PAPER

Magnetic Plasticine™: a versatile magnetorheological material†

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A novel black Plasticine™ was developed by dispersing iron microparticles into the paraffin wax–petroleum jelly composite matrix. Due to the presence of magnetic particles, this Plasticine™ exhibited magnetic-dependent mechanical properties and can be defined as a typical magnetorheological gel (MRG) material. The magnetic Plasticines™ were malleable and their mechanical properties were highly influenced by the iron contents. With increasing of the externally applied magnetic field, the shear storage modulus sharply increased. Under the optimum iron content, the magnetic induced modulus can be increased to as high as 4.23 MPa, whereas the relative magnetorheological effect was 305% and this value was higher than the reported magnetorheological elastomer (MRE). Interestingly, when the temperature reached a critical point, the magnetic Plasticine™ changed to a fluid like material which exhibited the typical characteristics of magnetorheological fluid (MRF). It was found the versatile magnetic Plasticine™ can seldom be transformed between the MRG and MRF without changing its dynamic properties.

1. Introduction

The integration of magnetic particles with polymer matrix leads to functional smart composites, whose mechanical properties can be varied significantly by externally applying a magnetic field.[1–10] These magnetic stimuli-responsive materials, which were often named as magnetorheological (MR) materials, have found wide applications in the biomedical areas of soft actuators or artificial muscles, or in the engineering applications of dampers, vibration controllers, isolators, and magnetoresistor sensors.[11–22] During the past decades, various efforts have been made to improve the mechanical behavior of the MR materials. It was found that the particles, carrying polymer, and the interface between the particles and polymer highly affected the dynamic properties of the MR materials. Therefore, most research in this area was focused on optimizing the magnetic content, tuning the particle arrangement structure, increasing the compatibility between the particles and polymer, improving the quality of the polymer matrix, and so on.[23–32]

The intrinsic properties of the polymer carrier play a key role in determining the mechanical behavior of the MR material. Based on the finite element analysis, Davis noted that the change of the modulus ($\Delta G'$) could only increase approximately 50% of G_0' for a typical elastomers.[33] However, it was also reported that the MR effect ($\Delta G'/G_0'$) of the silicone rubber based MR material could reach to 64% and the polyurethane based MR material exhibited a 121% MR effect, which indicated that the influence of the polymer matrix was energetic.[24,34] Understanding the effects of matrix nature on the mechanical properties of MR material has been the subject of numerous previous investigations, many novel carriers such as mineral oil swollen co-polymer poly-styrene-*block*-poly(ethylene-stat-butadiene)-*block*-polystyrene, physically crosslinked PVA hydrogels, low molecule weight polyurethane, *etc.* were used.[35–39] Different from the traditional rubber-based MR elastomers, the position of the magnetic particles in the above MR materials are movable and they can transform from isotropic to anisotropic under applying an external magnetic field, which enable them exhibit high mechanical properties.[37] Therefore, the soft polymer matrix with low initial modulus is desirable for improving the MR effect.

A phase-change material is a substance which can transform from solid-like to liquid states. During the recyclable melting–solidification process, the physical properties of the phase-change polymer varied quickly and correspondingly. It was reported that the modulus and damping of the MR gel sharply changed since the gel-like matrix became softer with the increase of the temperature.[37] Therefore, when the phase-change polymer is applied as the carrier for the MR material, a more vigorous variation will be acquired by varying the temperature. Plasticine™ is a wonderful material which was firstly applied as children's toys, moulding casts for plaster, and plastics.[40,41] Because of its non-linear viscous behavior, it also has been used to simulate the geological structures of the folds, bounding, diapers

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etc.[42–44] The Plasticine™ is soft, non-toxic, malleable, and its physical state can be maintained on exposure to air, which enable the Plasticine™ be an ideal matrix for MR materials. However, few works have been done to develop the Plasticine™-based MR materials and investigate their magnetic-dependent mechanical properties. In addition, due to the presence of the long-chain aliphatic acids, Plasticine™ exhibits a typical phase-change phenomenon, which indicates that the magnetic Plasticine™ would be a versatile MR material with changeable MR characteristic.

In this work, a novel phase-change MR material, defined as magnetic Plasticine™, was developed by dispersing iron microparticles into the paraffin wax–petroleum jelly composite matrix. The mechanical properties of the as-prepared composites were highly influenced by the iron contents, magnetic field, and the temperature. The magnetic Plasticine™ performs as the MR solid gel under room temperature while it transform to MR fluid if the temperature was above the phase change point. The affecting factors for preparing the magnetic Plasticine™ were discussed and the possible mechanism was analyzed.

