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Multifunctional Polymer Composite with Excellent Shear Stiffening
Performance and Magnetorheological Effect

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Abstract: A novel multi-functional polymer composite (MPC) with both excellent shear stiffening (ST) performance and magnetorheological (MR) effect is prepared by dispersing magnetic particles into shear stiffening polymer matrix. Besides having the magnetically dependent mechanical properties (MR effects), this multi-functional MPC automatically changes its rheological behavior in responding to the external shear stimuli. By varying the particle's types and contents, the mechanical properties of this smart composite also can be alternatively achieved. Under applying a shear stress with excitation frequency from 1 Hz to 100 Hz, the storage modulus (G') of the MPC increases from 10^2 to 10^6 Pa, demonstrating an excellent ST effect. Interestingly, the ST effects of the MPC are also tunable by varying the external magnetic field and the change area of G' could be highly enlarged and precisely controlled. Based on the experimental results, a possible mechanism is proposed and discussed. It is believed that the "cross bonds" and the particle chains induced by the magnetic field are attributed to the excellent multi-functional stimuli-responsive properties.

Keywords: multifunctional polymer composite, shear frequency, shear stiffening performance, magnetorheological effect.

Highlight: A novel multi-functional polymer composite with both excellent shear stiffening performance and magnetorheological effect is synthesized.

1. Introduction.

Stimuli responsive smart materials have been attracted increasing interests due to their alternative chemical/physical/mechanical properties in corresponding to various working environments. A large amount of these smart systems such as thermo-responsive hydrogel,^[1, 2] pH-sensitive drug delivery,^[3, 4] electrorheological/magnetorheological fluid,^[5-7] shear thickening fluids,^[8] etc. were developed. Among these smart materials, magnetorheological materials (MR) were usually prepared by dispersing magnetic particles into the carrier matrixes. Due to their magnetic dipole-dipole interactions, the mechanical properties of the MR materials were tunable by varying the external magnetic field, thus they have been widely applied in damper, vibration controller, isolator, and magnetoresistor sensor.

The most matured MR material was MR fluids (MRF), in which the magnetic particles were dispersed in the fluidic carrier. Although the MR effect was very high, the MRFs also met a sedimentation problem because of the mismatch between the heavy magnetic particles and carrying oil.^[9] To improve the stability, the cross-linked polymers were used as the carrying phases. Unfortunately, due to the deadly-trapping of the magnetic particles, the MR effects were relatively small in these MR elastomers (MRE). The mechanical properties of the MR materials were highly influenced by varying the carrying matrix. It was found that the MR effects increased by decreasing the cross-linking densities. When the low molecular polyurethane gel was used, the final product, which was defined as the MR plastomer, exhibited both high MR effects and stabilities.^[10]

Very recently, the incorporation of other functionalities into MR materials to form multi-functional smart materials can not only defeat the disadvantages of the present MR materials but also improve their MR performances. Fang et al mixed magnetite with polypyrrole (PPY) to synthesize an bi-responsive material.^[11] By combining the conductivity of the matrix with the magneto-sensitive characteristic of dispersing magnetic particles, the final products exhibited both magnetorheological and electrorheological characteristics. Gong and his colleagues developed a real MR plastincine, for which they can store as MR plastomer but worked in the fluidic state

by increasing the temperature.^[12] Typically, this multi-functional MR material could be selectively worked as either the MRP or MRF, which not only decreased the sedimentation but also increased the MR effects. Moreover, Vicent et al. also reported the phase-changed MR materials, in which the MR materials could transform from MRF state to MRG state as soon as the temperature increased up to a critical temperature.^[13]

Shear thickening (ST) or shear stiffening is a very interesting phenomenon in many dense colloidal suspensions, whose viscosity could be sharply increased as soon as the externally applied shear stress beyond the critical shear rate.^[8] Because of this reversible shearing rate activated ST behavior, the ST materials have wide potential applications in energy adsorption and body protection.^[14, 15] Tian et al reported a novel shear-stiffened elastomer which was synthesized by silicone rubber and silicone oil.^[16] Recently, various efforts have been focused on the solid ST materials, silly putty. It is a derivative of boron siloxane materials, whose storage modulus can be sharply changed by applying a shear, punch, or tensile.^[17, 18] In consideration of their unique shear stiffening characteristics and plastic behavior, they would be very useful in preparing multi-functional polymer composites. It was reported that the fluidic ST materials could be used as the carrier fluids for MR fluids. Due to the iron particles could be held on the ST fluid media, the sedimentation could be avoided.^[19] Without applying the magnetic field, the viscosity of the as-formed multi-functional MR-ST fluids could be reduced by shearing. Obviously, the solid MR-ST hybrid materials would be more attractive than the fluidic materials for their easy sealing behavior. However, to our knowledge, the multi-functional polymer composite with both excellent ST performance and MR effect has not been reported.

