

Piezoresistive Behavior of Graphene Nanoplatelets/Carbon Black/Silicone Rubber Nanocomposite

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ABSTRACT: Silicon rubber (SR) filled with carbon black (CB) and carbon black (CB)/graphene nanoplatelets (GNPs) hybrid fillers are synthesized via a liquid mixing method. The effects of filler type on the electrical properties and piezoresistive properties (near the region of the percolation) of the conductive SR composites are studied. It is suggested that the conductivity of the composite filled with CB/GNPs hybrid fillers in the mass ratio of 2 : 4 is much higher than that in other ratio. Percolation threshold for CB/GNPs/SR is found to be 0.18 volume fractions lower than CB/SR. Moreover, force range and linearity of GNPs/CB/SR is higher than CB alone filling system. And the repeatability of the GNPs/CB/SR composites is better than CB/SR. Not repetitive index (e_z) of them is 0.1 and 0.18, respectively. The results suggest that the GNPs/CB/SR composites provide a new route toward fabrication of flexible piezoresistive sensors with high performance. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Soft and flexible piezoresistive materials have attracted tremendous attention due to their potential applications in advanced stress and strain sensors which is critical for the fabrication of artificial skins^{1–4} and wearable electronic devices.^{5–8} In the past few decades, much effort has been devoted to developing piezoresistive sensing devices based on metallic and inorganic semiconductor materials.⁹ However, electrically conductive composites consisted of conducting fillers and the insulating polymer matrix should be a better candidate for the preparation of piezoresistive sensors owing to their flexibility, light weight, easy processing, low cost, greater resistance changes, and ease of spreading over arbitrary curved surfaces. Carbon materials, such as graphite, carbon black (CB) and carbon nanotubes (CNTs), are widely used as fillers in conductive polymer composites due to low density and high conductivity. Many studies have recently demonstrated that polymers especially soft elastomers incorporated with these conducting fillers could show significant piezoresistive performance.^{10–14} The expanded graphite/polypropylene piezoresistive composites with great resistance change under 1–10 MPa pressure range have been reported in Qu's paper.¹⁵ However, both CNTs and expanded graphite-based piezoresistive composites failed to exhibit high pressure sensitivity, excellent repeatability, and small hysteresis effect at the same time. Recently, two-dimensional (2-D) graphene nanoplatelets (GNPs) have emerged as another promising carbon

conductive filler in polymer matrices because of high aspect ratio, low cost, easy production, and low resistance.^{16,17} Therefore, graphene can form a conductive network at a much lower percolation threshold due to the extremely high aspect ratio, which is beneficial to lower the filler content and maintain the excellent flexibility of the polymer matrix. Meanwhile, Two-dimensional (2-D) structure of graphene makes conductive network more stable. Whereas, the strong intrinsic Van der Waals attraction between the sheets and the high surface area makes the GNPs easily aggregate and difficult to disperse in the matrix, resulting in the weakening of the electrical conductivity of the composite. It is widely acknowledged that, in some cases, a combination of two different carbon fillers could improve the dispersion and electrical performance of the composite.^{18,19} It was reported that the addition of CNTs into the composites filled with CB into the SR composites could remarkably enhance the electric conductivity of the matrix, and a low percolation threshold of 22 vol % was achieved.²⁰ The improvement arises from the combination of two conducting fillers with unique geometric shapes and aspect ratios as well as different dispersion characteristics.²¹ It is well known that 0-D CB and 2-D GNPs are typical nanostructured carbon conductive fillers used in the polymer matrix.²² In this article, GNPs and CB were used to prepare the conductive polymer composites to show how would the fillers affect the conductivity of the composite if a small amount of GNPs is added into the CB

composite and why the piezoresistive property of mixed better than CB. The difference of conductivity and piezoresistive property between CB/SR and CB/GNPs/SR was investigated in detail.

