Magnetic field dependent electro-conductivity of the graphite doped magnetorheological plastomers

Haoming Pang, Shouhu Xuan,* Taixiang Liu and Xinglong Gong*

In this work we reported a novel graphite doped conductive magnetorheological plastomer (GMRP) with magnetic field dependent electro-conductivity. The conductivity of the GMRPs increased by increasing the content of the graphite particles, while it decreased with the graphite size. When the graphite content reached 15 wt%, the conductivity of GMRPs is approximately 10,000 times higher than the non-doped MRP. Because the iron particles in the GMRPs were magnetic, the conductivity of the GMRPs was magnetically sensitive. Upon applying a 780 mT magnetic field, the electric conductivity could increase about 1000 times larger than the one under zero magnetic field. A particle–particle resistance model was developed to investigate the influence of the magnetic field and graphite doping on the conductivity, and the fitting curve matched the experimental results very well. Finally, a magnetically controllable on–off switch based on GMRPs was proposed and its working mechanism was discussed.

1. Introduction

As new types of smart materials, magnetorheological (MR) plastomers were prepared by dispersing micro-sized magnetically soft particles into a weak cross-linked polymer matrix.1,2 Different from the traditional MR gel, magnetorheological plastomers (MRPs) are a solid-like gel and behave like a plasticine. They can be moulded into various shapes and the shapes can be kept for a long time. Different to the MR fluid, no sedimentation of carbonyl iron powders (CIPs) was found in MR plastomers because of the high viscosity of the matrix. Upon applying an external magnetic field, the magnetically soft particles would overcome the constraint of the matrix and rearrange into a string-like structure. After removing the magnetic field, these microstructures would be kept well. Because of these unique structural characteristics, the MRPs were more stable than the MR fluid3–5 and presented a higher magnetorheological effect than the MR elastomers (MREs).6–8 To this end, they were very promising for practical applications, such as energy absorbers and vibration isolators.9,10

Since the CIPs were conductive, the MR materials were also conductive polymer composite (CPC)11,12 materials which were usually prepared by mixing the conductive particles into an insulating phase. Distinctively, the column-like aggregated microstructures of CIPs also enable the MR materials exhibit typical stimuli dependent conductivity.13–15 Martin et al. reported a high performance conductive nanocomposite by dispersing gold-coated magnetic particles in a polymeric resin.16,17 It was found that the nanocomposites were very sensitive to small volume changes, and their resistance could change ten orders of magnitude upon increasing the strain from 0 to 7%. Kchit and Bossis performed a systematic study on the conductive mechanism of MREs and they presented that the resistance of MREs mainly comes from the interface, similarly the roughness parameter, the thickness of the oxide layer and the thickness of the polymer layer.18 Wang used the impedance spectroscopy method to investigate the impedance and resistance of MREs. Simultaneously, a phenomenological model was proposed to understand the impedance response of MREs under different mechanical loads and magnetic fields.19 Recently, Ghafoorianfar et al. studied the sensing capabilities of magnetorheological elastomers by combining the effects of magnetic fields and mechanical compression loads.20 The finite element analysis indicated that the coupled magnetostriction and magneto-resistance determined the piezoresistivity effect of MREs under the combined loading conditions.

The conductivity of the MRP was very sensitive to the external magnetic field because the position of the CIP was magnetically movable. Different from the traditional MRE, the MRP possessed a large change region in the conductivity because the CIPs in the MRP could be ranged from isotropic to anisotropic. Xu et al. demonstrated that the inner structure...
of MRPs exhibited a great influence on samples’ resistance using the impedance spectroscopy method\textsuperscript{21} and the influence of the particle chain direction on the conductivity of anisotropic MRP was investigated. Based on the structural dependent conductivity, an equivalent method was developed to quantitatively characterize the anisotropy of MRPs. Such a magnetically sensitive conductivity was much favourable for their applications such as the on–off switch. Unfortunately, because of the obstacle of the polymer layers, the resistance in the CIP aggregated columns was still very high,\textsuperscript{22} more work should be done to improve the conductive sensitivity of the MRP.

