

Experimental and Theoretical Study on Piezoresistive Behavior of Compressible Melamine Sponge Modified by Carbon-based Fillers

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Abstract High-performance compression sensors have been playing an increasingly important role in human motion detection, health monitoring and human-machine interfaces over recent years. However, it remains a great challenge to develop theoretical models providing practical guidance to the sensor design. Herein, carbon black (CB), carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) were respectively incorporated into porous melamine sponges by a facile approach of dip-coating to fabricate compression sensors. Uniaxial compression-resistance tests show that the compressibility, stability and piezoresistive sensitivity of sensors could be tailored by the filler type and concentration. A model considering the number of conductive pathways (NCP) is given to describe the relationship between the resistance change and applied compression, showing extremely good agreement with the experimental data. Also, the correlation between the equivalent filler volume fraction and conductivity is described by the other two models proposed by McLachlan and Kirkpatrick, revealing the electrical percolation thresholds (Φ_c) for the conductive systems under compression. Among the three fillers, CB particles endowed the composite with the best piezoresistive sensitivity but the largest Φ_c due to its small size and aspect ratio. A combination of experimental study and theoretical model opens up a way of further understanding the piezoresistive sensing behavior as well as optimizing the electrical property and piezoresistivity of compressive conductive polymer composite.

Keywords Compression sensor; Melamine sponge; Model; Piezoresistivity

Citation: Luo, X. L.; Schubert, D. W. Experimental and theoretical study on piezoresistive behavior of compressible melamine sponge modified by carbon-based fillers. *Chinese J. Polym. Sci.* 2022, 40, 1503–1512.

INTRODUCTION

Conductive polymer composites (CPCs) can be used to design sensitive sensors to detect or monitor environmental conditions via loading conductive fillers into polymer matrices.^[1] Among these sensors, piezoresistive sensors, whose change in output electrical signal is caused by external stretching or compression, have received great attention due to their advantages of easy processing, simple structure, and low cost.^[2–4] It has been found that the piezoresistive sensing behaviors highly depend on the conductive particle dimensionality and the structure of conductive pathways.^[5] Nowadays, many efforts have been made to develop sensors with excellent piezoresistive sensing properties such as constructing hierarchical structures in CPCs.^[6–8] However, the practical applications of these sensors, especially related to normal human activities are limited because of a non-linear relationship between the electrical signal and the stimuli. To design and optimize piezoresistive sensors, it is fundamental to develop theoretical models capable of simulating the relationship between dynamic mechanical strain and electrical conductivity.^[9,10]

As reported, the most popular theory for modeling the changeable electrical properties of the CPC strain/compression sensors is the tunneling theory, according to which the electrical resistance of the conductive composites can be described as:^[11,12]

$$R = \frac{L}{N} \left[\frac{8\pi\hbar s}{3a^2ye^2} \exp(\gamma s) \right] \quad (1)$$

$$\gamma = \frac{4\pi}{h} \sqrt{2m\phi} \quad (2)$$

where R is the composite resistance, L is the number of particles on one single effective conductive path, N is the number of effective conductive paths (NCP), $\hbar$ is Planck's constant, e is the electron charge, s is the minimum distance between two particles, a^2 is the effective cross-sectional area between two particles, m is the electron mass, ϕ is the height of the potential barrier.

Based on the above theory, models have been developed to simulate the resistance evolution during stretching,^[13–16] however, the simulation of the compression process is still rare and only a very small compression could be modeled based on a method of representative volume elements.^[17] Inspired by these studies, attempts to model the compression response of CPCs were made firstly by modifying a widely reported model based on the above-mentioned tunneling the-

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Received March 8, 2022; Accepted April 21, 2022; Published online July 20, 2022

ory in this work. During the compressing process, it is assumed that the minimum distance decreases from s_0 to s under the applied compressive load, where s depends on the deformation of the polymer matrix. The deformation of each conductive particle itself is neglected, and thus:

$$s = s_0 (1 + k\varepsilon) \quad (3)$$

where ε denotes the compression of the specimen and k denotes a free adjustable parameter. During the uniaxial compression, the parameter k can be simplified to be -1 . Additionally, the number of the conductive pathway N in the system increases under compression:^[18]

$$N = N_0 \exp(C_1 \varepsilon + C_2 \varepsilon^2 + C_3 \varepsilon^3) \quad (4)$$

where N_0 is the initial number of conductive pathways for $\varepsilon=0$, and C_1 , C_2 , C_3 are constants. When substituting Eqs. (2)–(4) into Eq. (1), s_0 is extremely small resulting in that the item $k\gamma s_0 \varepsilon \cong 0$. Therefore, from Eqs. (1)–(4) follows simplified Eq. (5) with four adjustable parameters:

$$\frac{R_0}{R} = \frac{S_0 N}{S N_0} \exp(\gamma s_0 - \gamma s) \cong \frac{\exp(C_1 \varepsilon + C_2 \varepsilon^2 + C_3 \varepsilon^3)}{(1 - \varepsilon)} \quad (5)$$

where R_0 and R correspond to the initial resistance and dynamic resistance, respectively. In our previous study,^[19–22] it has been found that the relationship between electrical conductivity and filler volume fraction of CPCs can be graphically described by the general effective medium (GEM) theory equation proposed by McLachlan:^[23]

$$(1 - \Phi) \frac{\sigma_m^{1/s} - \sigma_c^{1/s}}{\sigma_m^{1/s} + \frac{1 - \Phi_c}{\Phi_c} \sigma_c^{1/s}} + \Phi \frac{\sigma_f^{1/t} - \sigma_c^{1/t}}{\sigma_f^{1/t} + \frac{1 - \Phi_c}{\Phi_c} \sigma_c^{1/t}} = 0 \quad (6)$$

where σ_m , σ_c , σ_f are the conductivities of the polymer matrix, the composite and the filler, respectively, Φ is the volume fraction of the fillers and Φ_c is the percolation threshold. The exponents s and t are taken to be the universal values of 0.87 and 2, respectively.