2. Experimental section

Materials

The materials paraffin wax and petroleum jelly were purchased from Shanghai Gao-Qiao Petrochemical Corporation, China; the magnetic particles were carbonyl iron particles (CI) with an average diameter of 3.5 μm, bought from BASF. All reagents were used as received without further purification.

Preparation of the magnetic Plasticine™

In a typical synthesis, equal amounts of paraffin wax and petroleum jelly were added into the three-necked flask and the temperature was increased to 70 °C by using a water bath. After all the solid materials were fully melted to form transparent solutions, the relative amount of CI particles was added to the above system under vigorously mechanical stirring. As soon as the particles and the carrier were well mixed, cooling the system to room temperature. Then the final magnetic Plasticine™ was obtained. Here, the properties of the magnetic Plasticine™ can be controlled by varying the weight percentage of the CI/paraffin wax–petroleum jelly and five magnetic Plasticines™ with 30%, 40%, 50%, 60%, 70% amount of CI contents were prepared.

Characterization

X-ray powder diffraction patterns (XRD) of the products were obtained on a Bruker D8 Advance diffractometer equipped with graphite monochromatized Cu Kα radiation ($\lambda = 1.5406$ Å). Infrared (IR) spectra were recorded in the wavenumbers ranging from 4000 to 500 cm^{-1} with a Nicolet Model 759 Fourier Transform Infrared (FT-IR) spectrometer using a KBr wafer. Their magnetic properties (*M–H* curve) were measured at room temperature on a MPMS XL magnetometer made by Quantum Design Corp. The thermal stabilities were studied by differential scanning calorimetry (DSC Q2000) under nitrogen atmosphere. The sample was heated from 0 to 120 °C at a heating rate of 10 °C min^{-1}, held for 5 min to erase the previous thermal history,

cooled to 0 °C at a cooling rate of 10 °C min^{-1}. Then, the heating and cooling processes were operated again. The microstructures of the products with different pre-treatment process were observed by a digital microscope (VHX-200, Keyence Co., Japan). A commercial rheometer (Physica MCR 301, Anton Paar Co., Austria) was used to test the mechanical dynamic properties of the products.

3. Results and discussion

Plasticine™ was always composed of calcium carbonate, petroleum jelly, and long-chain aliphatic acids. In this work, by substituting the calcium salts with CI particles, a novel kind of black Plasticine™ with magnetic dependent mechanical properties was successfully prepared. Fig. 1a shows the SEM image of the CI particles, which indicates the average size of the magnetic spheres is about 3.5 μm. These microspherical CI particles exhibit a typical body-centered cubic structure (Fig. SI1, ESI†) and they are very stable during the fabrication of the magnetic Plasticine™. After simply mixing the CI particles with petroleum jelly and paraffin wax under vigorously mechanical stirring, the black composite was cooled down from 70 °C to room temperature.

Due to the presence of the amphiphilic petroleum jelly, the inert CI particles can be well dispersed into the hydrophobic paraffin wax. Fig. 1c shows an optical microscopy image of the as-prepared magnetic Plasticine™, in which the white spots represent the CI particles and dark back ground stands for the matrix. It is observed from the image that the CI particles are
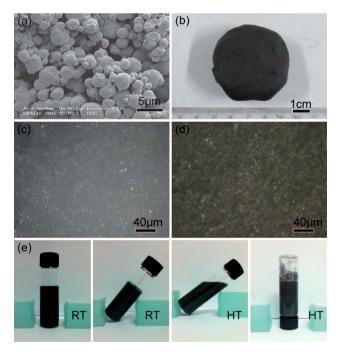

Fig. 1 SEM image of the carbonyl iron particles (a); photograph of the as-prepared magnetic Plasticine™ (b); optical microscopy images of the prepared magnetic Plasticine™ without (c) and with (d) application of an external magnetic field; photographs of the magnetic Plasticine™ under different temperatures (e); RT: Room Temperature, HT: High Temperature.

homogeneously distributed in the composite. No large CI particle aggregations are found in the matrix, which indicates the compatibility between the CI sphere and the carrier is very good. The particles are randomly dispersed in the matrix, thus the as-prepared magnetic Plasticine™ is isotropic. During the optical microscopy observation, the composite was placed between two parallel glass slides. If an external magnetic field was applied parallel to the glass plane, no obvious particle reassembly was found, which indicated that the CI particles located in the matrix were relatively stable (data not shown). Interestingly, if the above process was conducted under a high temperature, these CI particles can assemble to form chain-like structure by applying the magnetic field (Fig. 1d).