EXPERIMENTAL

Materials and Morphology of GNPs

The GNPs examined was supplied by Chengdu Organic Chemicals Co., Ltd. with a purity > 99.5 wt %. The GNPs had a thickness of 4–20 nm, a diameter of 5–10 μm and layers < 30. CB used in this study was CB-3100, which exhibits an average particle size of about 30 nm, and was provided by Swiss SPC chemical company. The samples matrix SR (SR-GD401) was provided by Sichuan Zigong Chenguang Chemical Institute. Figure 1 shows the morphology of the GNPs. The SEM image of GNPs was provided by Chengdu Organic Chemicals Co., Ltd.

Preparation of Composites and Instruments

The SR reinforced with GNPs and CB was prepared by the melt compounding method. First, the naphtha was added into GNPs and CB with different fractions thereby mechanical stirring for 30 min and sonication for 20 h to obtain a well-dispersed filler suspension solution. Second, the SR was added into the filler suspension solution. After 1 h of high-shear magnetic mixing with a rotational speed of 3000 rpm at room temperature, the mixture was put into a vacuum oven at 80°C for 5 h in order to remove the residual solvent. Finally, the mixture was placed at room temperature for 3 days to complete the curing process.

In this experiment, the microstructures of the samples were examined by a field emission transmission electron microscope (TEM, JEM-2100F). The volume resistivity (ρ) was measured by four-probe resistivity test device. The samples used were cut into round shaped films with a diameter of 25 mm. The round-

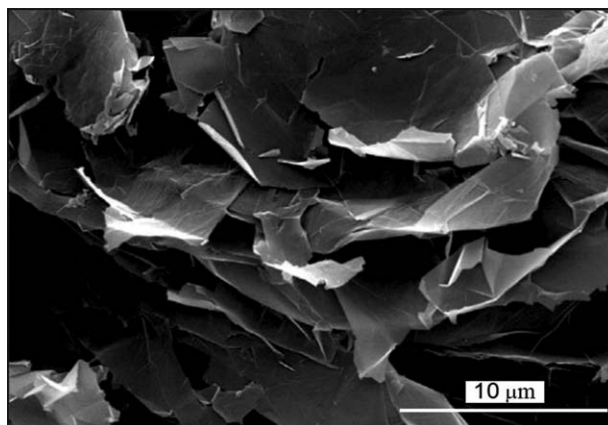


Figure 1. FESEM image of as-received GNPs nanoplatelets.

shaped nanocomposite film was sandwiched between two parallel metal electrodes and connected by conductive silver adhesive.

RESULTS AND DISCUSSION

Dispersion of GNPs and CB

In this experiment, naphtha was used as solvent for processing of composites. The dispersibility condition of CB and GNPs in naphtha is shown in Figure 2. Take the upper, middle, and lower dispersion observed under the optical microscope in the same magnification. The optical microscope images of three different height GNPs dispersion show different GNPs concentration. It is observed that GNPs is easy sediment at the bottom of the solution. But it can be observed that GNPs/CB evenly dispersed in the solvent from the right optical microscope images with same concentration. The GNPs/CB suspension exhibits homogeneous suspension with black color showing better colloidal stability in the test tube. In general, the dispersibility of