The values of Φ_c can also be determined by fitting another percolation model proposed by Kirkpatrick:^[24]

$$\sigma_c = \sigma_f (\Phi - \Phi_c)^p \quad (7)$$

where σ_c and σ_f are the conductivities of the composite and the filler, respectively, Φ is the volume fraction of fillers, Φ_c is the percolation threshold and p is a constant.

Conductivity is needed in Eqs. (6) and (7), which is given by

$$\sigma = \frac{d}{R \cdot S} \quad (8)$$

where R is the electrical resistance of the sample which can be directly measured, d and S are the area of the sample perpendicular to the direction of the electrical field and the length of the sample parallel to the direction of the electrical field, respectively. The principle of presenting the conductivity change with the filler volume fraction under the compressive load is to convert compression into equivalent filler volume fraction. The criteria and assumptions used to develop their relationship are as follows:

1. The object is a cubic porous composite such as a foam or sponge, with an initial thickness of d_0 and a cross-section area of S_0 . The filler volume is V_f , thus the initial filler volume fraction Φ_0 (defined as the ratio of the filler volume to the porous composite cube) is:

$$\Phi_0 = \frac{V_f}{d_0 \cdot S_0} \quad (9)$$

2. The compression is uniaxial and the Poisson's ratio of the polymer foam is equal to zero,^[25,26] thus the cross-section area S is constant while the thickness d linearly decreases with the compression increasing.

$$d = d_0 (1 - \varepsilon) \quad (10)$$

3. The filler shape, orientation, as well as volume V_f keep constant, only the voids are compressed during the uniaxial compression process. The equivalent filler volume fraction is given by

$$\Phi = \frac{V_f}{d \cdot S} \quad (11)$$

Substituting Eqs. (9) and (10) into Eq. (11), yields

$$\Phi = \frac{\Phi_0}{(1 - \varepsilon)} \quad (12)$$

Inserting Eq. (9) in Eq. (8), the conductivity can be obtained as

$$\sigma = \frac{d_0 (1 - \varepsilon)}{R \cdot S} \quad (13)$$

In this work, melamine sponge (MS) with a 3-dimensional skeletal network was utilized as the matrix, graphene nanoplatelets (GNPs), carbon blacks (CB) and carbon nanotubes (CNTs) were utilized as conductive fillers. Composites with different conductive network structures were fabricated *via* dip-coating process, a facile and low-cost method showing great potential for mass production of strain/compression sensing materials. The performances of these composites in the compression-electrical response were investigated and described by the proposed models according to Eqs. (5)–(7).

EXPERIMENTAL

Materials

Melamine sponge was purchased from J.E.Schum GmbH, Germany, GNPs were supplied by ProGraphite GmbH, Germany, with about 10 layers, d_{50} as an index of 50 μm and conductivity of 800–1100 $\text{S}\cdot\text{cm}^{-1}$. CB Printex XE2 was provided by Evonik with a mean diameter of around 35 nm and a density at room temperature of 2.13 $\text{g}\cdot\text{cm}^{-3}$. Multiwalled CNT Baytubes C150P was obtained from Bayer Material Science AG, Leverkusen, Germany. The bulk density of Baytubes C150P is 120–170 $\text{kg}\cdot\text{m}^{-3}$, the length is larger than 1 μm , and an outer nanotube diameter of 13 ± 3 nm according to the datasheet. Thermoplastic polyurethane (TPU Elastollan 1180A) with a density of 1.12 $\text{g}\cdot\text{cm}^{-3}$, was provided by BASF Co. Ltd. Tetrahydrofuran (THF) was obtained from Sigma Aldrich, Saint Louis, MO, USA.

Fabrication of MS/Filler Composites

Fig. 1 illustrates the preparation processes of the MS/Filler and MS/Filler/TPU compression sensors. Fillers were firstly added into ethanol (0.25 V/V), and the mixture was sonicated for 30 min to yield a homogeneous suspension. Cubic MS samples (12 mm $\times$ 12 mm $\times$ 12 mm) were then immersed in the suspension and squeezed to make fillers infused into the pores of the MS. After taking out, the MS/filler samples were dried under ambient conditions for 24 h and subsequently dried at 80 $^{\circ}\text{C}$ for 6 h to weigh and record the filler absorption. This process was repeated for certain cycles until the conductivity of the produced specimens tended to saturate.

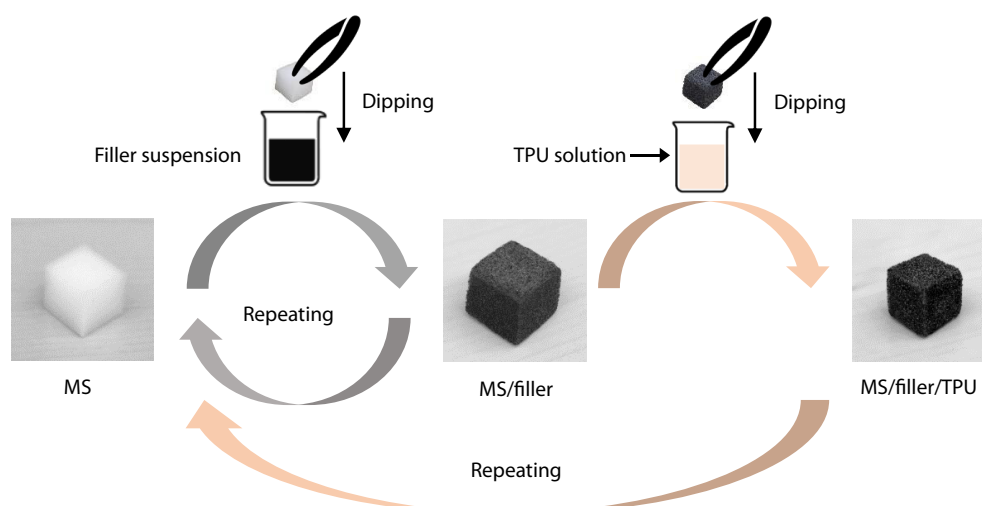


Fig. 1 Schematic illustration of the fabrication process of MS/filler composites.