The addition of the conductive doping is the most common method for improving the conductivity of the MR materials.\textsuperscript{23–25} Li et al. developed the high performance MREs with excellent mechanical and electrical properties by using graphite as an additive.\textsuperscript{26,27} In their model, the current flowing through the chain structure consisted of both a tunnel current and a conductivity current, both were dependent on the external loadings. Bica et al. have done several meaningful studies in this area and they found that the doped MR materials exhibited typical magnetic dependent conductivity and capacity.\textsuperscript{28} Some other doping like silvers, graphene and carbon nanotubes\textsuperscript{29,30} or other matrices like ionic liquids and ion gels\textsuperscript{31–33} can also improve the conductivity of MR materials.\textsuperscript{34,35} In consideration of their unique structural characteristics, the MRPs enhanced by the conductive doping must be much useful in the sensor application. Therefore, the development of high conductive MRPs and studying their stimuli dependent conductivity in both experiment and theory become an important point in this area.

In this work, a novel magnetic field dependent electro-conductive MRP doped with graphite (GMRP) was developed. The conductivity of the GMRPs was tunable by varying the content and size of the graphite doping. Under the optimum conditions, the GMRPs present well-defined magnetically responding conductivity and the coupling characteristics can be described by using a particle–particle resistance model. A possible mechanism was proposed to demonstrate the high sensitivity of the GMRPs. Finally, a simple on–off switch was developed and the results indicated that such smart materials had great potential in smart devices.

2. Experimental

2.1 Sample preparation

The materials used for the GMRPs are: toluene diisocyanate (TDI, 2,4-TDI at \(80\%\), 2,6-TDI at \(20\%\), Tokyo Chemical Industry Co. Ltd, Japan), polypropylene glycol (PPG-1000, Sinopec Group Co. Ltd, China), 1,4-butadiol (BDO, Sinopharm Chemical Reagent Co., Ltd, China), carbonyl iron powders (CIPs, type CN, BASF aktiengesellschaft, Germany) and flake graphite powders (FGPs, Dongguan Xieli graphite products Co. Ltd, China). The FGP sizes are of three different particle sizes (13.0 \(\mu m\), 6.5 \(\mu m\) and 2.6 \(\mu m\)). The average diameter of the CIPs is about 6.0 \(\mu m\).

GMRP samples with different CIP concentrations, FGP concentrations and FGP sizes are prepared by using homemade polyurethane (PU) as a matrix. To synthesize polyurethane, the TDI and PPG were added to a flask with a molar ratio of 3:1 at 80 °C for 2 hours. Their weights were calculated using the formula below:

\[
\frac{m_{\text{TDI}}/174 \text{ g mol}^{-1}}{m_{\text{PPG}}/1000 \text{ g mol}^{-1}} = 3.
\]

Later, BDO was added into the reactor and the temperature was set to be 60 °C for about 40 minutes. The weight of BDO was calculated by the formula below:

\[
\frac{m_{\text{TDI}}/174 \text{ g mol}^{-1}}{m_{\text{PPG}}/1000 \text{ g mol}^{-1} + m_{\text{BDO}}/90 \text{ g mol}^{-1}} = 1.1.
\]

The reaction was kept under stirring. As soon as the reaction was completed, the CIPs and FGPs were added under vigorously mixing before the temperature was cooling down.

In our experiment, three groups of GMRPs were prepared and the compositions of all GMRPs were shown in Table 1. Group 1 are samples with different FGP concentrations. The size of the FGP was 6.5 \(\mu m\) and their CIP's weight ratio was 70 wt%. These samples were defined as MRP-0, MRP-5, MRP-10, and MRP-15, respectively. The number means the weight of FGP in a 100 g matrix and their volume fractions are 0%, 1.9%, 3.6% and 5.3%. Group 2 are samples with different CIP concentrations. Their CIP's weight ratios are 50 wt%, 60%, 70% and 80% corresponding to 11%, 16%, 23% and 34% in volume fraction respectively. They were named as MRP-50, MRP-60, MRP-70, and MRP-80, respectively. Group 3 are samples doped with FGPs with different sizes, while the other parameters are kept constant, e.g. 5 g of 6.5 \(\mu m\) FGP in a 100 g matrix. The diameters of the FGP are varied from 13.0 \(\mu m\) to 6.5 \(\mu m\) and 2.6 \(\mu m\), thus the relative samples were named as MRP-13.0, MRP-6.5 and MRP-2.6.

