity of PDMS/SCF composites by 7.79 times higher when reduced the sample thickness to 0.3 ~ 0.5 mm [26]. In this work, we further investigate the effects of hybrid filler systems combined with the SCFNA method on the electrical conductivity of PDMS composites. The synergy between the micro- and nanoscale fillers are shown to enhance the continuity of conductive pathways in the forced assembled network. This method can facilitate the formation of a compact conducting network, which is applicable for enhancing the electrical and thermally conductivity, and mechanical toughening polymer composites.

## 2. Experimental

### 2.1 Materials

PDMS with a trade name of SYLGARD 184 obtained from DOW CORNING, USA was used at the polymer matrix. As a micro-scale filler, short carbon fibers (SCF) of 5~10  $\mu\text{m}$  in diameter and 3-5 mm in length were provided by Toray, Japan. As a nano-scale filler graphene, carbon black and CNTs were used. A few-layer graphene (G) of 1.0 ~1.77 nm in thickness and 10 ~50  $\mu\text{m}$  in width was provided by Changzhou Sixth Element Material Technology Co., Ltd, China. Superconductive carbon black (CCB, BP2000) with a particle size of 15 nm was obtained from CABOT, USA. CNTs with 20~30 nm diameter and 10 ~ 30  $\mu\text{m}$  length were provided by Beijing Daoking Technology Co., Ltd, China. The electrical conductivity of the four fillers (SCF, G, CCB and CNT) are  $\sim 2.6 \times 10^4$  S/m,  $1.0 \times 10^5$  S/m,  $5.0 \times 10^4$  S/m, and  $1.0 \times 10^4$  S/m, respectively.

### 2.2 Composite preparation and SCFNA process

A conical twin-screw compounder of HAAKE MiniLab combined with a specifically designed hot embossing device were used for preparation of the PDMS composites in order to realise a spatially confined forced assembly network (SCFNA) of conductive fillers.

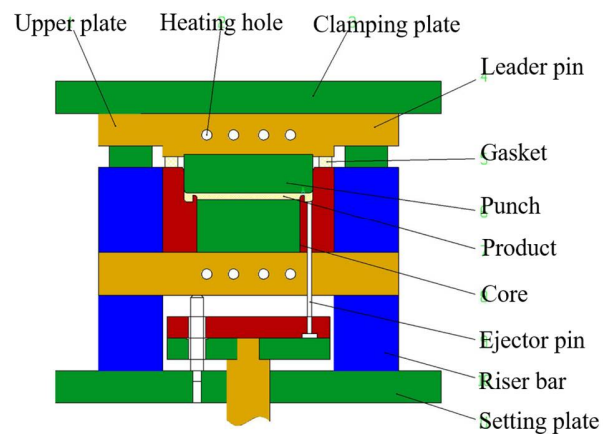
For PDMS/SCF composites, the PDMS was mixed with the short carbon fibres at weight ratios of 0.5, 1, 1.5, 2, 3, 4, 6 or 8 wt% at 25 °C with a rotational speed of 70 rpm for 10 min. For the preparation of PDMS composites containing hybrid micro- and nano-scale fillers, 1 wt% of CNT, G or CCB was included to the above PDMS/SCF compound with a rotational speed of 50 rpm for an additional 10 min at 25 °C to obtain PDMS/SCF-CNT, PDMS/SCF-G or PDMS/SCF-CCB composites.

The experimental hot embossing device as shown in Scheme 1(a) provided a pressing force up to 10 MPa with a pressing speed of 0.005 to 0.5 mm/s in a working stroke. The servo motor of this embossing device was accurately controlled by a programmable logic controller (PLC) system and the position accuracy of  $\pm 3$   $\mu\text{m}$  for the up platen was guaranteed. The compressing mold was made of two flat plates with electrical heaters. The temperature of the molds was controlled from ambient temperature to 350 °C with a control accuracy of  $\pm 1$  °C and heating rate of 15 °C/min. The effective working area was 210  $\times$  300 mm.