In this work, a novel plastic composite with MR-ST hybrid functionalities was synthesized by dispersing carbonyl iron particles into silly putty matrix. The rheological testing indicated this hybrid polymer composites exhibited both excellent shear stiffening performance and high magneto-sensitive effect. Interestingly, under applying a high frequency shear, this composite presented a higher MR effects than the traditional MR materials in the magnetic field, which indicating the presence of

the synergistic effect. Finally, the influence factors of the mechanical properties were analyzed and a possible mechanism is proposed. Because these hybrid composites possessed plasticity, tunable shear stiffening performance and magnetorheological effect, they will be potentially applied in vibration controlling, damping and body armor.

2. Experimental Section

2.1 Materials

Dimethyl siloxane, boric acid and benzoyl peroxide (BPO), purchasing from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China, are used to prepare the polymer matrix. The ferromagnetic particles carbonyl-iron (type CN with the iron content is greater than 99.5%) and magnetite powder are purchased from BASF and Sinopharm Chemical Reagent Co. Ltd, Shanghai, China, respectively. All the reagents are of analytical purity and without additional purification before used.

2.2 Preparing the polymer matrix

Firstly, the pyroboric acid was prepared by heating the boric acid at 160 °C for 2 h. Then, the 15 percent of pyroboric acid, 81 percent of dimethyl siloxane, and a small amount of ethyl alcohol were mixed in a beaker. After heating the above mixture in an oven for 5 h, the final product was cooled down at room temperature to obtain the polymer matrix.

2.3 Fabrication of Multifunctional Polymer Composite

Polymer matrix, different contents of fillers and BPO were homogeneously mixed by a two-roll mill (Taihu Rubber Machinery Inc., China, model XK-160) at room temperature. Then, all the samples were collected in beakers and the vulcanization process was performed in ovens at about 100 °C for 1 h. The mass fractions of the fillers (CI and Fe₃O₄ particles) in the matrix were kept at 0, 20, 40, 60 and 70%, respectively. For simplicity, the MPC filled by CI and Fe₃O₄ with different

mass fractions was defined as MPC-CI-X% and MPC-Fe₃O₄-Y%, where X and Y were the contents of fillers. In additionally, MPCs with both CI and Fe₃O₄ fillers were also prepared and they were named as MPC-CI-X%/Fe₃O₄-Y%. In our experiment, the total contents of fillers in MPC-CI/Fe₃O₄ were kept at 60%. For example, the 70% of mass fraction of CI in the polymer matrix was named as MPC-CI-70% and MPC-CI-20%/ Fe₃O₄-40% denoted that 20% CI and 40% Fe₃O₄ were filled in the MPC sample.

2.4 Structural Characterization

A Nicolet Model 8700 Fourier transform infrared (FT-IR) spectrometer was employed to record the Infrared (IR) spectra of the polymer matrix in the full range of 4000–500 cm⁻¹. The field emission scanning electron microscope (FE-SEM, 20 kV) images were conducted on a JEOL JSM-6700F SEM to obtain the images of CI and Fe₃O₄ particles. TG of polymer matrix, CI particles, MPC-CI-60%, MPC-Fe₃O₄-60% and MPC-CI/Fe₃O₄ samples were studied under nitrogen atmosphere by a differential scanning calorimetry (DSC Q2000). To further investigate the microstructures of MPC-CI, MPC-Fe₃O₄ and MPC-CI/Fe₃O₄ samples, an optical microscope (JVC of China, model TK-C921EC) was employed. In order to analyze the composition of the matrix, an X-ray diffractometer was applied to record the XRD spectra. In addition, by using a MPMS VSM (SQUID, Quantum Design Co., America) the magnetic hysteresis loops of CI, MPC-CI and MPC-Fe₃O₄ samples were studied. In this paper, the rheological properties of the MPCs were carried out by a commercial rheometer (Physica MCR 301, Anton Paar Co., Austria). The shape of the tested samples is cylinder with the diameter of about 20mm and thickness of 0.68 mm and the mass are the different since the density of different samples are various. The measurements contained two parts: frequency sweep tests and magnetic-induced property tests. In the frequency sweep tests, the strain was set at 0.1% while the frequency was varied from 0.1 Hz to 100 Hz at room temperature. During the magnetic measurement process, a rotating plate with a diameter of about 20 mm was used and the 0.68 mm gap was kept all the time. Simultaneously, a controllable magnetic field was generated