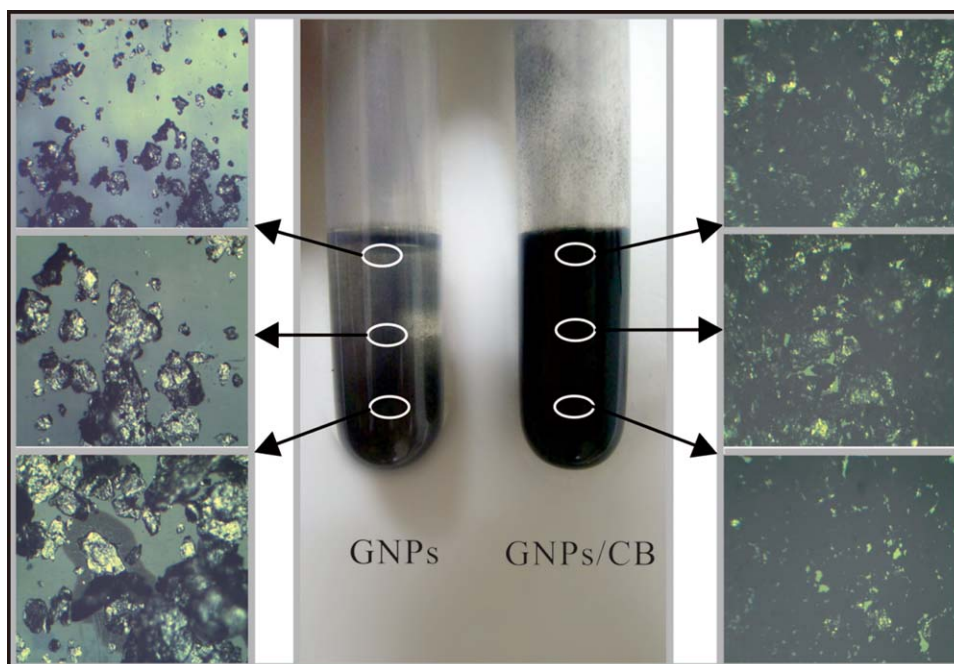


Figure 2. Optical microscope images of GNPs and GNPs/CB dispersion solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

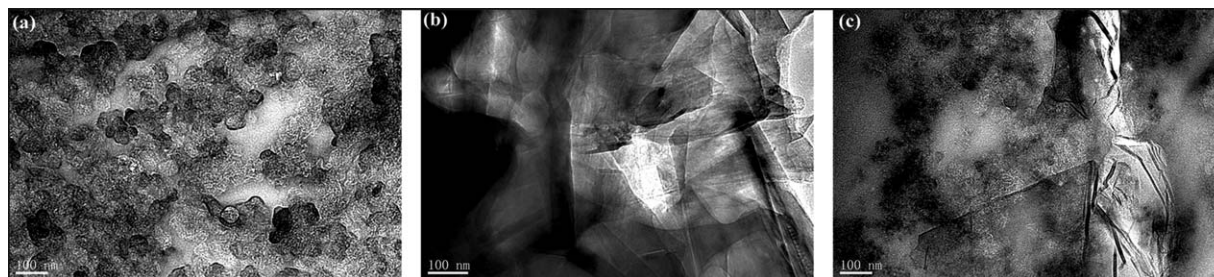


Figure 3. TEM images of (a) CB/SR nanocomposites, (b) GNPs/SR nanocomposites, (c) GNPs/CB/SR nanocomposites.

particles in solvent was affected by the particle–particle interactions and particles–solvent interactions. Because GNPs has 2-D plane structures and large surface area, the large surface van der Waals forces of GNPs will result in GNPs reunion. When the granular CB was added to enter between the graphene, it can construct hierarchical CB/GNPs architecture to inhibit the stacking of GNPs resulting in good colloidal stability. Photographs show the synergetic effect of CB and GNPs on the dispersibility, the addition of CB can improve the stability of GNPs in naphtha effectively.

Microstructure of Composites

TEM was used to investigate the morphology of the fractured surfaces of the composites. The fractured surfaces exhibited dispersibility of CB and GNPs in the SR matrix, as shown in Figure 3. It can be observed from the TEM images of the hybrid composites that CB particles are not well distributed throughout the matrix at nanoscale and just have formed a little catenated network within the matrix [Figure 3(a)]. As shown in Figure 3(b), composites containing GNPs alone shows non-uniform dispersion due to aggregated GNPs. The black region in the image shows the reunion of graphene. When spherical CB particles are incorporated into laminar GNPs, both the dispersion of CB and the exfoliation of the GNPs were improved [Figure 3(c)]. The CB particles were dispersed homogeneously on the surface of the GNPs and filled in the gaps between the graphene sheets to prevent the aggregation of the GNPs. At the same time, CB prevents the settling of GNPs in the SR matrix. This means CB could effectively improve the dispersion of the GNPs.