Fig. 2a shows the FTIR spectra of the mixture of the petroleum jelly and paraffin wax. The large absorption band between 3000 and 2800 cm^{-1} may correspond to the C–H stretching for the –CH$_3$ and –CH$_2$– groups. The peaks located at 1465 and 1382 cm^{-1} are attributed to the asymmetrical and symmetrical vibration of the –CH$_3$, respectively.[45] Due to the similarity of the FTIR spectra of the petroleum jelly and paraffin wax, it is difficult to distinguish the exact attribution of the two compounds. Fig. 2b exhibits the FTIR spectra of the magnetic Plasticine™ and it is almost the same to the mixture of the petroleum jelly and paraffin wax, which indicates the starting materials are stable during the fabrication. Due to the CI particles are crystallized metal, no IR absorption was found in the spectra.

The magnetic hysteresis loops of the pure CI particles and the as-prepared black Plasticine™ were measured by using a SQUID at room temperature. As shown in Fig. 3, the magnetization of the CI particles can be saturated to be 173 emu g^{-1} when the magnetic field reaches to 1 T. The saturated magnetization (M_s) of the magnetic Plasticine™ decreases to 60 emu g^{-1} upon the introduction of 70 wt% carrier into the composite. The magnetic Plasticine™ with 30 wt% CI particles displays a 30% M_s value of the pure CI particles, which indicates the synthesis do not break any physical nature of the CI particles. Both the CI particles and the magnetic Plasticine™ exhibit a soft magnetic characteristic and the coercivities are very small.[46] Similar to other Plasticine™, the magnetic Plasticine™ is malleable. As shown in Fig. 1b is the photograph of the magnetic Plasticine™, which indicates that the material can be molded into various shapes, such as sphere and cubic. These shapes could be kept stably without applying any
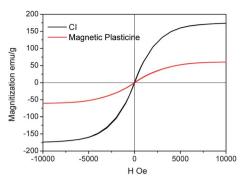

Fig. 3 M–H curves of CI particles (a) and the as-prepared 30 wt% magnetic Plasticine™ (b).

large pressure. After integrated the two different shaped bulk materials together, the new mixture can also be molded into many other shapes. The new formed material exhibits the same physical and chemical properties, indicating a curable nature (Fig. SI2, ESI†).

Due to the presence of the paraffin wax, the magnetic Plasticine™ melts when exposed to heat. Fig. 4a shows the DSC curve of the mixture of the petroleum jelly–paraffin wax. An exothermic peak located at around 49.78 °C is found during the cooling process, which may be corresponding to the crystallization point of the paraffin wax. From Fig. 4b, we can also find that the magnetic Plasticine™ has a similar exothermic peak (49.78 °C), which indicates that it must exhibit a phase-changed characteristics. To investigate the thermal-dependent nature of the as-prepared magnetic Plasticine™, the status of the product under different temperatures was recorded by using photographs (Fig. 1e). Under room temperature, the magnetic Plasticine™ remained in the solid state and the interface was level. If the vial was tilted, the interface was also perpendicular to the side of the vial. When the temperature was above 50 °C, the interface of the magnetic Plasticine™ adapt itself to be level to the water level whatever the incline of the vial. When the vial was converted, the magnetic Plasticine™ dropped from the bottom to the mouth. Based on the above analysis, it is very clear that the magnetic Plasticine™ exhibits a typical phase-changed behavior. It performed as an elastic-like magnetorheological gel at room temperature and transformed to the magnetorheological fluid when the temperature was above the phase-change point.
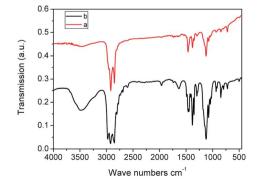

Fig. 2 FTIR spectrum of the mixture of the petroleum jelly–paraffin wax (a) and the as-prepared magnetic Plasticine™ (b).
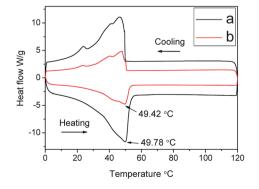

Fig. 4 DSC curves of the mixture of the petroleum jelly–paraffin wax (a) and the as-prepared magnetic Plasticine™ (b).