Typically, MS/GNPs/TPU samples were also fabricated with this method to construct “compact” conductive networks. The difference was introducing TPU/THF solution (1 wt%) in the repeating cycles, thus the sponge skeletons and GNPs could be coated with TPU. The obtained composites were denoted as MS/Filler_x and MS/GNPs/TPU_x, where *x* represents the volume fraction (vol%) of fillers.

Characterization

Scanning electron microscopy (SEM) (Carl Zeiss Microscopy, Germany) was conducted to investigate the morphologies of the sponge, operating at an accelerating voltage of 3 kV. The composite films were previously coated with a gold layer using Sputter Coater S150B from Edwards. The static electrical resistances *R* of the MS/Filler and MS/GNPs/TPU composites were measured using a Keithley 6487 Pico ammeter at a constant voltage (1 V) based on a homemade setup.^[27] The electrical conductivity σ was then calculated by Eq. (13) and five samples were involved in each group. Piezoresistive properties of the filled sponges were obtained on a universal testing machine (Zwick Z050) coupled with the Pico ammeter simultaneously. The specimens were attached to the universal testing machine with a gauge length of 12 mm. The fixtures of the testing machine were encased by insulating tape to minimize electronic noise and each end of the conductive sponge was carefully affixed to a silver sheet to reduce the electrical contact resistance. Cyclic compressions of the specimens were performed at crosshead speeds of 1 mm/min and 5 mm/min, respectively.

RESULTS AND DISCUSSION

Morphology and Structural Characterization

Fig. 2(a) shows that the filler volume fraction almost increased linearly with increasing the dip-coating number. Despite the same concentrations of fillers in ethanol before dipping, the amount of CB absorbed into the MS increased more rapidly while GNPs and CNTs showed a lower trend probably due to the very small size of CB. The morphologies of the representative samples were characterized by SEM, and the results are exhibited in Figs. 2(b)–2(f). MS (Fig. 2b) has a smooth 3D

interconnecting porous structure with a pore diameter of about 100 μm , which is very suitable for the storage and support of fillers (planar GNPs with a mean diameter of 40 μm).^[20] As shown in Fig. 2(c), GNPs are coated with TPU, some of them embed into the pores of the sponge, and the others are assembled on the sponge scaffolds. Due to the large size of GNPs, most of the GNPs embedded into the vacancies of the porous structure in the MS/GNPs composite (Fig. 2d) rather than wrapped the sponge skeletons.^[28] It can also be observed that the stack of GNPs was much looser in the MS/GNPs composite, whereas GNPs formed larger agglomerations in the MS/GNPs/TPU sample due to the coating of TPU, exhibiting more compaction of the structure. In addition, the appropriate pore diameter of the MS also made the GNPs rarely drop out in these two composites. Unlike the GNPs, CB and CNTs tend to aggregate among the pores of the MS as shown in Figs. 2(e) and 2(f). Those aggregates seemed to be confined by the skeletons of MS and their size was comparable to those of the pores. The aggregates were not only a benefit for taking in more fillers, but also for reducing the loss during the compression.

Mechanical Properties

Compression tests were performed to evaluate the mechanical properties and the network stability of the prepared piezoresistive sensors. Figs. 3(a)–3(f) show representative compressive load-compression curves of the MS and the composites. Typical compression levels from 0% to 10%, 30% and 50% were conducted for each concentration in a compression cycle. As Fig. 3(a) shows, the MS inevitably exhibited a hysteresis in the compressing-releasing cycle due to the energy dissipation during the deformation process,^[29] and it became larger for higher applied compression levels. Moreover, the MS has an ultra-low compressive load value of 1.1 N at 50% compression and it shows an insignificant difference in mechanical properties during the three cyclic compressions, indicating a good elasticity. The MS/GNPs composites with various GNP volume fractions (Fig. 3b) have a similar trend of the hysteresis, which might also be explained by the buckling of GNP networks, friction between the graphene sheets and possible cracks in the GNP layer during compressing.^[28] Therefore, it increased because these effects were enhanced at

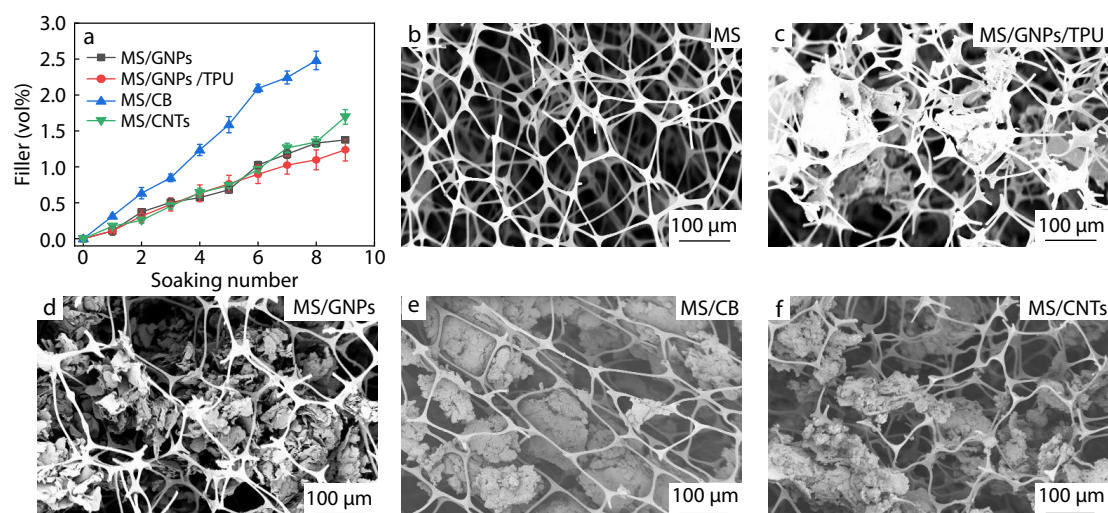


Fig. 2 (a) Filler volume fraction as a function of soaking number. SEM images of (b) as-received melamine sponge, (c) MS/GNPs/TPU, (d) MS/GNPs, (e) MS/CB and (f) MS/CNTs.