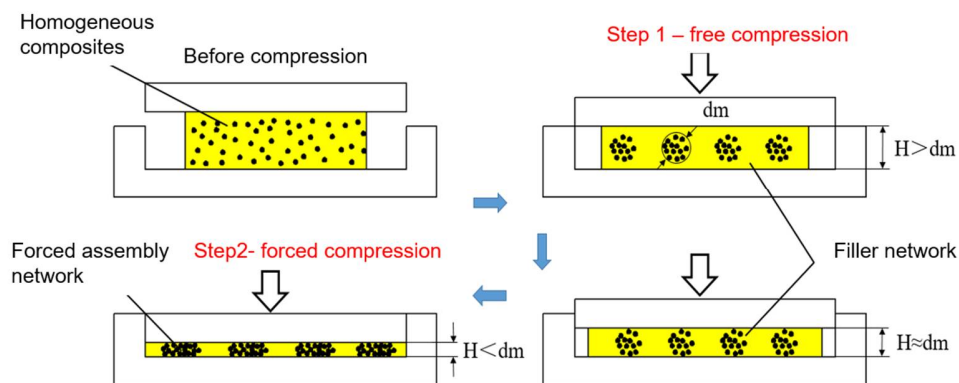
The compounded materials were compressed in the designed mould at 20 °C following the steps shown

in Scheme 1 (b). The compounds were compressed from an original thickness of 10 mm to 1.0 mm within 120 seconds, and kept at 10 MPa for 5 minutes to initiate the first assembly of the filler network. Then the composite sheets were continuously compressed to the thickness of 0.4, 0.3, 0.2, and 0.1 mm, respectively within 30 seconds. The second compression aims to force the assembly of the filler network in a spatially confined space. In this work, when the sample thickness ( $H$ ) was reduced below a critical network thickness ( $d_m = 0.3$  mm), the conductivity was significantly enhanced. Finally, the composite sheets were cured at 100 °C for 10 mins to stabilize the filler network. The specimens with a thickness of 1.0 mm after the first stage of compression were used as a control.

(a) Hot embossing device



(b) SCFNA process



Scheme 1 (a) Schematic diagram of the experimental apparatus used to shape the PDMS composites and form the SCFNA structure; (b) SCFNA process to condense the conducting filler network in polymer matrix, where  $H$  is the height of the sample sheet,  $d_m$  is the critical thickness of the conducting network.

### **2.3 Characterization**

A Video Measuring System JTVMS-1510T manufactured by Dongguan JATEN Precision Instrument Co., LTD. (China) was used to investigate the morphology evolution process during the preparation of compact short carbon fibre network in the PDMS matrix. A Hitachi S4700 scanning electron microscopy (SEM) was used to study the dispersion and localisation of the fillers in the composites under an accelerating voltage of 30 kV.

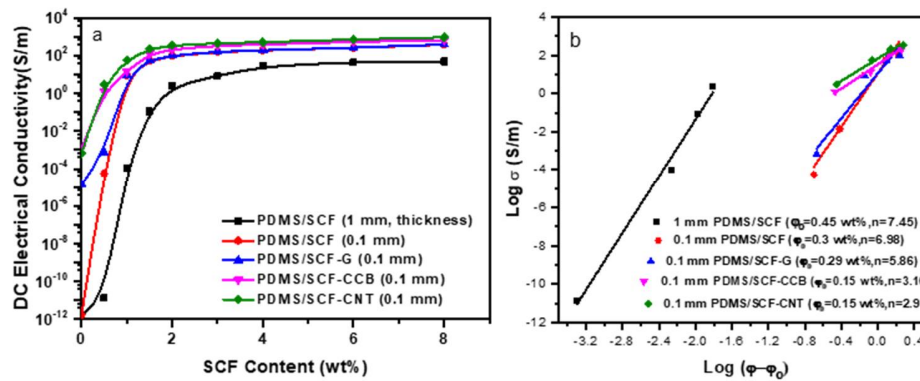
The electrical conductivity of the composite samples was measured using a Keithley 4200-SCS (America) with a standard four-probe method and a ZC-90D resistivity meter from Shanghai Taiou Electronics (China). All electrical conductivity measurements were carried out at ambient conditions.

The mechanical properties of the PDMS composites were evaluated using a universal material-testing machine (UTM-1422, Chengde Jinjian Testing Instrument Co., Ltd) with a cross-head speed of 5 mm/min at ambient temperature and the corresponding dimension of specimen is 30 mm × 15 mm × 0.2 mm.

## **3. Results and discussion**

### **3.1 Concentration-induced electrical percolation of PDMS composites**

The DC electrical conductivity of the PDMS composites containing short carbon fibres was investigated as a function of filler concentration or mechanical compression, and the effects of an additional nano-scale filler (CNT, G or CCB) on the electrical properties of the composites were also discussed. The nano-scale filler was added at a loading level of 1 wt% and the sample thickness of the PDMS composites were reduced from the original 1.0 mm further down to 0.1 mm using the SCFNA compression method.