### 2.2 Experimental setup

Fig. 1 shows the schematic of the experimental setup used to characterize the magnetic field dependent conductivity of the GMRPs. The system consists of three parts: a commercial rheometer Physica MCR301 (produced by Anton Paar GmbH, Austria) equipped with an electro-magnetic accessor MRD180.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Group 1</th>
<th>Group 2</th>
<th>Group 3</th>
</tr>
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<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>11</td>
<td>9.5</td>
<td>0.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 1 Compositions of GMRP samples
a Modulab material test system (MTS, Solartron analytical, AMETEK advanced measurement technology, Inc, United Kingdom) and a data storage and analyzing system (software). The GMRP sample is located between two copper electrodes. The two copper electrodes are fixed on the rotor and the sub-stratum of the rheometer by an insulating glue. The rheometer can supply a uniform magnetic field from 0 mT to 800 mT. At the same time, the distance between two copper electrodes and the normal force on the GMRP samples can be accurately controlled and measured. The modulab MTS can supply a direct voltage excitation and measure the responsive current. Finally, all the data will be saved in the data storage and analyzing system.

In our experiment, the distance between two copper electrodes was set to be 1 mm, and the diameter of the GMRP sample was kept as 20 mm. All samples were treated under a 780 mT magnetic field for more than 300 s as a pre-configuration process before resistance testing. The direct voltage was set as 4 V and the resistance of the copper electrode and the wire is less than 1 Ω. During the test, the time of each measurement point was set as 1 s. All the measurements were implemented at room temperature.

3. Results and discussion

3.1 Resistance of GMRPs

Fig. 2 presents the SEM images of the samples after pre-configuration. It is found that almost all the CIPs are assembled to form chain-like microstructures. These chains are parallel along the direction of magnetic field (red arrow). Different from the MRE, the CIPs in the MRP are not deadly fixed in the polymer matrix, thus they cannot closely attach to each other and many interval gaps are presented. Besides the spherical CIPs, some sheet-like particles are also observed in the SEM image. These particles are indexed to be graphite sheets. The graphite doping has not shown any significant influence on the microstructure of the final GMRPs and all the doped GMRPs with different sized graphite particles present a chain like inner structure.

The mechanical properties of the matrix PU and the graphite doped MRP were firstly investigated. Fig. 3 presents the shear storage modulus \( G' \) of the GMRP under different magnetic flux density. Clearly, with increasing magnetic field, \( G' \) increases. The saturated storage modulus is highly dependent on the content of the CIPs. As soon as the content of CIPs reaches 80%, the storage modulus was 7.5 MPa and the relative MR effects reached as high as 1000%. All these results indicate the MRPs possess a high MR performance. Interestingly, the content of graphite also exhibits an enhancing effect on the MR effects. Upon increasing graphite percentage to 15%, the increment of the saturated storage modulus is about 0.8 MPa, this should be
in response to the strengthening effects of the graphite doping. However, the storage modulus of the GMRPs doped with different sized graphite particles presents a similar magnetically dependent nature, which illustrates that the size of graphite particles can hardly affect the storage modulus of the graphite doped MRPs. Fig. 4 gives the viscosity of GMRPs with different compositions. The viscosity notably increases with the CIP content and the FGPs also exhibit a strengthening effect on the viscosity. At the same time, the size of the graphite particle only weakly influences the viscosity. The high storage modulus and viscosity of GMRPs demonstrate that they are different from the traditional MR gels and MR elastomers.

The conductive CIPs in the MRP are aggregated to form a chain-like microstructure, thus the MRP could be defined as a conductive material. Fig. 5 shows the I–U characteristic curve of MRP-5 under different magnetic flux densities. All the curves are straight lines via the original point, which means that the resistance of GMRPs can be tested by voltage dividing by current. With increasing magnetic flux density, the current sharply increases which illustrates that the electrical capability of the GMRPs is very sensitive to the magnetic field. Therefore, the influence of the magnetic field on the resistance of GMRPs was investigated.