Electrical Conductivity of Composites

The Electric Conductivity of the GNPs and CB Filled In SR. The electric conductivity of the CB and GNPs filled in SR composites as a function of the CB and GNPs fraction (total filler loading is 6 wt %) is shown in Figure 4. The experimental data shows that, with the increase in the content of CB, the resistance of the composite materials decreases rapidly. When the mass ratio of GNPs and CB is set as 2 : 4, the minimum resistance of the composite is obtained, and then resistance continues to increase. It can be explained in the following: It is commonly believed that the conductivity of the filled conductive polymer derives from the formation of a conductive network by the fillers in the matrix, and the increase of conductive paths facilitates the improvement of the composite conductivity.²³ As for the GNPs filler alone, the conductive network is formed due to the contact of the laminar GNPs with each other. when GNPs are more, a large number of graphene would be aggregated which

prevent the formation of conductive path, resulting in poor conductivity; when CB is added into the GNPs, CB particles can decrease the agglomeration of the GNPs, as shown in Figure 3(c), which is favorable to the formation of more conductive paths. On the other hand, while CB promotes GNPs dispersion, it also forms a 2-D conductive network with GNPs, which is superior to the 1-D conductive network of the CB only. So, when CB is more, extent of the 2-D conductive network is weakened, which results in the increase of composite resistance. When the mass ratio of GNPs and CB is set as 2 : 4, the GNPs and CB may be best dispersed, reaching a minimum. The conductivity of the composite material is highest, so it can easily attain the critical percolation transition with only a slight amount of the fillers filled, effectively avoiding deterioration of the mechanical properties of the composite.

Conductive Mechanism and Percolation Characteristic of GNPs/CB (Set as 1 : 2) Conductive Silicone Rubber. Relative curve between resistivity of SR and the volume fraction of GNPs/CB (set as 1 : 2) is divided into three areas (shown in Figure 5). Zone A with higher resistivity is called as insulation zone; Zone B with sharply increased resistivity is called as percolation zone; Zone C with lower resistivity is called as conductive zone. At a low filler density (Zone A), the electric conduction occurs based on the “tunneling effect or field emission,” which postulates that the hybrid GNPs/CB cannot make a perfect network in the insulating matrix. As a result, the electrons cannot directly move between the fillers and instead, they penetrate the potential barrier. Nearby the percolation

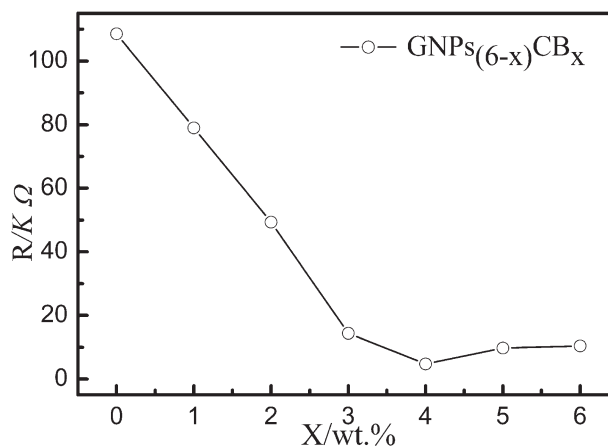


Figure 4. The variation of the resistance of the composite as a function of weight ratios of CB/ (GNP + CB) (total filler content is 6 wt %).

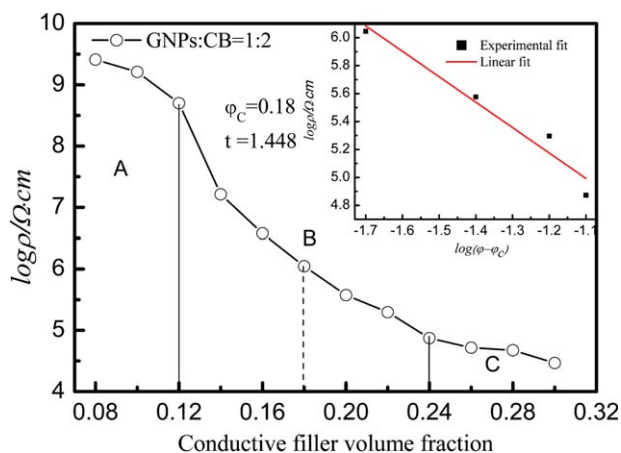


Figure 5. The resistivity of GNPs/CB/SR as a function of the filler content. Inset images in figures show the best fits of conductivity data to eq. (1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density (Zone B), CB particles and GNPs gather link, starts forming conductive path; space between congeries continuously decreases. Probability of the electronic transition greatly raise, as a result sharp increase of the conductivity of the composite material is observed. Above the percolation density (Zone C), the fillers can contact each other directly and form perfect networks, which results in the high conductivity of the composites.^{24,25}