**Fig.1** (a) Effect of short carbon fibre content and sample thickness on the DC electrical conductivity of PDMS composites, (b) percolation threshold fitting results.

The electrical conducting behaviour of polymer composites can be interpreted by the classic percolation theory[27]. The electrical conductivity of the composites near the percolation threshold follows a power-law relationship described in Eq.1,

$$\sigma \propto \sigma_0(\varphi - \varphi_c)^n, \text{ for } \varphi \geq \varphi_c \quad (1)$$

where  $\sigma$  is the electrical conductivity of composites,  $\sigma_0$  is a constant that is typically assigned to the plateau conductivity of fully loaded composites,  $\varphi$  is the filler weight content,  $\varphi_c$  is the weight ratio of the filler at the percolation threshold, and the value of critical exponent ( $n$ ) depends on the system dimension and is used to interpret the mechanism of network formation. An insulator-conductor transition is observed at the  $\varphi_c$ , and the electrical conductivity of the polymer composites increases with the filler content increasing when  $\varphi \geq \varphi_c$ . As shown in Fig.1a and Table 1, the DC electrical conductivity of the PDMS/SCF composites with a thickness of 1.0 mm was increased with an increase of SCF contents, from the original filler free PDMS of  $\sim 10^{-12}$  S/m to 49 S/m when the SCF content was increased to 8 wt%. The  $\varphi_c$  of PDMS/SCF composites was calculated to be 0.45 wt% and  $n=7.45$  according Eq. 1 [28-30], as shown in Fig.1b.

### 3.2 Compression-induced electrical percolation of PDMS composites

Similar to the concentration-induced percolation, a compression-induced percolation transition was observed during the SCFNA compression process, when the sample thickness or volumetric strain reached a critical value  $\varepsilon_c$  or under a critical pressure  $P_c$  [31], as expressed in Eq.2 and Eq.3:

$$\varphi_c = \frac{\varphi_0}{1 - \Delta P_c} \quad (2)$$

$$\varepsilon_c = 1 - \left(\frac{\varphi_0}{\varphi_c}\right) \quad (3)$$

Where  $\Delta P_c$  is the pressure increment ( $P - P_c$ ) to drive the percolation transition from  $\varphi_0$  to  $\varphi_c$ .

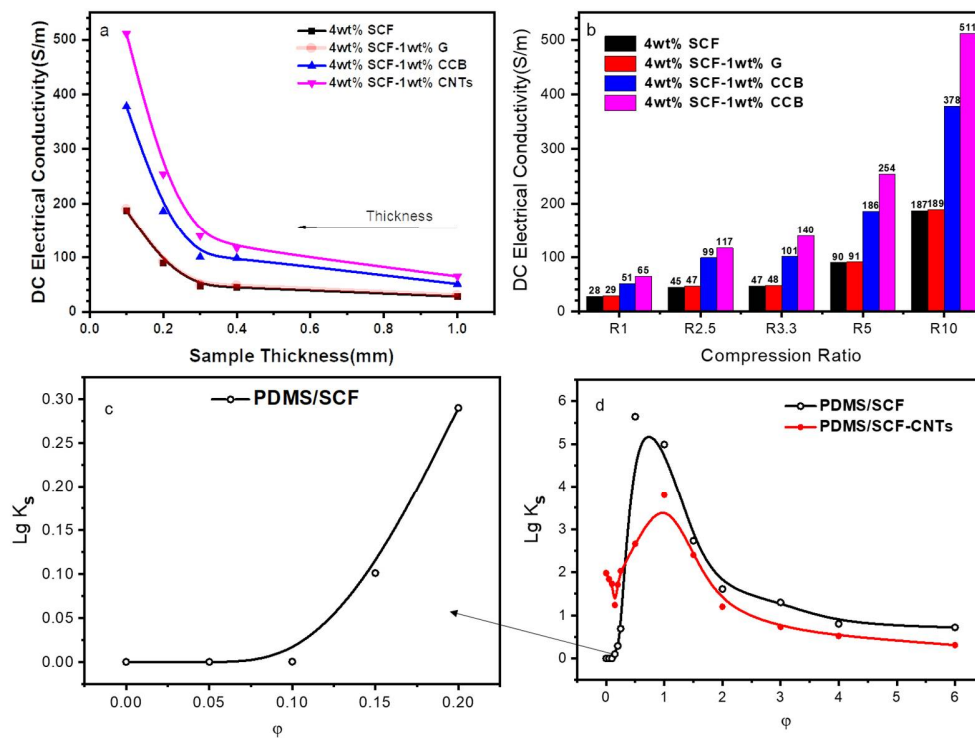


Fig.2 (a) Effect of sample thickness on the DC electrical conductivity of PDMS composites prepared by the SCFNA method; (b) effect of compression ratio ( $R$ ) on the DC electrical conductivity of PDMS composites by SCFNA method; (c,d) the strain sensitivity  $K_s$  of the conductivity of the PDMS composites during the SCFNA compression process.