by an external coil. In this study, the values of magnetic flux density were ranging from 0 mT to 1200 mT. The test frequency was set at 10 Hz. Preshears were also carried out before all the rheological tests.

3 Results and Discussion

3.1 Preparation and characterization of the MPC

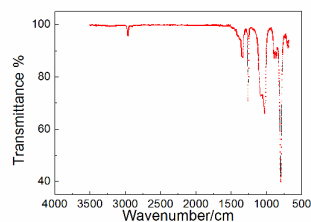


Fig. 1 The FTIR spectrum of polymer matrix in the range of 4000-500 cm^{-1} .

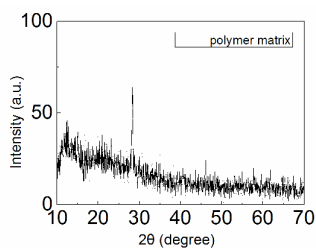


Fig. 2 XRD pattern of the polymer matrix.

Fig. 1 shows the FTIR spectrum of polymer matrix in the range of 4000-500 cm^{-1} . The absorption peak at 2950 cm^{-1} is ascribed to methyl asymmetric stretching. The characteristic band of 1350 cm^{-1} derives from B-O vibration. The strong absorption band at 1275 cm^{-1} demonstrates the presence of Si-CH₃ group. The peak presents at 1100 cm^{-1} relates to the Si-O bond. A strong absorption band locates at 890 cm^{-1} and 860 cm^{-1} indicates the formation of Si-O-B bond. Fig. 2 represents the typical XRD patterns of the polymer matrix. As shown in the figure, the peak at 28.2° (2θ) indicates the presence of BO₃-clusters forming during the high temperature treatment, which is in accordance with the results reported.^[20, 21]

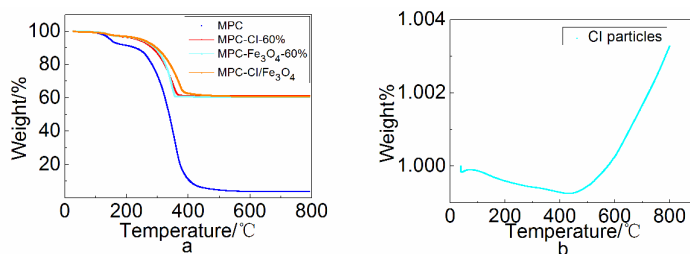


Fig. 3 TG results of : (a) polymer matrix, MPC-CI-60%, MPC-Fe₃O₄-60%, MPC-CI/Fe₃O₄ samples and (b) CI particles.

The final results of the TG analysis of polymer matrix, MPC-CI-60%, MPC-Fe₃O₄-60%, the hybrid MPC-CI/Fe₃O₄ and pure CI particles are illustrated in Fig. 3a and b respectively. It is found that the first weight loss appearing in 150 °C is attributed to the volatilization of adsorbed water and the decomposition of methyl in the Si-CH₃ structures. The weight loss between 250 to 400 °C is due to the decomposition of organosilicone, including the Si-O, Si-C and Si-O-B structures. For the pure polymer, almost all of them are burn out when the temperature reaches to 400 °C. As soon as the fillers are added into the polymer matrix to form the composite materials, such as the MPC-CI-60%, MPC-Fe₃O₄-60% and the MPC-CI/Fe₃O₄, the weight only decreases to 40%, indicating the polymer is completely decomposed and the residue is the particle fillers. Measwhile, it is also observed in Fig. 3b that the mass of CI particles are almost constant during the TGA test.