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The as-prepared magnetic Plasticine™ worked as a magneto-rheological gel at room temperature. Fig. 5a shows the magnetic dependency of the storage modulus of all the magnetic Plasticines™ with different CI contents. The storage moduli are dependent on the strain amplitude and it was found that the storage moduli of all the magnetic Plasticines™ keep a stable value when the shear strain was smaller than 0.1% (Fig. SI3, ESI†). Therefore, the strain amplitude was set as 0.1% while the driving frequency was 5 Hz for testing the magnetic dependent modulus of the magnetic Plasticine™. With the increase of the magnetic field, the storage modulus increases. Taking the composite with 30 wt% CI content as an example, the G_0' is 0.47 MPa while the G_s' can reach up to 2.48 MPa. The relative MR effect is 427% and this value is much higher than most of the reported MR elastomers. Here, the magnetic dependent modulus is highly influenced by the CI content. By increasing the CI percentage from 30 to 70 wt%, the G_0' increases. The $\Delta G'$ changes from 2.01 to 3.38, 4.23, 3.43, 2.23 MPa, while the relative MR effect are expected to be 427%, 426%, 305%, 135%, and 43.6%, respectively. It is clear that the stiffness of the magnetic Plasticine™ sharply increases with increasing of the CI content, which further leads to the decrease of the relative MR effects. Most of the above magnetic Plasticines™ exhibit good mechanical performance, which enables them to satisfy the requirements for practical application.[47,48] All the loss moduli of the magnetic Plasticines™ are smaller than their storage moduli, indicating that they behave with an elastic-like characteristic.[31] With increasing of the magnetic field, the loss modulus increases for the sample with low CI weight percentage (30 wt%). However, for the high CI content sample, the loss modulus tends to be saturated and then decreases. With increasing of the CI content, the saturation magnetic field decreases (Fig. 5b). Although it is

supposed that the change of the microstructure of the sample may be responsible for this interesting phenomenon,[37] our present understanding is still limited and more in-depth analysis is in progress.

The mechanical properties of the products are sensitive to the temperature as shown in Fig. 5c. Taking the 50 wt% magnetic Plasticine™ as an example, the G_0' and G_s' decreases from 1.4 and 5.6 MPa to 0.7 and 4.1 MPa when the temperature increase from room temperature (25 °C to 30 °C), respectively. A sharper decrease is found when the temperature increases to 40 °C, indicating the change of the magnetic Plasticine™. However, when the temperature is above 50 °C, the magnetic dependencies of the modulus are kept all the same. According to the DSC analysis, the magnetic Plasticine™ transforms to a fluidic state as soon as the temperature reach to 49.78 °C, thus the modulus of the product is stable when the temperature is relatively high. Similarly, the loss modulus of the magnetic Plasticine™ also changes with the temperature and keep stable when the temperature is higher than the critical point (Fig. 1d).

Obviously, the magnetic Plasticine™ transforms from MRG to MRF when the temperature is higher than 50 °C. Fig. 6a shows the testing curves of the fluidic magnetic Plasticine™ and the stress increases with increasing of the shear rates, indicating the CI particular structures in the magnetic fluid are destroyed by the shear deformation. With increasing of the magnetic field, the shear stress increases tremendously and they are 2–3 orders of magnitude higher than that without applying the magnetic field. In the fluid status, the influence of the temperature is tiny and their mechanical properties can be kept relatively stable even when the temperature reaches 80 °C (Fig. 6b and SI4, ESI†). Fig. 6c shows the shear rate dependent viscosity of the fluidic magnetic Plasticine™ under 50 °C. The viscosity decreases with
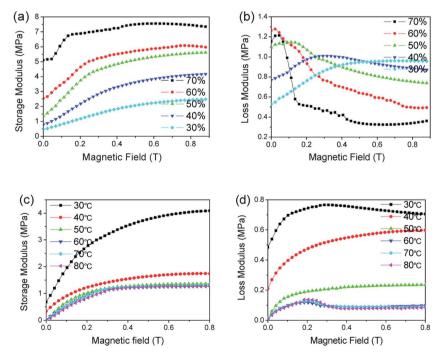

Fig. 5 Room temperature storage moduli (a) and loss moduli (b) of magnetic Plasticine™ with different iron particle contents under different magnetic flux densities; storage moduli (c) and loss moduli (d) of 50 wt% magnetic Plasticine™ under different temperatures.
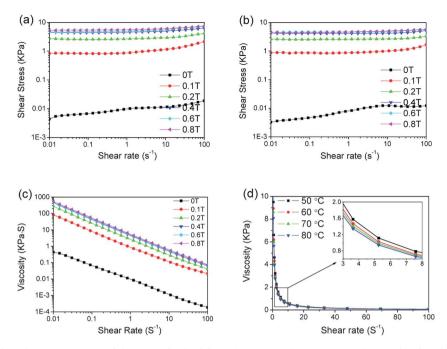
Fig. 6 Shear rate dependent shear stress curves of the magnetic Plasticine™ (50 wt%) under 50 °C (a) and 80 °C (b); viscosity curve (viscosity *vs.* shear rate) of the magnetic Plasticine™ (50 wt%) under different magnetic field (50 °C) (c); viscosity curves of the magnetic Plasticine™ (50 wt%) under different temperature (the magnetic field is 0.8 T).