The percolation transition happened when the conducting fillers were approaching each other until a critical



partial volume of the fillers was reached. As shown in Fig. 1, when the thickness of the PDMS/SCF composites was reduced from 1.0 mm to 0.1 mm by the SCFNA compression, the overall conductivity of composites was increased significantly and the  $\phi_c$  was reduced to 0.3 wt%. Above the percolation threshold, the increase of the short carbon fibre concentration from 6 wt% to 8 wt% led to a small increase of the ultimate conductivity of the PDMS/SCF composite (1 mm) from 44.6 S/m to 48.6 S/m, only increased by 8.97%. However, for the PDMS/SCF composite samples (0.1 mm) prepared by SCFNA method, the conductivity was increased by 47.1%, from 257 S/m to 378 S/m. This illustrates that when a conducting network is formed in the polymer matrix (above the concentration induced percolation threshold), a further increase of filler concentration has little contribution to the ultimate electrical conductivity. In contrast, compression may densify the conducting network, and further enhance the electrical conductivity without increasing filler concentrations. This is particularly promising in the case that the ultimate electrical conductivity of polymer composites above the concentration-induced percolation threshold can be further enhanced by a compression-induced percolation transition.

Fig. 2a shows the effects of sample thickness on the electrical conductivity of the PDMS/SCF composites at above its percolation threshold. As the sample thickness was reduced, the electrical conductivity of the PDMS/SCF composites was slowly increased, and exhibited an abrupt enhancement when the thickness was below  $d_m = 0.3$  mm, which indicates that a new compression-induced percolation transition occurs, i.e., a compact assembly of filler network at a higher compression ratio. A further reduction of the sample thickness to 0.1 mm led to a significant increase of the conductivity, from original 28 S/m (at 1 mm) up to 187 S/cm for PDMS/SCF (4 wt%), similarly the PDMS/SCF(4 wt%)-CNT (1 wt%) composite has the electrical conductivity increased from 65 S/m to 511 S/m. As shown in Fig.1b, for the compressed composites with 0.1 mm in thickness, the addition of 1 wt% of a second nano-scale filler such as CNT or CCB reduced the  $\phi_c$  from 0.3 to 0.15 wt%, demonstrating a synergistic effect between the micro-scale short carbon fibres and the second nano-scale filler.

The effects of a second nano-scale filler along with the compression ratio (R) on the electrical conductivity of the composites are compared in Fig.2b. The compression ratio R is defined as 1.0 mm over the assembly

thickness of composites prepared by SCFNA, i.e when the thickness of the composite samples were reduced to 1, 0.4, 0.3, 0.2, 0.1 mm, the compression ratio  $R$  were 1, 2.5, 3.3, 5, 10, respectively.

As shown in Fig.2b, the conductivity of the composites are generally increased with an increase of the compression ratio  $R$  of the composites. The conductivity of PDMS/SCF, PDMS/SCF-G, PDMS/SCF-CNTs, PDMS/SCF-CCB were enhanced by 6.68, 6.52, 7.41, 7.86 times after simply compression-moulding of the composite sheets from 1 mm to 0.1 mm. This indicates that the thickness or the packing density of the filler network plays a significant role in the electrical properties of the composites. The addition of 1 wt% of graphene to the PDMS/SCF composites did not show any obvious effect on the conductivity under variable compression ratios (see Fig.2a and 2b), while the use of 1 wt% CCB and CNTs significantly increased the conductivity along with the thickness reduction. The CNTs were the most effective, which can be ascribed to its large aspect ratio and bridging the conducting network easily compared with CCB.

To demonstrate the dependence of electrical conductivity on partial volume of the fillers (sample thickness), the strain-sensitivity coefficient  $K_s$  is plotted against the filler concentration according to Eq. 4, and shown in Fig.2cd.

$$K_s = \frac{d\sigma}{\sigma} / \frac{dV}{V} \quad (4)$$

Where  $dV/V$  is the volumetric strain, causing a relative increment of the conductivity ( $\frac{d\sigma}{\sigma}$ ).