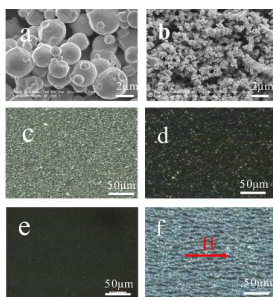


Fig. 4 The SEM images of (a) CI and (b) Fe_3O_4 particles; the photographs of (c) MPC-CI-60%, (d) MPC-CI-30%/ Fe_3O_4 -30%, (e) MPC- Fe_3O_4 -60% and (f) MPC-CI-60% sample under the magnetic field.

Fig. 4a and 4b shows the SEM images of CI and Fe_3O_4 particles respectively. The Fe_3O_4 particles are polyhedron and their average size is about 700 nm. The 3.6 μm CI particles are provided by BASF and their average diameter is much larger than the Fe_3O_4 . Fig. 4c, d, e and f represent the optical images of MPC-CI-60%, MPC-CI-30%/ Fe_3O_4 -30%, MPC- Fe_3O_4 -60% and MPC-CI-60% under magnetic field, respectively. As shown in Fig. 4c, the CI particles are homogeneously dispersed in the polymer matrix. Fig. 4d shows the microstructure of the MPC with 30 wt% CI and 30 wt% Fe_3O_4 particles. The Fe_3O_4 is much smaller than CI and the nano-sized Fe_3O_4 cannot be observed in the optical microscope, thus the particles observed in Figure 4d are less than in Fig. 4c. Similarly, it is also very difficult to detect the Fe_3O_4 particles in the MPC- Fe_3O_4 -60% sample (Fig. 4e), though some Fe_3O_4 particles aggregate. These magnetic particles are sensitive to the external magnetic field. As shown in Fig. 4f, the CI particles are driven to form the chains-like microstructure parallel to the direction of magnetic field, which also indicates the present product belongs to a kind of magnetorheological materials.

3.2 Shear stiffening effects of the MPCs

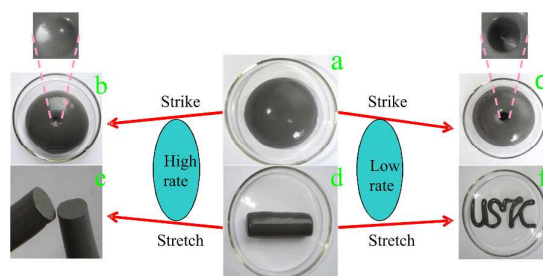


Fig. 5 (a and d) The MPC-CI-60% molded into spherical and cylinder shapes, (b) a small sunken once striked quickly and (c) a hole if striked slowly; (e) fractured as

solid-like when stretched at high strain rate and (f) exhibited soft property if stretched slowly.

The MPC presents a plastic characteristic, thus they can be mold into various shapes just like the plasticine. Fig. 5 a and d are the photos of MPC-CI-60% in the spherical and cylinder shapes. If a heavy steel bar is used to strike the material at a high speed, the material transforms into solid-like state and only a small sunken is found in the surface (Fig. 5b). Interestingly, once putting the bar on the original MPC-CI-60%, under the action of gravity of the heavy bar, the material is impaled easily (Fig. 5c). Moreover, once stretched at high strain rate, the material fractures abruptly, indicating the ST behavior (Fig. 5e). On the other hand, if stretched slowly, the material is so soft that it can be stretched to filament without fracture (Fig. 5f).

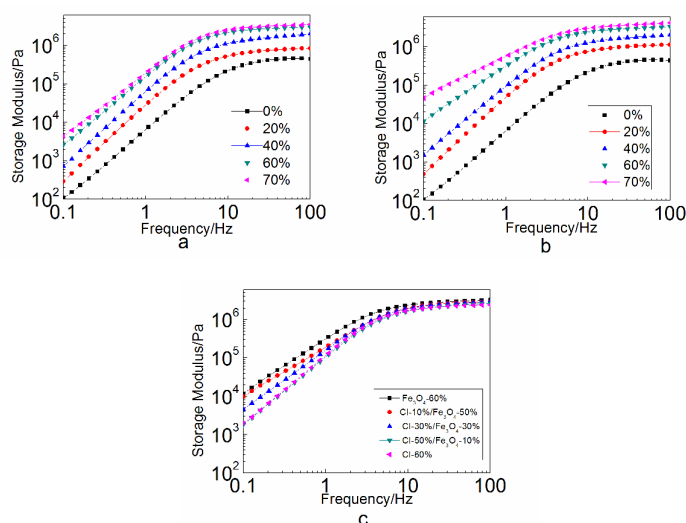


Fig. 6 Storage Modulus (G') of (a) MPC-CI, (b) MPC- Fe_3O_4 and (c) hybrid MPC in the shear frequency tests.