As shown in Fig. 6, with the increase of magnetic field, the resistance of the MRP firstly sharply decreases within 200 mT and then tends to level off till 800 mT. Although the CIPs are aggregated to form a chain structure in the GMRPs, many internal gaps are presented in the chains, thus the conductivity of the GMRPs is low. Upon applying the magnetic field, the induced dipole force between CIPs enables the chains assembled more tightly. Under a 780 mT magnetic field, the resistance drops from 22 kΩ to 2.5 kΩ in sample MRP-15 and the conductivity increases about 8000 times. To this end, the conductivity increases with increasing magnetic field.

In this work, the graphite particles were added into the MRPs to improve the conductivity. Clearly, with increasing graphite doping percentage, the conductivity critically increases. The above results also indicate that the conductivity of the GMRPs can be controlled by varying the graphite doping. If the FGP doping is 15 wt%, the resistance significantly decreases from 200 MΩ to 22 kΩ, indicating that the conductivity increases as high as 10 000 times. It was found that the conductivity increased sharply with the low graphite doping. As soon as the graphite content is increased to 15%, the enhancing effect sharply decreases. Therefore, this value is defined as the optimum content for the doping.

Here, the influence of the CIP content on the conductivity of the GMRPs was also investigated. As shown in Fig. 7, samples with a higher CIP content have higher magnetoresistances and the conductivity of all the samples increases more than 1000 times with an increase of magnetic field from 0 mT to 780 mT. The resistance drops from 112 000 Ω to 6600 Ω at 780 mT with rising CIP content from 50% to 80%. Interestingly, without applying the magnetic field, the resistance increases with CIP content, which may be caused by the higher viscosity of samples with a higher CIP content. The high viscosity of samples makes them insensitive to small magnetic field, which leads to the high resistance when the magnetic field is small. Finally, the effects of the graphite particle size on the conductivity were also studied. Fig. 8 demonstrated...
that the smaller FGPs often lead to a smaller resistance. Under similar content, more particles are presented in the matrix for the smaller graphite particles. In this case, more inner gaps between the CIPs in the chains would be connected by the conductive particles, thus the conductivity was increased.

### 3.2 Theoretical model

In order to understand the conductive properties of GMRPs, a particle–particle electrical resistance model based on dipole model was developed. Here, we assume that all CIPs are of the same size and form strings one by one as shown in Fig. 9. Since the resistance of the matrix is far more than that of CIPs, the resistance of GMRPs mainly comes from the interface resistance between the particles, named as tunnel resistance. To ensure the rationality of assumption, the microstructures of the samples were observed in Fig. 3. The CIPs in the matrix attached with each other to form particle chains (Fig. 9). Between the nearby two particles, an interface layer was found (Fig. 3b) and the interface layer is composed of the polymer matrix. In this case, the resistance of the CIPs can be neglected contrasted with the tunnel resistance.

The conductivity $J$ of tunnel current in the case of low voltage is given by ref. 40

$$J = \frac{3(2m\phi)^{1/2}/2e}[E_i/d]V \times \exp[-(4\pi e/d)(2m\phi/\omega)^{1/2}], \quad (1)$$

where $m$ is the mass of electrons, $E_i$ is the charge of electrons, $\phi$ is the height of the rectangular barrier, $d$ is Planck’s constant and $V$ is the voltage across film. $J$ falls sharply with the increase of the particle distance $e$. Therefore, we just consider the tunnel current where the particle distance is less than $h$. When $e$ changes, the distance of the main contact area is still around $h$, so we denote the average resistivity of this area as $\rho$. Then the resistance of the volume unit in Fig. 8 is given by

$$R = \frac{\rho e}{A}, \quad (2)$$

where $A$ is the area of tunnel current and is given by

$$A = \pi a^2 = \pi \left( r^2 - \left( r - \frac{h - e}{2} \right)^2 \right) \approx \pi r(h - e). \quad (3)$$

Here $e$ is far less than CIP radius $r$.