Percolation models usually serve as the best known tool for explaining and predicting electrical properties of conducting filler based polymer composites. Critical volume fraction, an important parameter in percolation models, is a key parameter to study the electrical properties of these composites at the percolation threshold. Near the percolation threshold, conductivity of composites experiences a sudden rise in electrical conductivity for several orders of magnitude. These trends in electrical conductivity of composites near the percolation threshold follow a power law described as below²⁶:

$$\rho = \rho_f (\varphi - \varphi_c)^{-t} \quad (1)$$

In the eq. (1): φ is the volume fraction of the conductive particle in composite material; φ_c is the critical volume fraction of the conductive filler forming a percolation network in the polymer matrix, which is also known as critical percolation threshold value; ρ is the volume resistivity of conductive composite material; ρ_f is the volume resistivity of conductive filler, and t is the conductivity exponent.

The electrical properties of SR composites as a function of volume fraction of the GNPs/CB hybrid filler at room temperature is shown in Figure 5. Critical volume fraction (φ_c) and conductivity exponent (t) of the composite was determined by linear fitting of log-log plot of the power law equation described in eq. (1). The values of φ_c and t of GNPs/CB/SR were 0.18 and 1.448, respectively. The percolation concentration of GNPs/CB/SR is lower than the percolation concentration of CB/SR, which

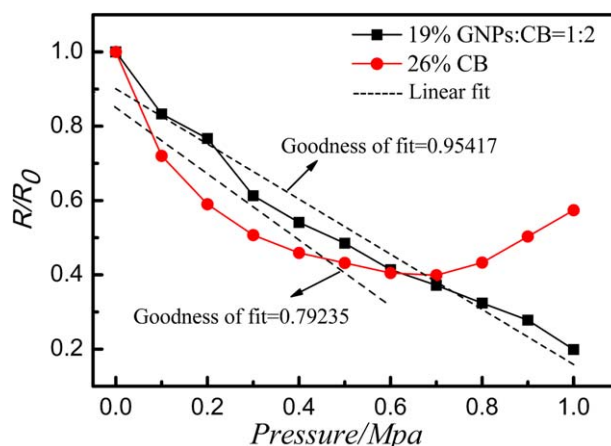


Figure 6. The relative resistance of a SR nanocomposite as a function of applied pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is 25.5 vol % in another article of our group.²⁷ It is because very thin and conductive 2-D GNPs can be effective bridges which can transport electrons between CB, and the particular high aspect ratio of GNPs increases the probability of electronic transition to form a network at low filler loading. On the other hand, the CB prevented the agglomeration of the GNPs, which can preferably form more conductive paths, resulting in a much lower percolation threshold value.

Piezoresistive Properties of Composites

The nanocomposite with the fraction of conductive fillers closest to the percolation threshold possesses a remarkable piezoresistive effect, 19 vol % for GNPs/CB/SR and 26 vol % for CB/SR was considered for the experiment. The resistivity as a function of pressure of all rubber composites is displayed in Figure 6. In the range of 0–0.6 MPa, CB/SR and GNPs/CB/SR shows a negative pressure-coefficient effect of resistance (NPCR) and the resistivity of CB/SR falls faster than the GNPs/CB/SR. After 0.6 MPa, CB/SR sample shows a positive pressure-coefficient effect of resistance (PPCR), while GNPs/CB/SR still shows the NPCR and has a continuous decreasing trend after 1.0 MPa. It can be seen that the force range of GNPs/CB hybrid fillers composite is higher than CB alone filling system. Figure 7 shows the conductive network changes scheme of GNPs/CB and CB filling systems before and after the pressuring. In the CB/SR, CB-CB is connected by point-to-point, which is easy to slide. The formation and destruction of its conductive paths is easy to occur. While in the GNPs/CB/SR they are connected by point-to-face and face-to-face, showing a more stable 2-D conductive network. On the other hand, in GNPs/CB/SR system, CB inhibits face-to-face aggregation of GNPs. This results in a large surface area, so, increasing the contact surface area between CB/GNPs and SR matrix and GNPs with high aspect ratios has more crosslinking points with rubber molecular chain, which needs greater force to form and destruct the conductive network. Moreover, within the force range, the linear goodness of fit of GNPs/CB/SR and CB/SR piezoresistive characteristic curves is 0.95417 and 0.79235, respectively. This indicates that GNPs/CB/SR is a better material as a force sensor.