Fig. 6 a, b and c show the frequency-responsive storage modulus (G') of MPC-CI, MPC- Fe_3O_4 and hybrid MPC-CI/ Fe_3O_4 , respectively. Clearly, with increasing of the shear frequency, the shear rate on the polymer composites increases. In Fig. 6a, it is observed that with the G' of all the samples increase obviously with increasing of the

frequency. Taking the MPC-CI-40% for example, when the excitation frequency is 0.1 Hz, the storage modulus (G'_{\min}) is 7.16×10^{-4} MPa. As soon as the shear frequency increases, the storage modulus sharply increases and finally balances in 1.99 MPa when the frequency reaches to 100 Hz. This phenomenon indicates the material becomes stiffer under applying an external shear stress and the storage modulus can increase about 4 orders of magnitude. This mechanical behavior is in accordance with the phenomenon in Fig. 5 which when increases from low rate or low shear frequency to high rate or high shear frequency, the MPC exhibits distinguished shear stiffening behavior. Moreover, the presence of the CI particles also highly improves the shear stiffening effects. When the content of CI particles is increased to 60wt%, the storage modulus can also reach to as high as 2.95 MPa. As a result, it can be concluded that the as-prepared MPC presents typical shear stiffen behavior under the external shear or punch stimuli. Within a certain shear frequency (0-20 Hz), the storage modulus exhibit a sharp increment and the increment will be level off under higher shear frequency. Moreover, the CI particles can improve the shear stiffening effects.

The storage modulus of the MPC-Fe₃O₄ samples as a function of frequency was shown in Fig. 6b. Comparing with the MPC-CI samples, the storage modulus also exhibited the similar behavior and tendency in the frequency tests. It is observed from Fig. 4a and b that the diameter of CI and Fe₃O₄ is about 3.6 μm and nano-sized respectively. Therefore, the specific surface area of Fe₃O₄ is much huger than the CI and the large contact area between polymer matrix and Fe₃O₄ is account for the better shear stiffening effect. To compare the shear stiffening effect, a relative shear stiffening effect (RSTe) is defined to quantify the stimuli-responsive effect.

$$RSTe\% = \frac{G'_{\max} - G'_{\min}}{G'_{\min}} \times 100\% \quad (1)$$

where G'_{\max} is the maximum G' of one sample induced by the shear frequency while G'_{\min} is the initial G' . Detail information of all the MPC-CI and MPC-Fe₃O₄ samples are listed in **Table 1** and **Table 2**, respectively.

Table 1 The G'_{\min} , G'_{\max} and RSTe % of MPC-CI samples in the frequency tests.

CI content	G'_{\min} /MPa	G'_{\max} /MPa	RSTe %
0%	1.08×10^{-4}	0.44	404529.63%
20%	2.91×10^{-4}	0.84	288526.24%
40%	7.16×10^{-4}	1.99	277018.53%
60%	2.61×10^{-3}	2.95	112980.17%
70%	4.32×10^{-3}	3.50	80811.62%

Table 2 The G'_{\min} , G'_{\max} and RSTe% of MPC-Fe₃O₄ samples in the frequency tests.

Fe ₃ O ₄ content	G'_{\min} /MPa	G'_{\max} /MPa	RSTe %
0%	1.08×10^{-4}	0.43	404529.63%
20%	4.87×10^{-4}	1.12	230416.82%
40%	1.53×10^{-3}	2.01	131578.64%
60%	1.15×10^{-2}	3.28	28456.52%
70%	4.58×10^{-2}	4.16	8983.77%