As shown in Fig.2c, the electrical conductivity or  $K_s$  is not sensitive to the sample thickness when the SCF content is lower than 0.15 wt%. As the SCF content increases,  $0.25 \text{ wt\%} < \varphi < 0.5 \text{ wt\%}$ , the  $\lg K_s$  increases abruptly and reaches a maximum peak at 0.5 wt%, close to its percolation transition as determined in Fig. 1b, indicating the formation of a compression-induced conducting network. The  $\lg K_s$  gradually decreases as the filler concentration increases, indicating that once a compact conducting network has formed, the conductivity becomes less sensitive to the sample thickness and filler concentration.

In the case of PDMS/SCF-CNTs, the addition of 1 wt% of CNTs facilitates the formation of conducting SCF network at lower concentrations due to the gap-filling effect. In the SCF concentration range of  $0.15 \text{ wt\%} < \varphi < 1 \text{ wt\%}$ , the  $\lg K_s$  increases abruptly, and then drops as the SCF concentration increases. The  $\lg K_s$

peak value is lower than that of PDMS/SCF composite, which is because the addition of CNTs makes the network more compact, and thus reduces the strain sensitivity.

As shown in Table 1, the electrical conductivity of PDMS/SCF-G, PDMS/SCF-CCB, PDMS/SCF-CNTs composite samples (thickness is 0.1 mm) prepared by SCFNA increased significantly from  $1.38 \times 10^{-5}$  S/m to 383 S/m,  $1.21 \times 10^{-3}$  S/m to 657 S/m,  $6.51 \times 10^{-4}$  S/m to 909 S/m with an increase of the short carbon fibre content from 0 to 8 wt%, respectively. Therefore, the electrical conductivity of PDMS composites can be more effectively enhanced by constructing a compact conducting network instead of increasing the filler loading. By further increasing the packing density through adding a second nanofiller or increasing the filler concentration, the electrical conductivity can be significantly further enhanced.

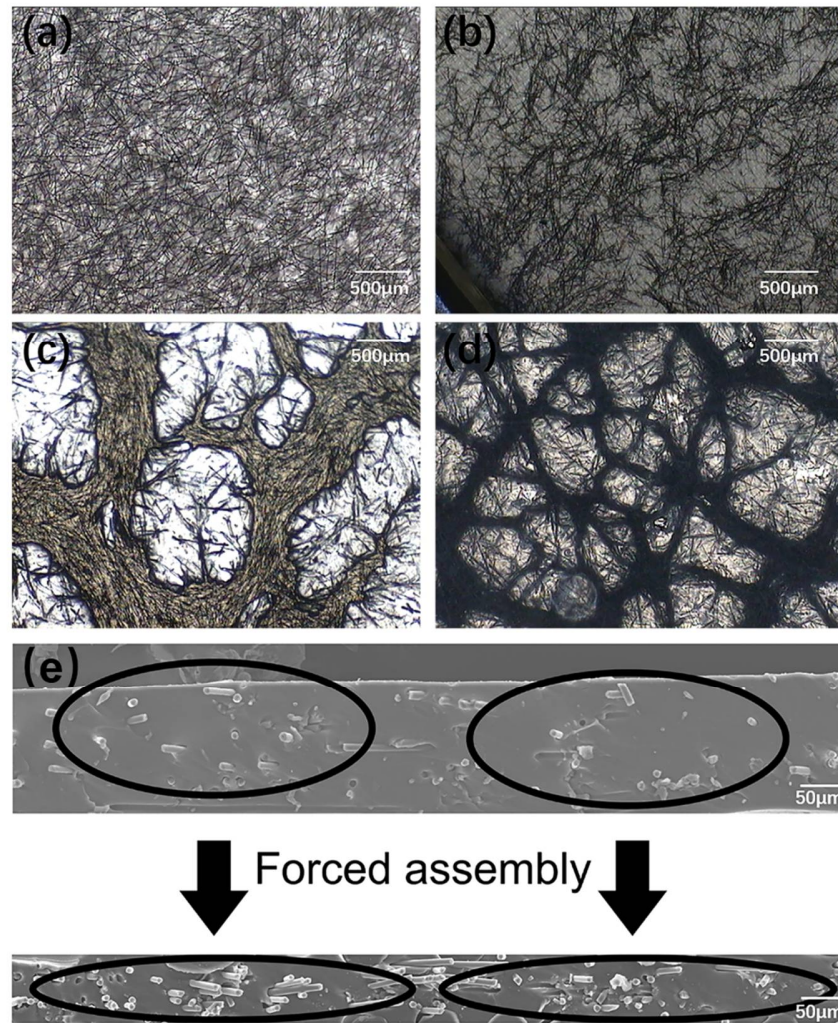
**Table 1.** Comparison of electrical conductivity of PDMS/SCF composites as the effects of sample thickness and a second nanofiller. The thickness of PDMS/SCF composites was reduced from 1 mm to 0.1 mm by SCFNA method, the second filler (G, CCB, or CNT) content is 1 wt%.