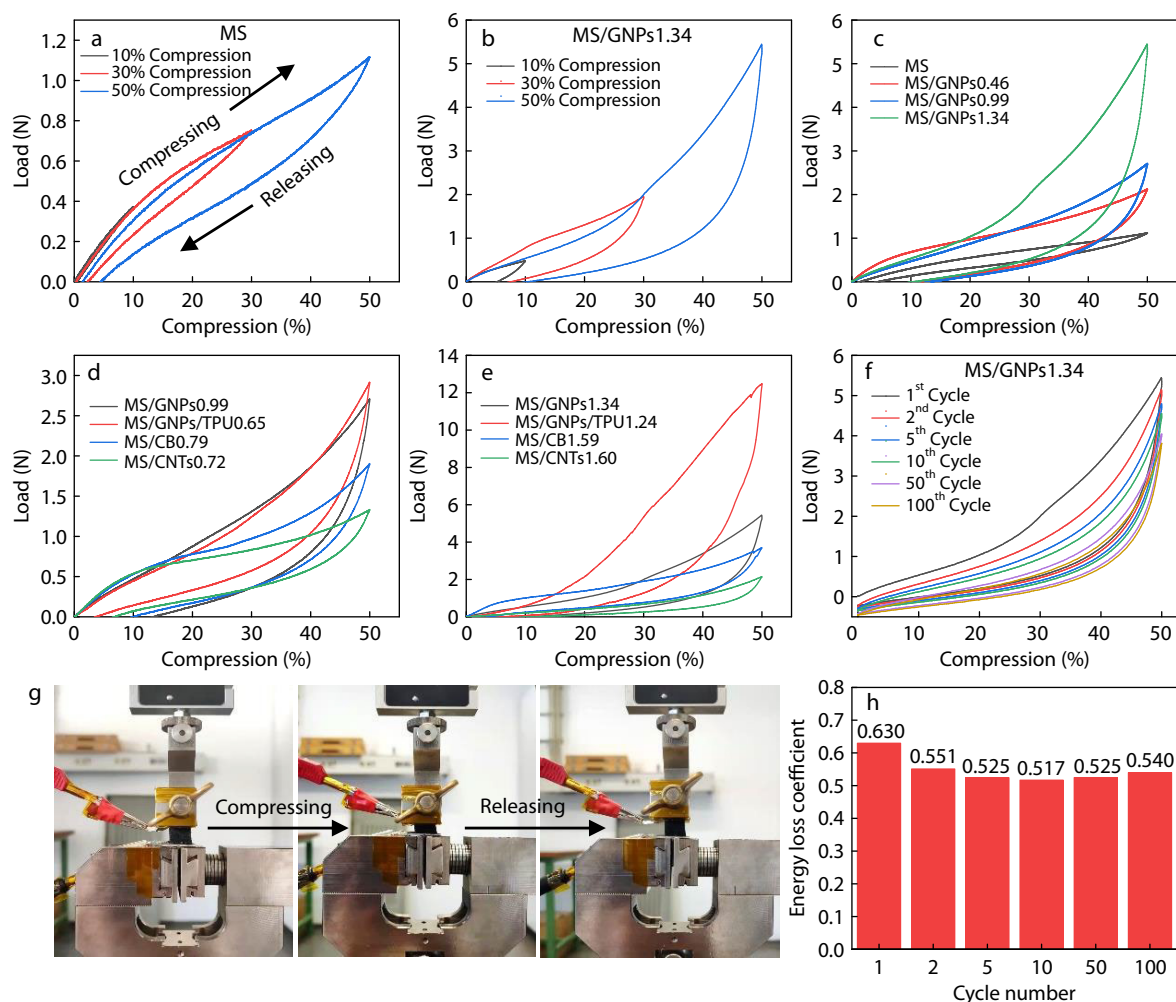


Fig. 3 Load-compression curves of MS and composites. (a) MS at different compression levels, (b) MS/GNPs1.34 at different compression levels, (c) MS/GNPs at various GNP volume fractions, (d, e) composites comprising different fillers, (f) MS/GNPs1.34 upon different number of compressing-releasing cycles, (g) compressing-releasing test on the universal testing machine and (h) energy loss coefficient of various cycles of MS/GNPs1.34.

higher compression. Fig. 3(c) shows that the compressive load values increased with increasing GNP concentrations. The compressive load increased to 5.4 N at 50% compression when the GNP content was 1.34 vol%.

