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Preparation and characterization of a novel magnetorheological elastomer based on polyurethane/epoxy resin IPNs matrix

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Abstract
This paper proposes the preparation of a novel magnetorheological elastomer (MRE) with improved damping and mechanical properties. This MRE is based on polyurethane (PU)/epoxy resin (EP) graft interpenetrating polymer networks (IPNs). The tensile strengths, thermal stability, magnetorheological behavior, and damping properties of the MRE are studied systematically in terms of composition. The Fourier transform infrared (FTIR) spectra verifies the formation of IPN structures, and thermogravimetric analysis (TGA) revealed that the thermal decomposition temperature was raised by the addition of IPN structures. The test results from the materials test machine and the rheometer show that the presence of IPN can significantly improve the tensile strength and damping properties of the MRE. In addition, the mechanism for enhancing tensile strength and damping properties is proposed. The experiment results suggest that the damping performance of the MRE has a significant correlation with the magnetic strength, content of EP, and temperature. As the thermal endurance properties, tensile strength, and loss factor are improved by incorporating EP/PU IPN structure, it is expected that the PU/EP IPN MRE can be used as an intelligent structural damping material.

Keywords: magnetorheological elastomers, graft interpenetrating polymer networks, damping properties, mechanical properties

(Some figures may appear in colour only in the online journal)

1. Introduction
Magnetorheological (MR) materials are functional and smart materials, and their rheological or mechanical properties can be controlled continuously, rapidly, and reversibly by applied magnetic fields [1–4]. As an important branch of MR materials, magnetorheological elastomers (MRE) are polymer composites in which polarized particles are suspended in a nonmagnetic solid or gel-like matrix. Generally, they consist of three major components: magnetizable particles, matrix, and additives. The matrices for MREs include soft silicon rubber [5], natural rubber and synthetic rubber [6–8], polyurethane (PU) [9, 10], polydimethylsiloxane (PDMS) [11], and so on. MREs possess the advantages of both MR materials and elastomers, such as rapid response, good reversibility, excellent polymer properties, and strong controllable capacity, without the disadvantages of sedimentation, poor stability, and sealing problems found in MR fluids (MRFs). These advantages bring broad application prospects for MREs in the fields of noise reduction, vibration attenuation, and smart sensing, such as adaptive-tuned vibration absorbers, dampers, and sensors [12–14].

The damping and mechanical strength properties of MR are critical to the applications of MREs. Much research has been done to enhance the MR and damping properties of MREs. Zhang et al [15, 16] prepared hybrid MREs by embedding them with MRFs and MR fluid glues (MRGs), and they investigated the durability properties of MRE
materials based on a mixed matrix: cis-polybutadiene rubber and natural rubber. Ju et al [17] fabricated porous MREs using the decomposition reaction of NH₄HCO₃ to produce a porous structure and obtain better damping properties. Ge et al [18] improved the mechanical properties of MREs by adding CI particles into the natural rubber/rosin glycerin hybrid matrix. These studies suggested that the damping performance of an MRE has a significant correlation with the magnetic strength, shear rate, carbonyl iron content, and shear strain amplitude [19]. Fan et al [20] investigated the effect of the cross-link density and the plasticizer of the matrix on the controllable damping properties of the MRE. They also controlled the damping properties by using temperature-controllable materials in the matrix [21]. The damping principle and energy dissipation mechanisms were discussed by Gong et al [22–25]. In summary, introducing a plasticizer and reinforcements into the matrix and preparing the hybrid polymer matrix are effective ways to develop the high performance of MREs.