SCF (wt%)	DC Electrical Conductivity (S/m)				
	1 mm	0.1 mm	SCF-G (0.1 mm)	SCF-CCB (0.1 mm)	SCF-CNTs (0.1 mm)
0	$1.71 \times 10^{-12}$	$1.71 \times 10^{-12}$	$1.38 \times 10^{-5}$	$1.21 \times 10^{-3}$	$6.51 \times 10^{-4}$
0.5	$1.40 \times 10^{-11}$	$5.50 \times 10^{-5}$	$7.21 \times 10^{-4}$	1.31	3.02
1	$1.01 \times 10^{-4}$	8.81	8.84	14.5	56.8
1.5	0.11	53.2	56.7	120	221
2	2.51	95.2	100	211	343
3	8.11	154	161	333	443
4	27.7	187	189	378	511
6	44.6	257	261	533	702
8	48.6	378	383	657	909

### 3.3 Characterisation of the conducting filler network in PDMS

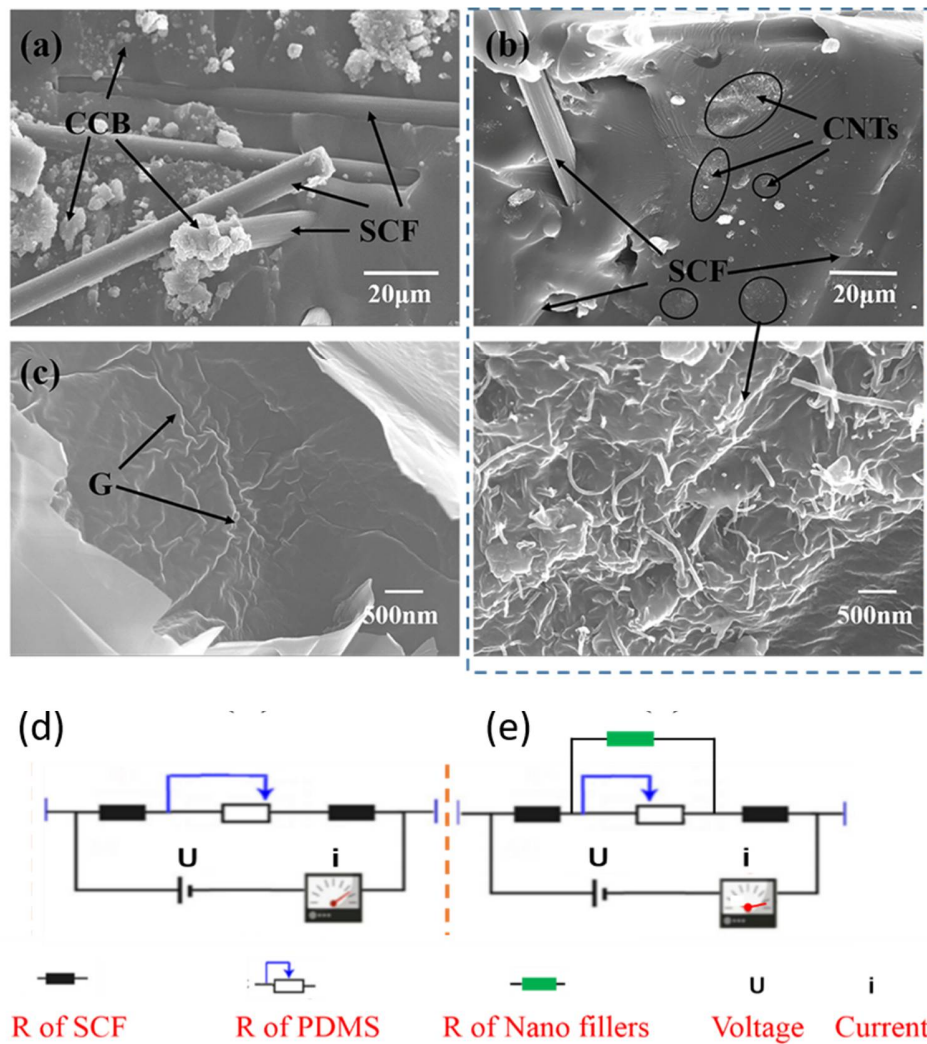
Reducing the gap between adjacent filler particles would benefit electron conduction[8, 32-33], since the