It is found that although the RSTe % of pure matrix is higher than the composite materials, the changes of mechanical property are very small. For example, the G'_{\max} of the pure matrix was just 0.44 MPa, while it was 3.50 MPa for the MPC-CI-70%. On the other hand, the reinforcing effect of Fe₃O₄-filled samples was better than the same amount of MPC-CI samples. Taking the MPC-CI-70% and MPC-Fe₃O₄-70% for example, the G'_{\max} of MPC-Fe₃O₄-70% is 4.16 MPa, which is larger than G'_{\max} of MPC-CI-70%. The reason may be attributed that the interfacial bond between polymer matrix and Fe₃O₄ is much larger since the specific surface area is huger than the CI. Therefore, the mechanical reinforcement of Fe₃O₄ is larger. Fig. 6c represents the storage modulus of the hybrid MPC vs frequency. From Table 1 and 2, the G'_{\max} of MPC-Fe₃O₄-60% and MPC-CI-60% are 3.28 MPa and 2.95 MPa, respectively. In the Fig. 6c, it is apparent that the G'_{\max} of all MPC-CI/Fe₃O₄ are larger than 2.95 MPa and smaller than 3.28 MPa and the higher Fe₃O₄ content will induce larger G'_{\max} .

3.3 Magnetorheological effect of the MPCs

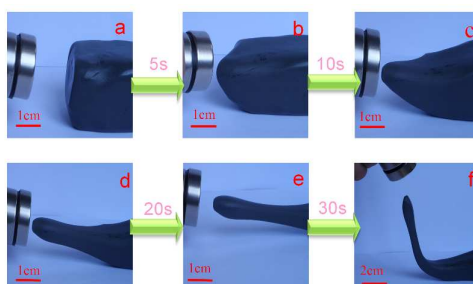


Fig. 7 The magnetic field-responsive effect of MPC-CI-60% under the stimuli of magnetic field.

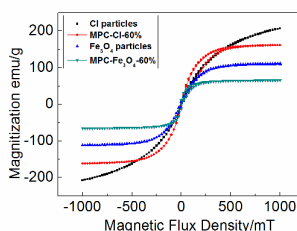


Fig. 8 The magnetic hysteresis loops of MPC-Fe₃O₄-60%, MPC-CI-60% and CI particles.

Interestingly, the MPCs also can be molded into different shapes under a magnet due to the magnetic forces (Fig. 7). The intrinsic magnetic responsive properties of the as-prepared MPCs are investigated by a MPMS VSM. Fig. 8 gives the hysteresis loops of MPC-Fe₃O₄-60%, MPC-CI-60% and CI particles. All the products exhibit typical soft magnetic behavior and the saturated intensity of magnetization of MPC-Fe₃O₄-60%, MPC-CI-60%, CI particles and Fe₃O₄ particles are 59.5 emu g⁻¹, 160.7 emu g⁻¹, 207.2 emu g⁻¹ and 111.3 emu g⁻¹ respectively. Because of the higher magnetization, the responsive storage modulus (G') of MPC-CI is much larger than that of MPC-Fe₃O₄ under the stimuli of the same magnetic field.

Similarly, the mechanical properties of the MPCs are also highly dependent on the externally applied magnetic field. Fig. 9 shows the magnetic field dependent storage modulus (G') of MPC-CI, MPC-Fe₃O₄ and MPC-CI/Fe₃O₄. It is distinct that

G' of MPC-CI samples exhibit remarkable MR effect (Fig. 9a). These curves depict that there is an increasing tendency with the increase of the external magnetic field at first and trend to saturation with further increasing of magnetic field for the storage modulus of MPC-CI. Moreover, the CI content has a great influence on G' , which means that the higher CI content will induce more apparent MR effect. As for the MPC-CI-0%, no magnetic field-dependence occurs. The magneto-induced modulus (G') is mainly caused by the particle chains (Fig. 4f), which would dramatically intensify the magnetic particle interactions. The changes of storage modulus for the MPC- Fe_3O_4 samples induced by the magnetic field are not distinctive in comparison with the MPC-CIs (Fig. 9b). Even if the mass fraction of Fe_3O_4 is very high (70 wt%), the G' shifts in small amplitude. Based on the above analysis, there is no doubt that the MR effect of MPC-CI/ Fe_3O_4 with higher CI mass fraction is more obvious than those with smaller CI content (Fig. 9c).