Figs. 3(d) and 3(e) show the load-compression curves of composites comprising different fillers at medium and high filler fractions. For both filler concentration levels, the maximum load followed the sequence of MS/GNPs/TPU > MS/GNPs > MS/CB > MS/CNTs, indicating different reinforcements. The compression loads varied from 2.0 N (MS/GNPs0.46) to 11.1 N (MS/GNPs/TPU1.24), for all sponges with a compression area of 144 mm², the compressive stresses are in a range of 13.9–77.1 kPa, which are in a medium-pressure regime (from 10 kPa to ~100 kPa), showing great potential for monitoring human activities such as blood pulse, human weight, and joint movements.^[30] It should be noted that the improvement of the mechanical properties of the MS/GNPs sensor is entirely attributed to the contribution of the GNPs, while that of the MS/GNPs/TPU composite improves more due to the TPU coating. Fig. 3(f) shows the cyclic mechanical properties of the MS/GNPs1.34 composite at the compression level of 50%. The maximum compressive load decreased by 30% as the cycle number was increased to 100, indicating deformation of the sponge during the repeated compressing-releasing process. Figs. 3(g) and 3(h) show a compressing-releasing test cycle on the universal testing machine and the energy loss coefficient of different cycles of the MS/GNPs1.34 com-

posite, respectively. The energy loss coefficient reflects the hysteresis of the material during cyclic deformation. The value of the first cycle was 0.630, it decreased to 0.551 for the second cycle and almost keep constant for the subsequent cycles.

Compression-resistance Analysis

To evaluate the influence of the filler content on the sensing characteristics of the composite sensors, electro-mechanical responses of the four kinds of filled sponge samples with three various filler concentrations were measured at the axial compressions up to 50%. Only two of the MS/GNPs/TPU sensors are shown because the low filler concentration of 0.33 vol% yielded unreliable data with large experimental scattering. The resistance change rate R_0/R as a function of the compression level is presented in Fig. 4, where the compression level of 50% is converted to 0.5. With the increase of the filler addition, R_0/R drops dramatically since denser conductive networks formed at a higher filler content.^[31,32] This phenomenon corresponded to the increase in NCP in Eq. (5).

However, the sensing characteristics of these sensors were highly dependent on the conductive particle dimensionality. The MS/GNPs/TPU sensor exhibits the lowest sensitivity and the most unstable resistance change, while the MS/CB shows the best performance. For example, the resistance change rate of the MS/GNPs/TPU0.49 sensor is 16 while that of MS/CB0.83 is 4.9×10^5 at the 50% compression. The dependence of the sensitivity on filler type is in agreement with that

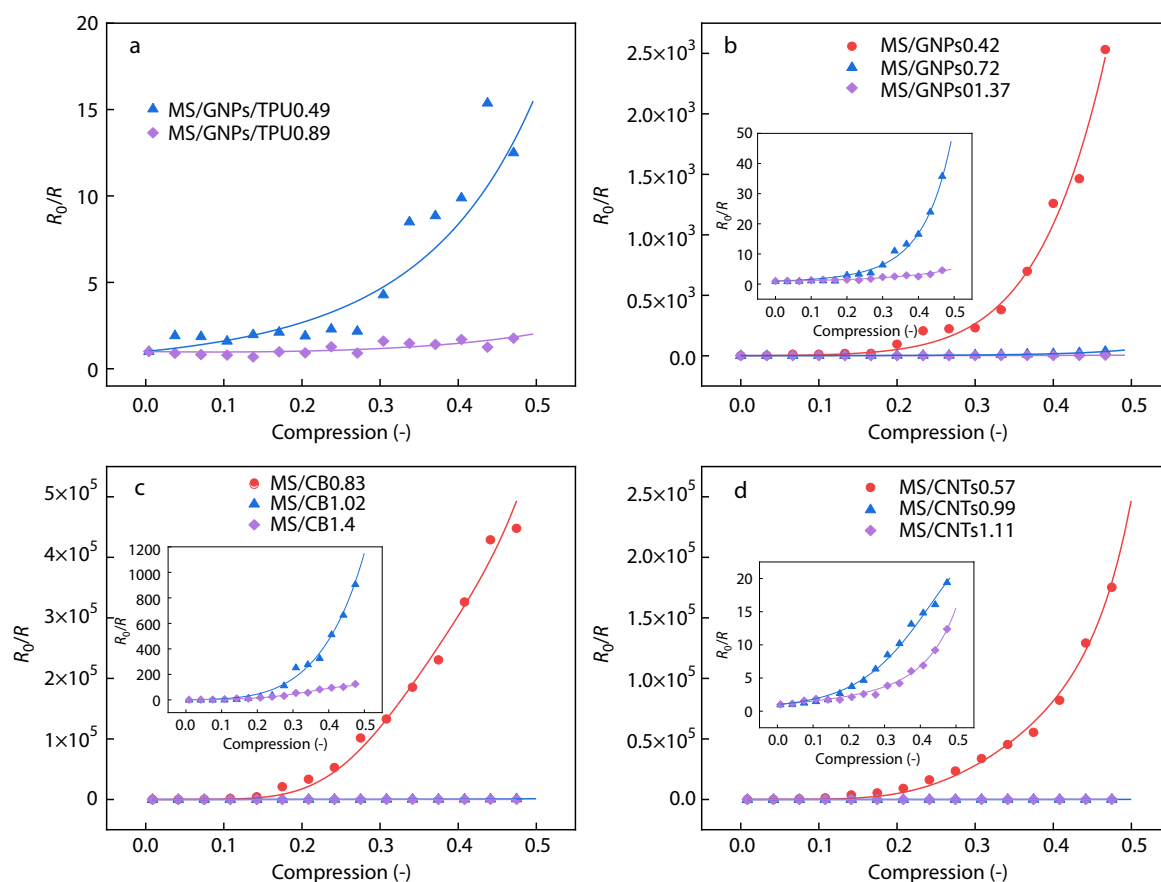


Fig. 4 R_0/R -compression curve and model fitting with Eq. (5) for (a) MS/GNPs/TPU; (b) MS/GNPs; (c) MS/CB and (d) MS/CNTs composites.

reported for stretching sensors.^[5] 0-Dimensional CB particles, corresponding to an aspect ratio of one with the smallest size, formed a large number of weak CB-CB interaction, thus the conductive networks could be easily built up under compressing, causing a sharp decrease in the resistance of the composite. In contrast, 1-dimensional CNTs with a large aspect ratio (AR) tended to entangle with each other to form relatively firm networks, thus the MS/CNTs sensors were less sensitive to the compression stimulus. Likewise, 2-dimensional GNPs formed robust conductive networks due to their larger aspect ratio, while they became the firmest with the coating of TPU. This is in line with the dispersion state of fillers in different composites as shown in Fig. 2. The fitting curves with Eq. (5) are depicted by the black solid lines, which show great agreement with the experimental data, as the coefficients of determination R^2 in Table 1 approximate to 1. C_1 is the dominant coefficient relative to the linear term, the absolute value of C_1 decreases with more addition of fillers.^[33] The results demonstrated that the model according to Eq. (5) is also able to describe the dependence of the resistance change to compression and not only to tension.^[18] Moreover, a better agreement was obtained for composite sponges with fillers inside the pores than coating on the skeletons.