For the plastic MR materials, the CIPs in the matrix could rearrange their locations to form perfect chains upon applying an external magnetic field. Therefore, the resistance would reduce in the presence of a magnetic field. In this case, the matrix is viscoelastic and the particle distance $e$ will decrease under the dipole force between two particles. To further understand the influence of distance $e$ on the resistance, a four-element model was proposed to represent the viscoelasticity interface. An equivalent analytical model is constructed by a cascade of a spring, a dashpot and a Voigt–Kelvin model. The Voigt–Kelvin model contains a dashpot that is parallel to a spring (Fig. 10).

![Fig. 9](image_url) Sketch of the particle–particle electrical resistance model. The dark spheres in the picture represent the iron particles in the sample and the light gray area represents the matrix. The dark gray area represents the area for the tunnel current.

![Fig. 10](image_url) The four-element model used for representing the viscoelasticity interface. It is constructed by a cascade of a spring and a Voigt–Kelvin model. The Voigt–Kelvin model contains a dashpot that is parallel to a spring. Another dashpot is added for the non-crosslinked matrix.
Using the four-element model, when the stress $\sigma = kt$, which means the stress increases linearly with time, then the relationship between the stress $\sigma$ and strain $\varepsilon_1$ is as follows:

$$\sigma = Ge_1 + \frac{de_1}{dt}$$  \hspace{1cm} (4)

The solution of eqn (4) is

$$\varepsilon_1(t) = \frac{kt}{G} - \frac{kt}{G} \left(1 - e^{-\frac{t}{\tau}}\right).$$  \hspace{1cm} (5)

where $\tau = \eta/G$, named as retardation time. In our experiment, $\tau$ is far more than $t$, thus we reserve the first two parts of the Taylor expansion of eqn (5) and rewrite as

$$\varepsilon_1(t) \approx \frac{kt}{G} - \frac{kt}{G} \left(1 + \frac{t^2}{2\tau^2}\right) = \frac{kt^2}{2G\tau}.$$  \hspace{1cm} (6)

Then the variation of distance $e$ is

$$\delta e = e_0(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) \approx e_0\left(\frac{kt^2}{2Gt} + \frac{\sigma t}{2\eta} + \frac{\sigma}{E}\right) = e_0\left(\frac{kt^2}{\eta} + \frac{kt}{E}\right).$$  \hspace{1cm} (7)

Finally using eqn (2) and (3), we obtain

$$R = \frac{\rho\left(1 - \frac{k}{2t^2} - \frac{k}{E}\right)}{\pi\varepsilon\left(\frac{H - e_0}{e_0} + \frac{k}{\eta} + \frac{k}{E}\right)}.$$  \hspace{1cm} (8)

Hereto, we obtain the equation of the resistance of the volume unit. Based on our assumption, the sectional area of the volume unit is given by

$$A' = \frac{4}{3}\pi r^3 = \frac{2\pi r^2}{3\phi}.$$  \hspace{1cm} (9)

Thus, the resistance of the sample $R'$ is

$$R' = R \cdot \frac{H}{2t + e_0} \cdot \frac{A'}{A} \approx \frac{\pi r H}{3\phi A} R,$$  \hspace{1cm} (10)

where $H$ is the thickness of the sample, $A'$ is the sectional area of the sample, $\phi$ is the volume fraction of CIPs. Hence, we have

$$R' = \frac{\rho H\left(1 - \frac{k}{2t^2} - \frac{k}{E}\right)}{3\phi A'} \cdot \frac{h - e_0 + \frac{k}{\eta} + \frac{k}{E}}{e_0}.$$  \hspace{1cm} (11)

In eqn (11), all the parameters are fixed for a defined sample except $k$ and $t$. To find out $k$, we first need to figure out the relationship between the dipole force $F$ and magnetic field $B$. Here we do not pay much attention on how the magnetic field affects the dipole force and we just use common equations.