In recent years, though the MR effect and the damping properties of MREs have been studied by many researchers, the poor mechanical strength and damping of the MRE still limited its application in some high-damping areas. Interpenetrating polymer networks (IPNs) are polymer alloys consisting of two or more polymers in a network form, held together by permanent entanglements with only occasional covalent bonds between the chains of the two different types of polymers [26]. Owing to its synergy effect, the IPN can overcome the disadvantages of the two different matrices and integrate the advantages of both. It can also broaden the effective damping temperature range of the material. Here, PU is the most commonly used matrix of MREs, but it is a flexible, elastic polymer with low mechanical strength and poor heat resistance, and thus its applications for structural damping materials are limited [27, 28]. At the same time, due to their high strength, epoxy resins (EPs) have usually been applied in structural composites. However, due to the brittle property of EPs, its high glass-transition temperature restricts its application in damping materials. PU/EP IPNs are excellent damping materials that have attracted many researchers’ attention [29–33]. Previously, the dynamic mechanical properties, mechanical properties, thermal properties, and morphology of PU/EP IPNs have been studied by many researchers [33–36]. In these studies, damping properties, tensile strength, and thermal properties have been improved by the presence of PU/EP IPNs. Therefore, we selected PU as the matrix of the MRE, added EP into the matrix to form PU/EP IPNs, and synthesized a novel MRE with excellent damping and mechanical properties. To verify the potential applications of the novel MRE in intelligent structural damping materials, the tensile strengths, thermal decomposition behavior, and the mechanical and MR properties of MREs were examined. In addition, the damping properties were explored comprehensively, and the energy dissipation mechanisms were also discussed.

2. Experimental

2.1. Materials

Diglycidyl ether of bisphenol-A-based EP was purchased from Baling Petrochemical Co., Ltd., Hunan, People’s Republic of China. Castor oil was purchased from Sinopharm Chemical Reagent Co., Ltd., People’s Republic of China. MDI was purchased from Yantai Wanhua Polyurethanes Co., Ltd., People’s Republic of China. 2,4,6-Tri(dimethylamino)methyl)phenol (DMP-30) was purchased from Wuhan Hongda Co., Ltd., People’s Republic of China, to be used as a curing agent. Di-butylphthalate (DBP) was purchased from Tianjin Bodi Chemical Holding Co., Ltd., People’s Republic of China, to be used as a plasticizer. The magnetic particles were carbonyl iron particles (CIP) (type: JCF2–2; size distribution: D50 = 5–8 μm) provided by Jilin Jien Nickel Industry Co. Ltd., People’s Republic of China.

2.2. Preparation of PU/EP IPN MREs

The detailed formations of MRE samples with different proportions of IPNs are shown in table 1. The content of CIP is 60% in each sample, and the matrix of MRE samples consists of different amounts of PU and EP. First, each component of the raw materials is calculated and weighed, and then treated with vacuum dewatering for 2 h. Second, castor oil was mixed with MDI and remained still at 80 °C for 15 min to obtain g-PU. Then, the plasticizer DBP and CIPs were added to the jar and mixed by agitator for 30 min to obtain a DBP/CIP dispersion. Finally, the IPN MREs were prepared by blending three mixtures together: g-PU, the DBP/CIP dispersion, and the mixture of EP and DMP-30. The main preparation process of the PU/EP IPNs is shown in figure 1.

2.3. Characterization

Fourier transform infrared (FTIR) spectra were obtained on a NicoletN10 FTIR spectrophotometer (Thermo Fisher Scientific, USA) scanning from 400 cm⁻¹ to 4000 cm⁻¹. Tensile strength values were obtained on a CTM2100 materials test machine (CTM, Shanghai, People’s Republic of China) with the crosshead speed of 5 mm min⁻¹. Each sample was cut into a dumbbell shape with a thickness of 2 mm and a middle width of 4 mm. All tensile strength values were the average of the five measurements.
Thermogravimetric analysis (TGA) curves were obtained on DTG-60H analyzer (SHIMADZU, Japan). The test samples without CIPs were ground into powder and tested at a heating rate of 10 °C min\(^{-1}\) with the temperature ranging from 40 to 600 °C under a nitrogen atmosphere.