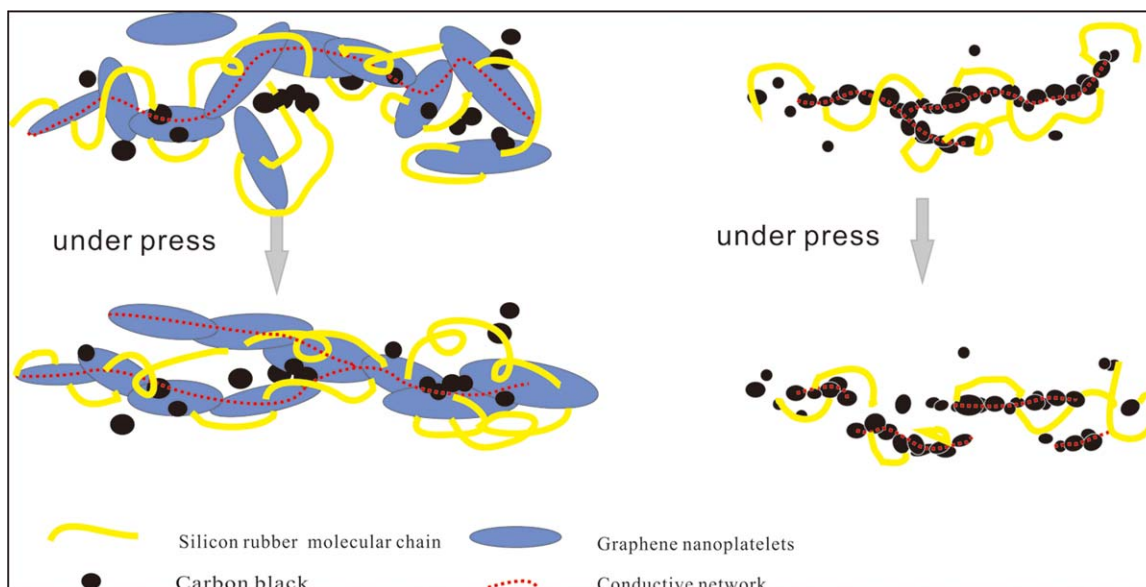


Figure 7. The model of conductive networks microstructural scheme in SR with GNPs/CB and CB before and after the pressuring. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The Repeatability of Piezoresistive Behavior

A regular and repeatable piezoresistive effect, which is mainly thought to be due to the regular changes in the conductive networks under repeated compressions, is observed in electrically conductive polymer composites. Figure 8 shows the repeatability of the piezoresistivity of a 19 vol % GNPs/CB/SR nanocomposite in (a) 26 vol % CB/SR nanocomposites and (b) of three successive compressions, respectively. Only very small differences in electrical-resistance changing of both were observed because of the rather homogeneous particle dispersion and the excellent elastic properties of SR. The graphene nanosheets are thought to be dragged along with the SR matrix during the deformation. And because of the large specific surface area and 2-D structure of GNPs, graphene can form two interfaces with polymer matrix. The bonds between the GNPs and the super-elastic polymer chains are stronger than the bonds between the CB and the polymer chains. All these lead the external stress

applied to the composite material to be transmitted to graphene fillers more efficiently. Thus, GNPs/CB/SR nanocomposite recovers better. Not repetitive index e_z is generally used to measure the quality of repetition. It is defined as: $e_z = \frac{\Delta_{\max}}{y_{F,S}} \times 100\%$. Where Δ_{\max} is maximum no repetitive error of output and $y_{F,S}$ the full scale output. e_z of GNPs/CB/SR and CB/SR is 0.1 and 0.18, respectively.