Typically, the cyclic piezoresistive behaviors of the conductive MS/GNPs composites at different filler volume fractions and maximum compressions are presented in Fig. 5. As shown in Fig. 5(a), when MS/GNPs0.46 is compressed to 50%, the resistance decreases by more than three orders of magnitude (R_0 was about $10^8 \Omega$). This is an ultrahigh piezoresistive sensitivity compared to most relevant reports.^[2,29,30,34–37] With the filler concentration increasing, the MS/GNPs composite exhibits lower sensitivity but improved reproducibility.

The long-term cyclic piezoresistive property of the MS/GNPs1.34 composite is shown in Fig. 5(c). The maximum value of R_0/R (at about 50% compression) almost kept the same level during the 100 cycles, implying that the sponge had stable conductive structures. However, the minimum value (at about 0% compression) decreases after about the 30th cycle, indicating poor recoverability after long-term oscillatory loading. This might be attributed to the increasing contact resistance with the repetitive compression. The shape of the conductive sponge could not recover completely after being subjected to the compression for certain times, which was in line with the decrease of compressive load in Fig. 3(f). Even a tiny deformation, especially along the compression direction would increase the contact resistance between the sample and electrodes due to a reduction of the contact area. Better reproducibility can be achieved by improving the compression-resilience properties of the sponges.^[38]

Equivalent Filler Volume Fraction-conductivity Analysis

McLachlan's general effective medium (GEM), Eq. (6), is probably the most reliable equation that can describe the composite conductivities both below and above the electrical percolation threshold.^[39–41] An important objective of this work is to assess the possibility of describing the conductivity data under compressions using the model of Eq. (6). Thus, in addition to the resistance measurements in the absence of the compression, compressions of 30% and 50% were applied for a series of filler concentrations. The relationship of the conductivities of the four kinds of compression sensors and the filler volume fractions is presented in Fig. 6, where the resistances were converted to conductivities according to Eq. (13) and the equivalent filler

Table 1 Parameters of modeling with Eq. (5) and coefficients of determination (R^2).

Composite	C_1	C_2	C_3	R^2
MS/GNPs/TPU0.49	3.57 ± 0.42	1.17 ± 0.94	0	0.880
MS/GNPs/TPU0.89	-1.72 ± 0.19	3.52 ± 0.46	0	0.757
MS/GNPs0.42	21.07 ± 0.86	-12.16 ± 1.96	0	0.987
MS/GNPs0.72	2.75 ± 0.45	7.56 ± 0.99	0	0.972
MS/GNPs1.37	0.46 ± 0.19	2.83 ± 0.44	0	0.962
MS/CB0.83	74.83 ± 1.79	-159.84 ± 9.60	121.20 ± 13.20	0.989
MS/CB1.02	23.24 ± 1.51	-29.93 ± 7.22	17.75 ± 8.57	0.991
MS/CB1.4	13.49 ± 1.35	-0.35 ± 6.98	-21.00 ± 8.80	0.981
MS/CNTs0.57	65.47 ± 1.67	-144.84 ± 8.29	121.64 ± 10.62	0.992
MS/CNTs0.99	3.92 ± 0.74	10.80 ± 3.86	-18.36 ± 4.95	0.989
MS/CNTs1.11	3.51 ± 0.87	-4.71 ± 4.38	11.80 ± 5.43	0.980

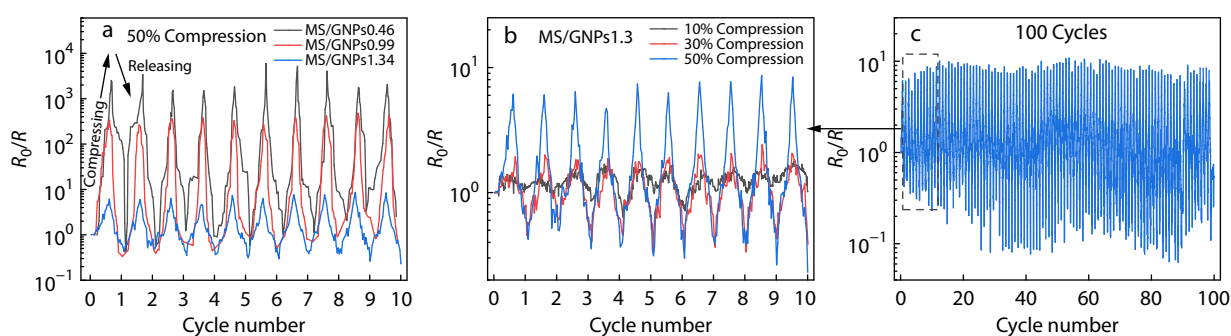


Fig. 5 Cyclic piezoresistive behavior of composites. (a) MS/GNPs at 50% compression level and different filler volume fractions; (b) MS/GNPs1.34 at different compression levels; (c) MS/GNPs1.34 upon 100 compressing-releasing cycles.

volume fractions under compressions were calculated from Eq. (12). The value of σ_m is 4.427×10^{-11} S/cm according to the measurement, t value is fixed to 2, σ_f and Φ_c are adjustable in Eq. (6). The fitting curves are shown in Fig. 6, and the values of Φ_c are shown in Table 2. All the fitting curves are in agreement with the experimental data ($R^2 > 0.943$).