The microstructures of the samples were observed using a scanning electron microscope (SEM, TESCAN VEGA). Microphotographs were taken of the tensile fractured surface, which was coated with gold powder prior to testing.

The magnetorheology and damping properties of the MRE samples were tested by using an advanced commercial rheometer (MCR301, Anton Paar). The details of this rheometer can be obtained from our previous work [37]. The damping properties of MREs were tested in different testing conditions to investigate influence factors, including magnetic flux density and temperature.

### 3. Results and discussion

#### 3.1. FTIR analysis

The FTIR spectra of a PU prepolymer and IPN are shown in figure 2. The spectrum of the PU prepolymer, seen in figure 2(b), shows the characteristic absorption bands at 2273 cm\(^{-1}\), which correspond to the isocyanate group (-NCO) group. The IPN spectrum, seen in figure 2(a), shows that the absorption band at 2273 cm\(^{-1}\) disappears, and the band at 917 cm\(^{-1}\) is produced by the stretching vibration of epoxide rings in the EP. It indicates that a chemical reaction between epoxy and PU has occurred. The -NCO group of PU reacted with -OH of the EP, and graft-IPNs are formed. The FTIR spectra testified to the formation of EP/PU IPNs, shown in figure 1.

#### 3.2. Microstructure of the MRE

Figure 3 shows SEM images of MRE samples. As shown in figure 3(c), a homogeneous microstructure can be seen in the fractured surface of the EP/PU MRE, indicating that no phase separation took place. Comparing figures 3(a) and (b) with figures 3(c) and (d), the dispersion of CIPs in the EP/PU IPN matrix was more homogeneous, and the interaction between CIPs and matrix was stronger in the latter. Here, the EP plays the role of the plasticizer, it immerses the CIPs more deeply in the matrix.

#### 3.3. Mechanical properties

The shear modulus of MREs in zero fields can be calculated by the Einstein-Guth-Gold equation [4]:

\[
G_{\text{ran}} = G_0 \left(1 + 2.5\varphi + 14.1\varphi^2\right)
\]

Where \(G_{\text{ran}}\) is the shear modulus, \(G_0\) is the shear modulus of the unfilled rubber, and \(\varphi\) is the volume fraction of the particles. Because the modulus of the MRE is improved by the IPN structure, the \(G_0\) increased with an increase of IPN content. The test results of tensile strengths of different MRE samples are shown in figure 4.

One can see that the test results verify the inference above. With the incorporation of 50% EP in the PU matrix, the tensile strength of IPN-5 can reach 12.5 Mpa, an increase of 830% compared to pure PU MRE samples. Because the tensile strength of the EP is considerably larger than that of pure PU, the tensile strength of the MRE increases with increasing EP content. In addition, the covalently bonded chains of PU and EP ran through and entangled with each other. The stress can transfer into the IPN when the samples suffer a drawing force, and the IPN structure is also conducive to tensile strength due to its synergistic effect.

#### 3.4. Thermal stability

MRE is a novel polymer composite material and the thermal stability of its matrix is critical to its durability and age resistance. The thermal stability of a polymer can usually be evaluated by TGA. The TGA thermograms of PU and the EP/PU IPN matrix are shown in figure 5. One can see that the PU/EP IPNs showed higher thermal stability than PU. Due to the presence of EPs, the weight loss of PU/EP IPNs is lower than PU, and the thermal-decomposition temperature is higher. Raymond et al reported that the formation of IPNs can improve the thermal stability of PU [38]. The interpenetration and entanglement of molecular chains in the IPN improved the structural stability of the polymer. This also can be

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**Figure 2.** FTIR spectra of (a) IPN and (b) castor oil-based PU prepolymer.