electrons can transport between adjacent conducting fillers within an average distance less than 100 nm, according to conductive passage theory[34]. Fig.3 shows the morphology evolution of the short carbon fibre network during the preparation of the PDMS/SCF (4 wt%) composites. A homogeneously dispersed short carbon fibre network was formed in the PDMS matrix after melt-compounding, as shown in Fig.3a. When further subjected to the strong shearing force in the conical twin-screw extrusion process, the short carbon fibre filler agglomerated and self-assembled, as shown in Fig.3b. After the first stage of compression, the self-assembly network was formed (Fig.3c) and was subsequently condensed by the second stage of spatial confining compression (SCFNA) to create a forced assembly network in Fig.3d. From the cross-sectional images in Fig.3e, the short carbon fibre framework was compacted by the forced assembly and the average distance between the short carbon fibres was reduced from more than 15  $\mu\text{m}$  to less than 100 nm, which creates the electron conduction pathways through both field emission and conductive passage.



**Fig.3** Morphology evolution of short carbon fibre network in PDMS: (a) homogeneous dispersion of short carbon fibres in PDMS after melt mixing; (b) a self-assembly network formed during conical twin-screw extrusion; (c) the free assembly network under compression; (d) forced assembly network under spatial confining compression; and (e) cross-section morphologies showing the evolution of the short carbon fibre network from self-assembly to forced assembly.



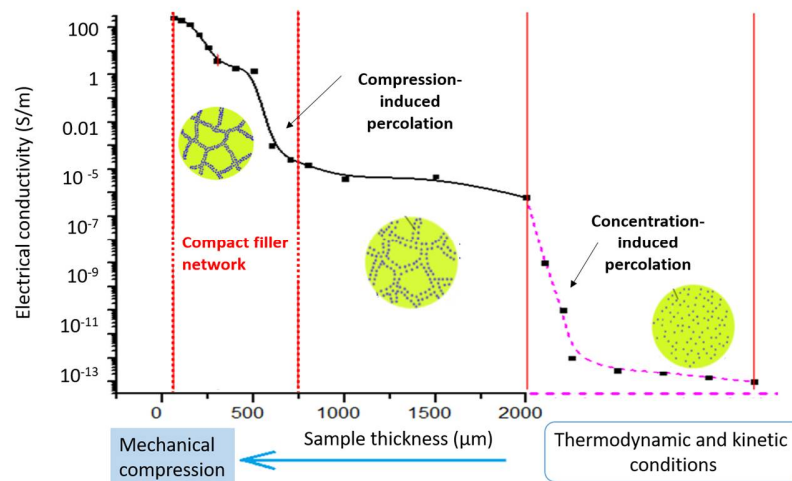


**Fig.4** SEM images of PDMS/SCF (4 wt%) composites containing 1 wt% of a second nanofiller: (a) CCB, (b) CNTs and (c) Graphene; Resistance of conductive network in the polymer matrix (d) PDMS/SCF and (e) PDMS/SCF containing a second filler.

The gap-filling effect of an additional nano-scale filler on the conducting network of short carbon fibres is illustrated by SEM imaging in Fig.4. In the PDMS/SCF-CCB composites, the majority of the CCB particles are located inside the network of short carbon fibres which fill the space between short carbon fibres, as shown in Fig.4a. A synergistic effect of a combination of CCB and short carbon fibres could enhance the continuity of conductive pathways in the compact carbon fibre conductive forced assembled network. As shown in Fig.4b, most CNTs are dispersed regularly around short carbon fibre framework. The

average spacing of adjacent CNTs in the network is less than 100 nm, and the interconnection between the long CNTs with the compact short carbon fibre network accounts for the enhanced conductivity of PDMS/SCF-CNT composites. In comparison, the few-layer graphene sheets are mostly dispersed in the PDMS matrix rather than inside of the carbon fibre network (Fig.4c), implying a lower synergy efficiency of the combination of graphene and SCF in PDMS composites. In addition, the agglomerates of graphene sheets may also account for the low conductivity and poor contribution for the PDMS/SCF composites.