The values of Φ_c slightly increased as the compression level increased for composites except for the MS/CB, probably due to the small size and the large amount of CB particles. Overall, the Φ_c values of the four kinds of composites followed the sequence of MS/GNPs/TPU < MS/GNPs < MS/CNTs < MS/CB. This could be attributed to the different AR of fillers. Since elongated cylindrical particles may form interconnected networks inside polymer composites more easily than spherical ones, a lower percolation threshold is expected with a higher AR.^[42] The Φ_c of the MS/GNPs/TPU composite was the lowest due to

the “compact” segregated structures with the coating of TPU.^[43,44] Furthermore, it can be observed that the composites with the highest electrical resistance changes in Fig. 4 had filler contents close to the percolation thresholds, which was also found in many studies.^[31,45–48] Similarly, the experimental results, for filler volume fractions $\Phi > \Phi_c$, were fitted with Eq. (7) by plotting the $\log(\Phi - \Phi_c)$ against the $\log \sigma$ until the best linear fits were generated. Here the p values, equal to the slopes of the fitting curves in Fig. 7, are shown in Table 2, which are also close to the universal value of 2.^[49]

When only the resistance change of compression sensors is focused in other studies, the conductivity change is presented in this work. Interestingly, it can be observed from Figs. 6 and 7, the conductivity of MS/GNPs/TPU slightly decreased, while those of the other three kinds of composites increased at higher compression levels. Particularly for the MS/CB com-

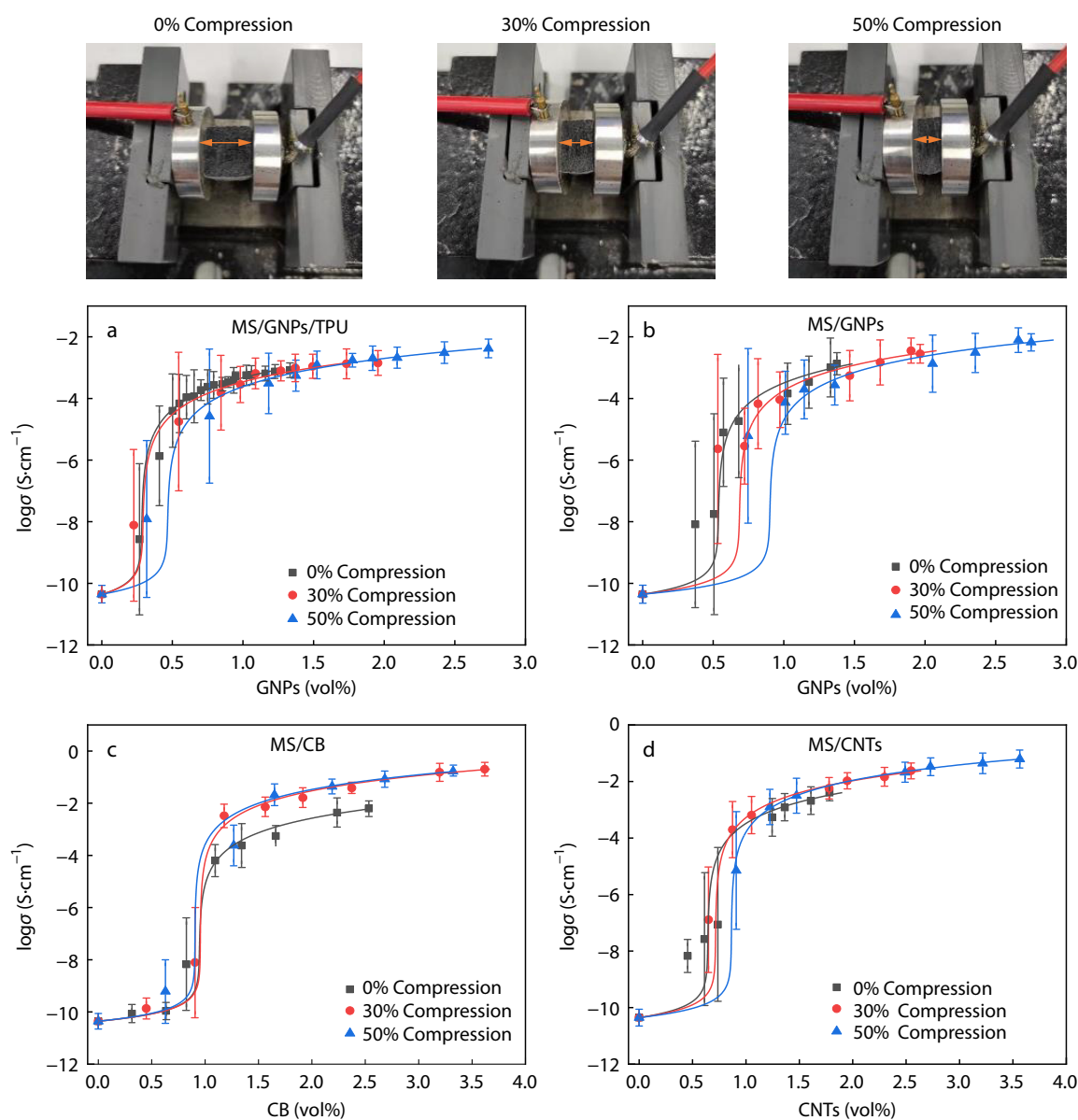
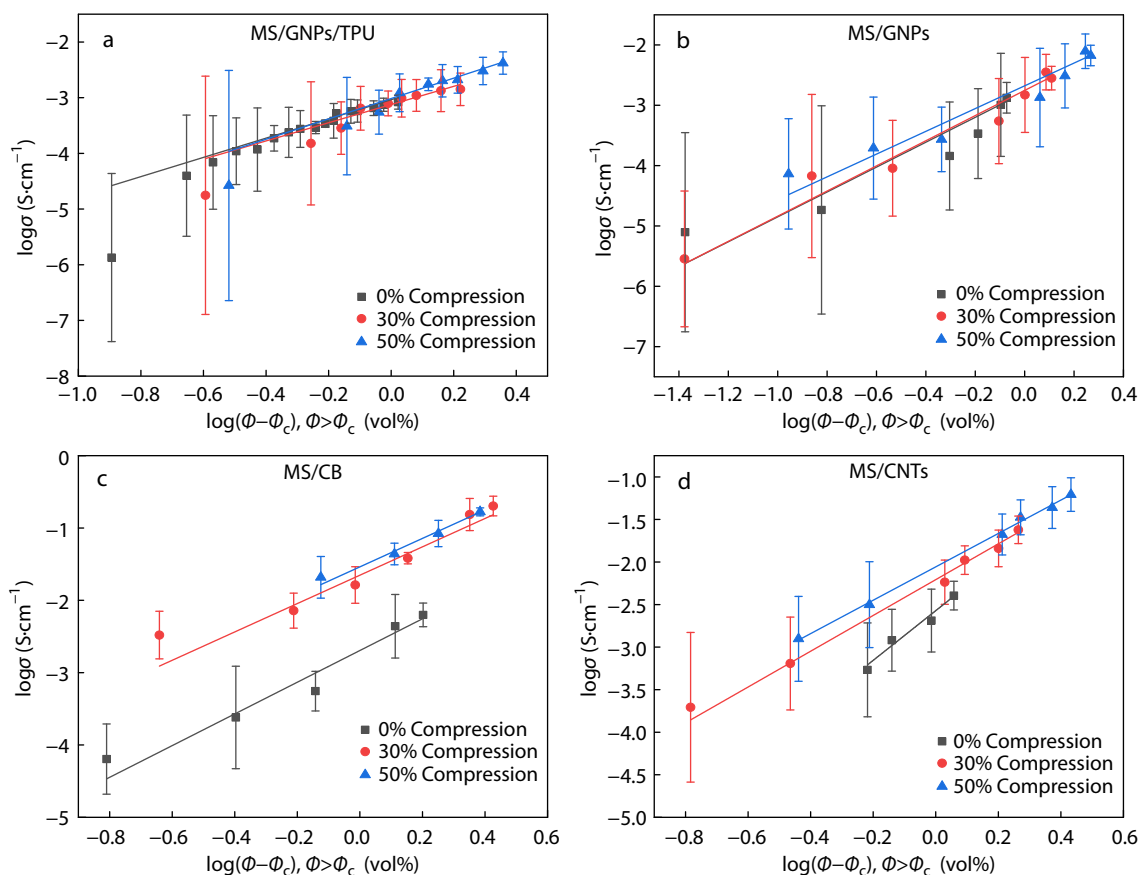