**Table 1.** Detailed formation of MRE samples with different proportions of IPNs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Matrix (40%)</th>
<th>CIP (60%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPN-0</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>IPN-1</td>
<td>20</td>
<td>2</td>
</tr>
<tr>
<td>IPN-2</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>IPN-3</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>IPN-4</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>IPN-5</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 3. SEM images of MRE samples: (a) (100×) and (b) (1000×) are MRE sample IPN-0; (c) (100×) and (d) (1000×) are MRE sample IPN-2.

Figure 4. Tensile strengths of MRE samples with various EP contents.

Figure 5. TGA thermograms of PU and PU/EP IPNs.
attributed to the fact that the thermal stability of the EP is higher than that of PU, and the grafting between –NCO of the PU prepolymer and the –OH of the EP strengthens the IPNs.

3.5. Magnetorheology property

For the MRE samples with different proportions of IPNs, the magneto-induced modulus and the relative MR effect were tested at room temperature, with the magnetic flux density ranging from 0 to 1.2 T. A strain amplitude of 0.1% and a frequency of 10 Hz were selected, and the initial compression force was set to 5 N. The MR effect is the fraction of the magnetic-induced value to the nonmagnetized condition value of the related parameter. The main influencing factor of this effect is the response of the MREs due to the external magnetic field. The MR effect is generally evaluated by the formula

$$G_{\text{MR-effect}} = \frac{G_{\text{max}} - G_0}{G_0} \times 100\%$$

where $G_0$ is the initial modulus, $G_{\text{max}}$ is the maximum modulus, and $G_{\text{max}}$ is the storage modulus when the particles are at magnetic saturation. The curves of the magnetic field-dependent shear storage modulus and the MR effects of the samples are shown in figure 6.

The result corresponds to the mechanical test results above and reveals that the initial module increased with EP content. Figure 6(a) shows that the range of magnetic-induced shear modulus increased with an increase in EP content at first, but as the EP content continued to increase, the range shrunk. In the curve of IPN-2, the value increased sharply when the magnetic flux density exceeded 500 mT. The main reason was that matrix restricted the movement of CIPs at the initial testing phase, resulting in the gentle growth of the magnetic-induced shear modulus. With the increase in the magnetic field, CIPs began to break the shackles when magnetic flux density reached its critical value. Then, owing to the movement and restructuring of CIPs, the magnetic-induced shear modulus increased sharply. However, the confinement strength of the matrix increased with the EP content, which weakened the movement and restructuring of the CIPs in IPN-3 and IPN-4. Owing to the greater movement and combination of CIPs, the value of IPN-2 finally surpassed that of IPN-3 and IPN-4. By introducing an IPN structure, the range of the magnetic-induced shear modulus of the IPN-2 MRE can reach 6.37 MPa, an increase of 66.3% over the pure PU MRE sample. The maximum shear modulus of the sample with 50% EP content can reach 9.91 MPa. But as figure 6(b) shows, due to the increase of the initial shear modulus, the MR effects calculated by equation (2) are decreased. The optimal sample is IPN-2, with its MR effect reaching 394%.