Generally, the force between two CIPs in a uniform magnetic field is ref. 41

$$F = \frac{3\mu_0 m^2}{2\pi \mu_0 r^3} = k_1 m^2.$$  \hspace{1cm} (12)

Table 2 shows the corresponding linear fit results $k_1$ of different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>MRP-50</th>
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<th>MRP-80</th>
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<td>0.0081</td>
<td>0.023</td>
<td>0.024</td>
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Sample | MRP-9 | MRP-5 | MRP-10 | MRP-15 |
<table>
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<th></th>
</tr>
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<tbody>
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<td>$k_1$ (N mT$^{-1}$)</td>
<td>0.019</td>
<td>0.017</td>
<td>0.021</td>
<td>0.018</td>
</tr>
</tbody>
</table>

Sample | MRP-13.0 | MRP-6.5 | MRP-2.6 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$ (N mT$^{-1}$)</td>
<td>0.024</td>
<td>0.016</td>
<td>0.020</td>
</tr>
</tbody>
</table>

where $m$ is the magnetic moment of the particle. Usually the CIPs will be saturated with increasing magnetic field, and then we used a fitting equation

$$M = k_2B^{1/2}.$$  \hspace{1cm} (13)

Therefore, we get

$$F = k_1(k_2B^{1/2})^2 = k_1B.$$  \hspace{1cm} (14)

Table 2 shows $k_1$ of all samples and the fitting curves can be found in Fig. S1 (ESI†).

In our experiment, the increase rate of the magnetic field was kept at 7.8 mT s$^{-1}$. The relationship between $F$ and $\sigma$ is

$$\sigma = \frac{F}{A'} \cdot \frac{A'}{\pi r} \approx \frac{2F}{3\phi A'}. $$  \hspace{1cm} (15)

Thus, we can get

$$k = \frac{5.2k_1}{\phi A'}. $$  \hspace{1cm} (16)

SEM analysis demonstrates that the FGPs are randomly dispersed in the polymer matrix. FGPs are nonmagnetic materials and the magnetic field cannot influence the position of FGPs directly, but the experimental results show that the resistance of MRPs will change a lot by FGPs. To understand the effects of the flake graphite particles on the resistance, the parameter $z$ was introduced to show the effect of flake graphite and we set $x$ as unit value 1 when there is no FGPs in the sample. Finally using eqn (11) we get

$$R' = \frac{\rho H h - e_0 + \frac{5.2k_1}{\phi A'} + \frac{5.2k_1}{\phi A'} h}{\phi A' + e_0}.$$  \hspace{1cm} (17)

In eqn (17), some parameters are constants, we substitute these parameters and thus obtain

$$R' = \frac{1.06\rho \left(1 - 16600k_1 \frac{h}{\phi E} + 16600k_1 \frac{h}{\phi E}\right)}{x\phi h - e_0 + \frac{280k_1}{\phi E} + \frac{280k_1}{\phi E} h}.$$  \hspace{1cm} (18)

or

$$R' = \frac{1.06\rho \left(1 - 21000k_1 \frac{B}{\phi E} + 21000k_1 \frac{B}{\phi E}\right)}{x\phi h - e_0 + \frac{280k_1}{\phi E}B + \frac{280k_1}{\phi E} B}.$$  \hspace{1cm} (19)
In eqn (18) and (19), $\rho$, $\eta$ and $E$ are calibration values and these parameters are constant once confirmed.

### 3.3 Theoretical results and analysis

Fig. 11 shows the comparison of theoretical and experimental results of samples with different CIP contents and Table 3 exhibits the relevant fitting parameters. Clearly, the theoretical results match the experimental results well when the CIP content of the sample is less than 70%. If the amount of the CIPs is too high, complex aggregation structures will be formed. In this case, the proposed model was not proper. Moreover, for MRP-80, the error of $k_f$ cannot be neglected. The relative initial particle distance $((h - e_0)/e_0)$ decreases with the increase of CIP content (Table 3) and the viscosity increases with the rise of CIP content. In a higher viscosity matrix, the CIPs meet higher constraint force during the pre-configuration process and the rearrange process becomes more difficult. No critical difference was found for the parameter $\alpha$, illustrating that the FGPs and CIPs influence the resistance separately.

Fig. 12 and 13 show the magnetic field dependent resistance of the MRP with different FGP contents and sizes. The theoretical results match well with the experimental results. The deviation between the theoretical results and the experimental results becomes larger when the magnetic field is larger than 500 mT. Because the particle distance $e$ cannot reduce forever and it has a limitation with increasing of the magnetic field, the resistance will gradually level off.