GNPs/CB/SR composites have better dispersibility, higher conductivity, lower percolation threshold, and better piezoresistive behavior, which may be attributed to a unique 2-D laminar structure of the graphene and its homogeneous dispersion in the SR matrix. The spherical CB particles are incorporated into laminar GNPs to prevent GNPs aggregating in the SR forming a 2-D homogeneous dispersion system, which improved the conductivity of the composites and made more GNPs firmly bound to the SR crosslinked network. Meanwhile, due to its high

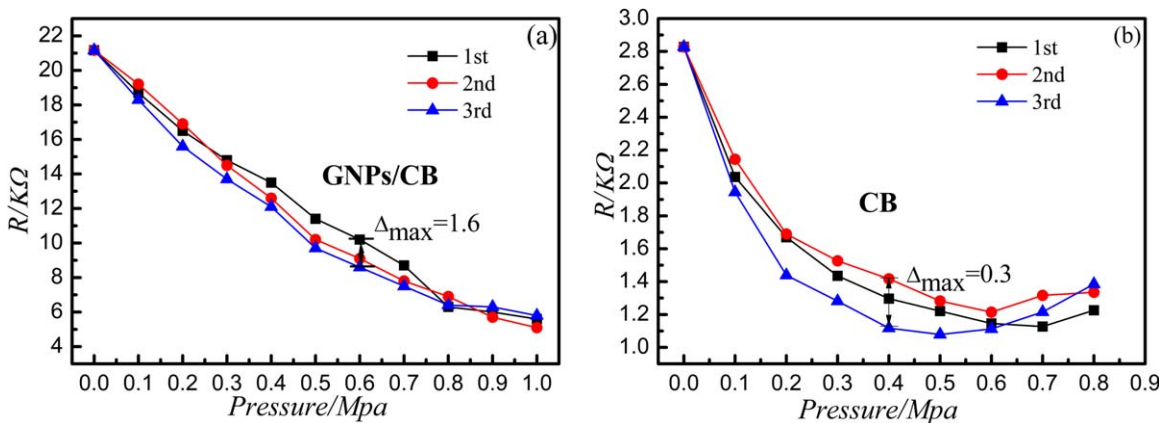


Figure 8. The repeatability of piezoresistive effects of (a) GNPs/SR and (b) CB/SR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

special surface area, the GNPs nanosheets can contact with polymer chains exceedingly. The two side interface is conducive to the prompt movement of graphene following the SR chains. Graphene and CB form a 2-D stable conductive network in the SR. Consequently, the change of normalized resistance presents high repeatability and has a wider force region. At present, the studies about improving the graphene properties in the polymer by adding other fillers have been reported rarely.²⁸ Functionalized graphene is the most commonly used method to improve its performance.^{29,30} However, this method is somewhat undermined inherent conductivity of graphene, which makes the changes in electrical property of graphene/polymer composites not significant.

CONCLUSIONS

In the study, highly elastic GNPs/CB/SR composites with low percolation threshold (18 vol %) were prepared through a liquid mixing method. The synergetic effect of graphene and CB hybrid fillers improved their dispersion in SR matrix. When the mass ratio of GNPs and CB is set as 2 : 4 (total filler loading is 6 wt %), the composite has the highest conductivity. The GNPs/CB/SR composites with 19 vol % of GNPs/CB display a better piezoresistivity property compared with CB/SR. The resistance–pressure curves of GNPs/CB hybrid fillers composites exhibit a wider force range and a better linearity than that of CB filling system. Moreover, the repeatability of the GNPs/CB/SR composites is better than CB/SR composites. Not repetitive index (e_z) of them is 0.1 and 0.18, respectively. Hence, such an excellent piezoresistive behavior makes the GNPs/CB/SR composites a potential applicant as piezoresistive sensors.

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