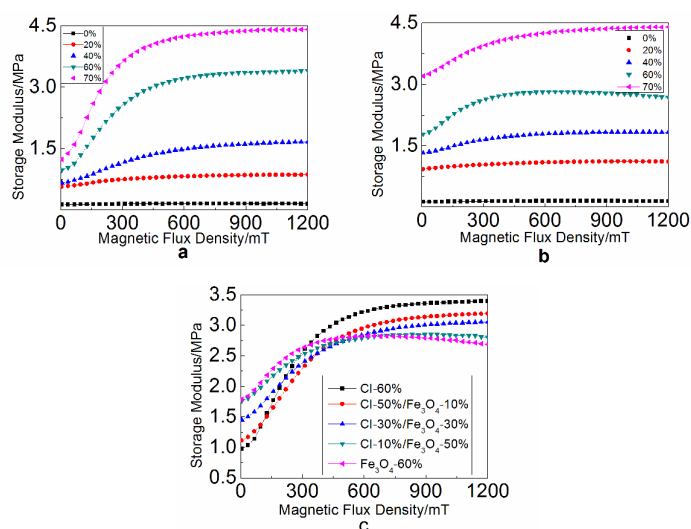


Fig. 9 The storage modulus of (a) MPC-CI, (b) MPC- Fe_3O_4 and (c) MPC-CI/ Fe_3O_4 samples simulated by different magnetic field.

The relative magnetorheological effect (RMe%) could be calculated by the equation:

$$RMe\% = \frac{G'_{\max} - G'_{\min}}{G'_{\min}} \times 100\% \quad (2)$$

where G'_{\max} is the maximum G' induced by external magnetic field while G'_{\min} is the initial G' . **Table 3** and **Table 4** give out the whole information of MPC-CI and MPC-Fe₃O₄, respectively. Clearly, the maximum MR effects can be increased to as high as 255%, which is much high than the previously reported MR elastomers.

Table3 The G'_{\min} , G'_{\max} and RMe% of MPC-CI samples induced by magnetic field.

CI content	G'_{\min} /MPa	G'_{\max} /MPa	RMe%
0%	0.14	0.15	13.5%
20%	0.57	0.87	51.07%
40%	0.67	1.67	150.64%
60%	0.98	3.40	246.59%
70%	1.24	4.42	255.84%

Table4 The G'_{\min} , G'_{\max} and RMe% of MPC-Fe₃O₄ samples induced by magnetic field.

Fe ₃ O ₄ content	G'_{\min} /MPa	G'_{\max} /MPa	RMe%
0%	0.14	0.15	13.5%
20%	0.93	1.12	19.99%
40%	1.34	1.84	37.60%
60%	1.79	2.69	50.31%
70%	3.21	4.41	37.30%

3.4 Magetically enhanced shear stiffening properties of the MPCs

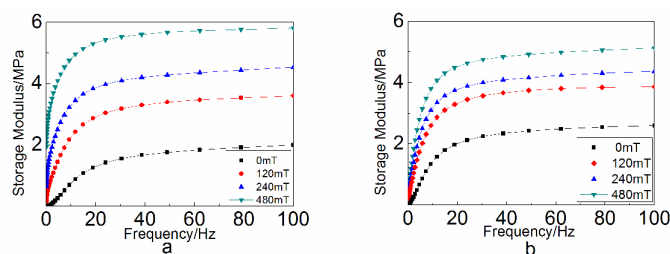
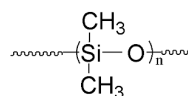


Fig.10 The storage modulus of MPC-CI-60% (a) and MPC-Fe₃O₄-60% (b) samples under the stimulation of shear frequency and external magnetic field.

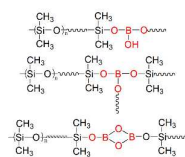
To further evaluate the inner performance of MPC samples, the synergistic effect of the frequency and magnetic field on the mechanical properties was also investigated. Fig. 10 depicts the storage modulus of MPC-CI-60% and MPC-Fe₃O₄-60% samples under different shear frequency and magnetic field. From these data, the dual stimuli dramatically enhance the storage modulus of all the MPC samples comparing with the performance induced by single stimuli. Keep the shear frequency constantly, the storage modulus increases with increasing of the magnetic field. Similarly, the storage modulus is also proportional to the frequency. Based on the above analysis, it is found that the MPC-CI-60% sample exhibits a larger change in mechanical properties than the MPC-Fe₃O₄-60%, indicating that MPC-CI is more sensitive to the external stimuli and the enhancement is more remarkable. To this end, we can conclude that by directionally controlling the external magnetic field and shear frequency, the mechanical properties can be varied in a large area.