Ohm's Law can be used to explain why the reduced separation between filler particles of the conductive network could effectively improve the electrical conductivity of composites. As seen in Fig.4d, when the adjacent short carbon fibers are closer, the effective resistance of the PDMS region between the short carbon fibres decreases, as a result, the electrical conductivity of the PDMS/SCF composites is increased. Moreover, with the addition of a second nano-scale filler, a gap-filling conductive network is formed among the SCFs, as shown in Fig.4e of the conductive model for PDMS/SCF-CNT and PDMS/SCF-CCB composites. This indicates that the PDMS resistance between adjacent SCFs is parallel with a small resistance, which greatly improves the conductivity of the composites.



**Fig.5** Mechanism of SCFNA process initiated compact conducting filler network and highly enhanced electrical conductivity of polymer composites.

Fig.5 shows the mechanism of SCFNA process and the structure development of conducting filler network in polymer composites. The SCFNA process provides a simple route to construct a continuous and compact short carbon fibre micro-network in the polymeric matrix by simply applying mechanical force, which enhances the electrical conductivity up to 378 S/m, 7.8 times higher than the pristine PDMS. Moreover, the gap filling effect of a second nano-scale filler such as CNTs has interconnected the micro-SCF network. As a result, the electrical conductivity of the PDMS composites containing hybrid fillers and processed via SCFNA can be further enhanced to as high as 909 S/m.

### 3.4 Mechanical properties

**Table 2** Mechanical properties of PDMS composites at thickness 0.2 mm

PDMS composite		Maximum tensile strength (MPa)	Elongation at break (%)
SCF (wt%)	Nano-filler		
0	0	4.5 ±0.1	110 ±2
1	0	3.9 ±0.2	96 ±4
0	1wt% CCB	4.0±0.1	98±1
0	1wt% CNT	4.2±0.1	105±1
0	1wt% G	5.1±0.1	125±1
2	0	3.6±0.2	91±4
3	0	3.2±0.2	83±4
4	0	2.8±0.2	72±4
4	1wt% CCB	2.9±0.2	73±3
4	1wt% CNT	3.1±0.2	77±3
4	1wt% G	3.8±0.2	94±3

The mechanical properties of PDMS composites with SCF (0~4 wt%), and 1 wt% of a nano-sized filler (CNT, CCB and G) are shown in Table 2, the sample thickness is 0.2 mm. The maximum tensile strength of PDMS/SCF composites decreased from 4.5 ± 0.1 MPa to 2.8 ±0.2 MPa when the SCF content increased from 0 to 4 wt%. The reduced properties can be ascribed to the higher contents of micro-SCF and the poor interfacial interaction between SCF and PDMS. After addition of 1 wt% nano-fillers into PDMS/SCF (4 wt%) composites, the tensile strength and elongation at break of the composites were enhanced. Graphene showed a better mechanical reinforcement effect than CNT and CCB. With the addition of 1 wt% graphene,



the maximum tensile strength of PDMS/SCF composites improved from  $2.8 \pm 0.1$  MPa to  $3.8 \pm 0.2$  MPa. The 2-dimensional graphene nanosheets offer a stronger interface layer with PDMS as compared to one-dimensional CNT or granular CCB, and the graphene is mainly located in the PDMS rich regions of the composites, which would be effective in reinforcement of PDMS. Meanwhile, graphene presents a folded morphological distribution in PDMS as shown in Fig.4c, which would benefit the enhancement of the tensile strength and elongation at break. Nevertheless, both the CNT and CCB improved the tensile strength of PDMS/SCF composites.

#### 4. Conclusions

The incorporation of conducting fillers into an insulating polymer matrix can generally enhance the electrical conductivity to a limited extent when beyond the percolation threshold. In this work, a spatially confined forced network combined with a hybrid micro-nanoscale filler approach are investigated in order to prompt high electrical conductive polymer composites. With our newly designed spatially confined forced network (SCFNA) process, the electrical conductivity of PDMS/short carbon fibre (SCF) composites was increased by 7.8 times in comparison to the pristine PDMS. The addition of nano-scale filler such as CCB or CNT, further increased the conductivity over two times higher at above the percolation threshold of SCF; this was a result of a synergy effect of the hierarchical filler network. The spatially confined forced network provides a simple route to construct a continuous and compact conducting filler network in PDMS/SCF composites and results in super high electrical conductivity yet mechanical flexible composites with lower filler concentrations. This approach will significantly prompt the applications of conductive polymer composites in the areas of flexible sensors and intelligent wearable products.

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