Fig. 6 Model fitting with Eq. (6) at 0%, 30% and 50% compression for (a) MS/GNPs/TPU, (b) MS/GNPs, (c) MS/CB and (d) MS/CNTs composites.

Table 2 Values of Φ_c and p fitted with Eq. (6) and Eq. (7) and coefficients of determination (R^2) for composite sponge at 0%, 30% and 50% compression.

Composite	Compression (%)	Φ_c (vol%, Eqs. 6 and 7)	R^2 (Eq. 6)	p (Eq. 7)	R^2 (Eq. 7)
MS/GNPs/TPU	0	0.282 ± 0.024	0.982	1.727 ± 0.221	0.802
	30	0.289 ± 0.078	0.964	1.634 ± 0.263	0.847
	50	0.464 ± 0.069	0.984	1.829 ± 0.202	0.921
MS/GNPs	0	0.534 ± 0.060	0.943	2.063 ± 0.413	0.862
	30	0.684 ± 0.075	0.962	2.085 ± 0.192	0.959
	50	0.899 ± 0.109	0.962	1.886 ± 0.202	0.946
MS/CB	0	0.944 ± 0.069	0.980	2.191 ± 0.297	0.948
	30	0.954 ± 0.090	0.983	1.960 ± 0.271	0.929
	50	0.904 ± 0.112	0.982	1.967 ± 0.142	0.990
MS/CNTs	0	0.640 ± 0.064	0.969	2.921 ± 0.317	0.977
	30	0.714 ± 0.049	0.993	2.103 ± 0.150	0.980
	50	0.862 ± 0.043	0.998	1.961 ± 0.083	0.993

**Fig. 7** Model fitting with Eq. (7) at 0%, 30% and 50% compression for (a) MS/GNPs/TPU; (b) MS/GNPs; (c) MS/CB and (d) MS/CNTs composites.

posite, the conductivity increased by more than one order of magnitude at 30% compression. This phenomenon opens a new way of improving the sensitivity of compressive CPCs by utilizing their piezoresistive characteristics.

CONCLUSIONS

In this work, lightweight porous melamine-based compression sensors with tunable compressibility, stability and piezoresistive sensitivity were fabricated by varying filler types (CB, CNTs and GNPs) and dispersion states. An analytical model is given and successfully described the compression-resistance response of

these sensors. It was found that the small size and the large number of CB particles endowed the sensor with the highest piezoresistive sensitivity due to the dramatic increase in the NCP during compression. When converting the resistance to conductivity, it is observed that the conductivity of the MS/CB composite was also significantly improved at the compressing state, although their Φ_c was the highest compared to other filled systems. Accordingly, this work provides a better understanding of the effect of the filler geometry and conductive network on the piezoresistive behavior of CPCs and guidance for a more precise design of the internal architecture of CPCs-based compression sensors.

NOTES

The authors declare no competing financial interest.

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