3.6. Damping properties

For the MRE samples with different EP content, curves of the magnetic field-dependent loss factors and maximal loss factors of each sample are shown in figure 7. As figure 7(a) shows, there is a peak in each curve, and the loss factor increases at first and then decreases with the increasing magnetic field. This is mainly because the CIPs tend to form a columnar parallel to the magnetic field. The relative movement between the matrix and the CIPs created more dissipation of energy, and thus the loss factor increased. With the increase in the magnetic field, more particles begin to agglomerate and more small structures are formed. When the magnetic flux density reaches the saturation magnetization of the iron particles, the number of small structures does not increase and the loss factor of all MRE samples tends to level off [37]. As the content of EP increases, the peak in the curve becomes flatter. This is mainly because the crosslinking density of the matrix increases with the increasing content of EP, which restricts the movement of the CIPs. In figure 7(b), one can see that the maximal loss factors of the MRE samples with different EP content increases at first, and then decreases. The peak value of the maximal loss factors of IPN-2 reaches 0.528, which is an increase of 129.6% over the pure PU MRE sample.
The glass transition temperature is a critical factor for the damping material, and the loss factor strongly depends on temperature. The relationship between the loss factor and temperature is shown in figure 8. One can see that the loss factors of the IPN-0 MRE and IPN-1 MRE samples decreased in the test temperature range. The loss factors of other MRE samples initially increase with an increase of temperature, and then decrease with the continual rise in temperature. The MRE samples, including IPN-2, IPN-3, and IPN-4, had temperature damping peaks at the testing temperature range. With the increase of IPN content, the temperature damping peak move to the high temperature. IPN is an effective means to broaden the damping temperature range (tan \(\delta\) > 0.3), and the temperatures for the tan \(\delta\) peak (glass transition temperature, \(T_g\)) of PU and EP are -10 °C and 130 °C, respectively [30]. One can see that the \(T_g\) of the MRE increases with increasing EP content. Figure 8 shows that the effective damping temperature ranges (tan \(\delta\) > 0.3) of IPN-2, IPN-3, and IPN-4 were about 25–85 °C in the range of test temperatures.

In summary, by incorporating the EP/PU IPN structure, both the value of tan \(\delta\) and the effective damping temperature range are improved. Generally, the overall damping capacity of the MRE can be expressed as

\[
D_{\text{MRE}} = D_c + D_I + D_M
\]

(4)

where \(D_c\), \(D_I\), and \(D_M\) are the intrinsic damping, interface damping, and the magnetomechanical damping, respectively. The magnetomechanical damping is much smaller than the others, and it does not cause significant changes in the overall damping [22]. The intrinsic damping is determined by the content and the constitutive damping capacity of each individual component, but because the loss factor of CIP is far lower than that of the polymer matrix, \(D_c\) is mainly determined by the constitutive damping capacity of the polymer matrix of the MRE. It indicates that when a magnetic field is imposed on the MRE, the randomly scattered CIPs form a columnar, which parallels the direction of the magnetic field. The movement of CIPs causes the relative motion of molecular chains. Owing to the presence of EP, as shown in figures 9(a) and (b), the interface between the CIPs and the matrix of the EP/PU MRE (figure 9(b)) is better than that of the PU MRE (figure 9(a)). As a result, more energy dissipation is produced when the molecular chains stretch and curl. Consequently, the intrinsic damping of the matrix improves. Furthermore, the interface damping is significantly dependent on the condition of the interfaces between the CIP and the matrix. In particle-reinforced polymer matrix composites, the interfacial bonding between the reinforcing particles and the polymer matrix is poor. Thus, when the relative motion takes place in the interface, the energy dissipation of internal friction between the two material phases makes great contributions to the damping capacity of the MRE. As seen in the sketch of the IPN structure in figures 9(c) and (d), the enrichment of interface formation in the EP/PU MRE increases the interface area and the interface friction between the CIPs and the matrix. From the analyses above, the
distinctive structure of the EP/PU IPN in the MRE improves the overall damping capacity of the MRE.

4. Conclusions

In this study, a novel kind of damping MRE was developed with a EP/PU IPN matrix and CIPs. The characterization result revealed that the tensile strengths, thermal stability, and damping properties were improved by incorporating the IPN structure. The effective damping temperature ranges of IPN-2, IPN-3, and IPN-4 were broadened, and the maximum effective damping temperature was raised to 85 °C. The maximal loss factors of the IPN-2 MRE sample reached 0.528 at room temperature, an increase of 129.6% over the pure PU MRE sample. At the same time, the MR effect of IPN-2 reached 394%. The energy dissipation mechanisms were also discussed from different perspectives. The analyses indicated that the IPN structure caused more frictional energy dissipation in the molecular chains and the surface of CIPs. These study results indicated that the design of the molecular structure of the matrix is an efficient measure to adjust the damping property of the MRE.

Acknowledgments

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