4. Mechanisms of the MPCs

It is well known that the frequency-dependent of mechanical properties of the polydimethylsiloxane (PDMS) is attributed to the entanglement and movement of molecular chains. The angle of silicon-oxygen bonds could swing back and forth easily, thus, forming the soft and flexible PDMS molecular chains. During the high-temperature processing, the dimethyl siloxane could polymerize with pyroboric acid easily. The Si-O bond would break and react with each other, forming the backbone structure of PDMS chains with high molecular weight. The basic structure is as follows.



At the same time, B was introduced into the chains, forming polyborondimethylsiloxane (PBDMS), which contained the Si-O-B bond. According to Zatsepin^[22] three possible structures were as follows:



As mentioned by Houston^[17] and Wick^[23], due to the lacking of electrons, the empty *p* orbital of the B atom could obtain them from the O in the Si-O structure. On the other hand, the decomposition of BPO would connect the molecular chains, forming the cross bonds. The microstructure of MPC sample is depicted in Fig. 11a.

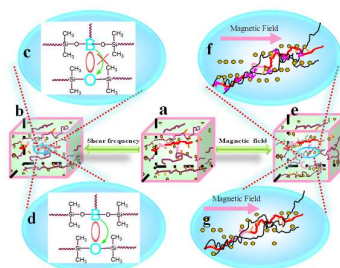


Fig. 11 The changes in microstructure of (a) MPC sample; (c and d) induced by shear frequency and (f and g) magnetic field.

The transient “cross bonds”, induced by the B and O atoms, are dynamically variable and more vulnerable than the covalent bond, which demonstrates that if stress is applied in a long time scale, the “cross bonds” has enough time to break and the resistance among the entangled molecular chains are delicate. Under this circumstance, only the chemical cross bond and the friction among the chains resist

the movement of polymer chains. Therefore, they could shift easily and the materials exhibit plasticity and fluidity (Fig. 11d). On the other hand, with increasing of the shear frequency, the “cross bonds” could not in accordance with external stimuli, as the relaxation time of the “cross bonds” is much longer than the frequency. Therefore, the large amounts of the “cross bonds” may attract the ambient polymer chains, impeding the movement of other chains. On this occasion, the increasing amount of the “cross bonds” generated in very short time scale also play an important obstructive role during the shift process (depicted in Fig. 11c). Consequently, the material behaves as solid state macroscopically.

By only changing the intensity of magnetic field, the CI would be driven to form particle chains with different dimensions, exhibiting different magnetorheological effect (Fig. 11f). Therefore, evident increase in G' could be observed. Finally, the filler amount also promotes the mechanical properties in regardless of the types. The free volume theory is applied to explain the phenomenon. When the filler amount is improved, the free volume among the polymer chains diminishes, causing the hindrance of the molecular chains. As a result, the fillers would undergo the majority of the external stress, leading to the reinforcement of the rheological properties. However, the frequency sweep indicates that the enhancement of Fe_3O_4 is much better. The reason should be ascribed that the diameters of Fe_3O_4 are much smaller than the CI particle, so the specific surface area is much larger and the contact between the polymer chains and particles are much huger, giving rise to higher friction and energy dissipation during the deformation.

5. Conclusion

In this work, a versatile plastic polymer composite, defined as MPC, was fabricated by using carbonyl iron particles and silly putty as the dispersing phase and carrying matrix, respectively. The G' of MPC can change 4 orders of magnitude under the stimuli of shear frequency, which shows excellent ST effect. Besides the plasticity,

the external magnetic forces also can induce the MPC into various shapes. The magnetically dependent MR effects of MPC-CI-70% can reach 255% and the maximum storage modulus is 4.42 MPa. More importantly, the mechanical properties of MPC can be tremendously enhanced under the stimulation of frequency and magnetic field simultaneously. Finally, the “cross bonds” and CI particle chains, induced by the B-O bonds and magnetic field respectively, are the main reason for MR-ST multifunctional properties. On account of the plasticity, enhanced mechanical property and credible tunability, MPC will be applicable in vibration controlling, damping, isolator and body armor.

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