increasing of the shear rate, indicating the fluid exhibits a typical shear thinning behavior. As soon as the magnetic field is applied on the fluid, the viscosity increased rapidly. The large magnetic field leads to a large viscosity till the magnetic field is large enough to saturate the magnetic particles. Similar to the traditional CI–silicon oil composite system, the as-formed fluid-like magnetic Plasticine™ exhibits a typical magnetorheological behavior. In this case, it is found that the viscosity of the magnetic system slightly decreases with increasing of the temperature (Fig. 6d and SI5, ESI†), which may be due to the decreasing of the viscosity of the composite carrier.

Based on the above analysis, the as-prepared magnetic Plasticine™ is proven to be a versatile magnetorheological material, which can transform between MRG and MRF by varying the temperature. At room temperature, the carrier, which is composed of petroleum jelly and paraffin wax, exhibits a gel-like structure, thus the as-formed magnetic Plasticine™ performed as an elastic MRG. Because the carrier is soft, the product exhibits

much higher MR effects than the MR materials based on the natural rubber, *cis*-polybutadiene rubber, and *etc.*[24,26] With increasing of the temperature, the carrier become softer thus the magnetically saturated modulus decreases. As soon as the temperature increases to the critical point, the carrier transforms from gel to fluid. In this case, stable MRF is obtained. Different from the traditional silicone oil based MRF, the present MRF should work under high temperature, at least higher than the phase-change point. Fortunately, the CI particles can be well confined in the carrier matrix under room temperature, thus this kind of materials does not have any sedimentation problem which often puzzled the traditional MRF. By simply cool to room temperature, the MRF transform back to MRG again without any break of the mechanical performance.

Fig. 7 shows the magnetic dependency of the loss factors under different CI content and temperature. The damping factor of the magnetic Plasticine™ decreases sharply with increasing of the magnetic field under room temperature. With further increasing
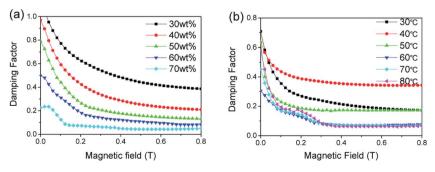

Fig. 7 The damping factors of the magnetic Plasticine™ under different magnetic field (a) and different temperature (for 50 wt% magnetic Plasticine™) (b).

of the CI weight percentage, the damping factor decreases. The damping of the magnetorheological materials represents the ability for energy dissipation. From the structure analysis, it is found that the CI particles could not be moved by applying the magnetic field, thus the energy dissipation responsible for the interface slipping is tiny. For the present product, the damping is mainly comes from the movement of the soft segments in the carrier, where the damping for the CI particles is ignored. The CI particle–particle interaction increases with increasing of the magnetic field, thus the movement of the soft segments in the matrix become harder, which further lead to the decrease of the damping factor. Therefore, the damping factor decreases sharply with increasing of the magnetic field. As the CI particles can be saturated under a relatively high magnetic field, the damping factor tends to level off with further increasing of the magnetic field. The temperature influence is relatively complicated. When the temperature is increasing from 30 °C to 40 °C, more melted carrier is presented in the matrix and the restriction of the soft segments decreases, thus the damping factor increases. With further increasing the temperature to 50 °C, the magnetic composite transforms to be the MRF, the damping factor decrease due to the change of the carrier status.

4. Conclusion

A versatile magnetorheological material, magnetic Plasticine™, was developed by using paraffin wax–petroleum jelly as the carrier matrix. The mechanical properties of the as-prepared composites can be controllably obtained by varying the iron contents, magnetic field, and the temperature. All the gel-like magnetic Plasticine™ exhibits high magnetic induced moduli and the relative MR effects of the product with 50 wt% CI particles can be reach as high as 305% at room temperature. The as-prepared magnetic Plasticine™ is proven to be a phase-change-able material which can be cycled between MRG and MRF by varying the environmental temperature. The transforming mechanism is discussed and these characteristics enable them be widely applied in artificial muscle, noise control, mechanical actuators, vibration absorbers, and magnetoresistor sensors.

Acknowledgements

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