The factors $\alpha$ for FGPs are listed in Table 4. The factor $\alpha$ increases sharply with increasing FGP content, which means that the resistance can be tremendously decreased by adding FGPs in the matrix. Meanwhile, the factor $\alpha$ increases with the decrease of the FGP size.

To further analyze the conductive characteristics of the GMRPs, a possible mechanism was proposed (Fig. 14). In this work, the FGPs work like bridges to connect the conductive chains in the matrix. Without the magnetic field, CIPs and FGPs are loosely dispersed in the matrix. The gap between the particles is so large that a few channels for the current are present in the materials. As soon as a magnetic field is applied, the iron particles tend to aggregate much closer under the dipole force between iron particles. Therefore, the conductivity

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**Table 3** The relevant fitting parameters: relative initial particle distance and $\alpha$ used in the theoretical model

<table>
<thead>
<tr>
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<th>MRP-80</th>
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<tr>
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**Table 4** The relevant fitting parameter $\alpha$ used in the theoretical model

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<table>
<thead>
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<tr>
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</table>

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of GMRPs sharply increased with increasing magnetic field. Here, many defects were present in the CIP chains and some of them are of low conductivity. The graphite flasks are conductive and they can uniformly disperse in the polymer matrix. They can also bridge the non-contact particle chains thus improving the conductivity. With an increase in the number of graphite particles, the conductivity of the GMRPs decreases with a decrease in the size of the graphite particles. Similarly, the resistances sharply decrease with the increase of FGP content of GMRPs.

Based on the above analysis, we can find that the conductivity of the GMRPs is highly dependent on the content and size of the doped graphite particle. In consideration of the magnetic sensitivity, the GMRPs are promising for practical applications such as magnetic field sensors or magnetically controllable on–off switches.

### 3.4 Magnetically controllable on–off switches

By utilizing the above-mentioned characteristics of the GMRPs, a magnetically controllable on–off switch was constructed and its magnetic field dependent sensitivity was studied. As shown in Fig. 15a, two parallel copper electrodes were attached on the surface of the GMRPs to form a switch. Without applying magnetic field, the bulbs were turn off. After a magnetic field was applied, the bulb became bright. Fig. 15b showed the time dependent current in the circuit upon applying a square wave magnetic field. It was found that the current increased quickly (within 1 s) as soon as the magnetic field was added. Similarly, once the magnetic field was withdrawn, the current decreased to zero, which indicated a quick response of our repeated on–off switch.

Different from the previously reported quick response switch, the sensing current and response time could be tuned by varying the magnetic field. As shown in Fig. 15c, under a step wave magnetic field, the bulb became bright at the wave crest of magnetic field and its luminance increases with the increase of magnetic field. It means that the sensing current can be controlled by adjusting the magnetic field. Moreover, the turn on process could also be controlled by adjusting the increasing rate of magnetic field. Fig. 15d shows the time dependence of current by slowly increasing the magnetic field. We control the growth speed of magnetic field and make sure that the...
magnetic field uniformly increased from 0 mT to 780 mT in 5 s, 20 s and 100 s respectively. As shown in the picture, the current slowly increased to the maximum in different times corresponding to the growth speed of magnetic field. Clearly, the on–off time was tunable by varying the magnetic field and the light-emission change of the bulb in Fig. 15 showed the turn on process directly. This advantage enables the on–off switch to be widely applied in the smart devices by protecting the electronic device from getting destroyed by quick and large electro-current.

4. Conclusions
In this work, graphite particles were introduced into MRPs to improve the electro-conductivity of the final GMRPs. The influence of the content and size of the graphite particle on the resistance of GMRPs was investigated. The experimental results showed that the resistance of non-doped MRPs was approximately 10 000 times higher than the resistance of sample MRP-15 with 15 wt% graphite doping. Meanwhile, the conductivity of the GMRPs was magnetically sensitive and it increased more than three orders with the magnetic field increasing from 0 mT to 780 mT. A particle–particle electrical resistance model based on the dipole model was developed to understand the improving mechanism and the theoretical results matched the experimental results well. At last, a magnetic field controlled on-off switch based on GMRPs was developed and the results demonstrated that the current in the circuit increased quickly according to the external magnetic field and its sensing time was tunable by varying the increasing velocity of the magnetic field.

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Notes and references