Magnetic properties of polyurethane magnetorheological elastomer based on carbon nanotubes

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Abstract
The paper has modified a magnetorheological elastomer (MRE), a sensitive component of a sensing device, by adding conductive particles of multi-wall carbon nanotubes (MWCNTs), to increase conductivity and reduce response time. After adding MWCNTs, the magnetoresistance calculation model is established based on the theories of effective medium and percolation. Also, MRE with different ratios of carbon nanotubes and carbonyl iron powder are prepared, and the test system for magnetoresistance is built. The test results show that when the ratio is 2:3, the resistivity reaches a minimum while the response time is the shortest. For the same 2:3 ratio and different conductive particle volume fractions, the relationship between electric resistance and magnetic induction is tested. The results show that the resistance decreases with the increase of the applied magnetic field strength, and the larger the volume fraction of the conductive particles, the more obvious the resistance drop. The resistance value as a function of applied magnetic field is predicted well by our model, which provides a new method for the calculation of the resistance value of MRE.

1. Introduction

Magnetorheological elastomers (MREs) are widely considered as smart polymeric materials because their properties change with an external magnetic field. When MRE is in a magnetic field, the magnetic particles in the material are rapidly magnetized to produce a magnetic interaction which changes mechanical and electrical properties. As induction increases, changes will become greater. However, when the external magnetic field is removed, the interaction will disappear and MRE will return to its original state. This phenomenon is called the magnetron characteristics [1] of MRE.

In order to explore magnetron property, many researchers have analyzed its microscopic mechanism. Bica [2–4] studied the change of the resistance of MRE in magnetic field, and found that the resistance value in the direction along the magnetic field always decreases with an increase in field strength, which proved that MRE has obvious magnetoresistance characteristics. Andrei et al [5] developed a MRE-based panel capacitor and tested the effect of field strength on capacitance. The results showed that the capacitance increases with the increase of magnetic field intensity at the same frequency. Based on the magnetic chain–induced model and the principle of tunneling, MRE conduction was studied by Li et al [6, 7]. Deng et al [8, 9] established the theoretical model of the piezoresistive characteristics of MRE, and verified the accuracy of the piezoresistive model based on experimental data. Cvek et al [10, 11] studied the electrical properties of isotropic and anisotropic, which proved that the type of conductive particles and their microstructure have a considerable impact on the dielectric properties of MRE. Yang et al [12] established a mathematical model that can describe the lagging response of MRE. The model was modified based on experimental data and evaluated by various indicators to ensure its accuracy. Wang et al [13] investigated the sensing properties of MREs. The results showed that MRE samples exhibit significant changes in measured values of impedance and resistance in response to compressive deformation, as well as the applied magnetic field. Ausanio et al [14] proposed an analytical model to describe the
relationship between gradient magnetic field and analog resistance based on the magnetostrictive properties of MREs.

Due to the excellent application prospects of the magnetic control properties, researchers have enhanced a certain feature by adding various fillers to the traditional MRE, and applied the modified one to various sensing devices. Kchit N et al [15, 16] modified MRE with conductive carbon-black and tested the conductivity of it at different pressures and temperatures. Tian et al [17] studied the sensing capabilities of MRE with graphite by theory and experiment. The results showed that with an increment of graphite weight fraction, the resistance of MRE sample decreases steadily. Meanwhile, higher magnetic fields result in a resistance increase. Liu et al [18] enhanced the performance of MRE by polyurethane and plotted the magnetization and magnetoresistance curve of polyurethane MRE. Besides, they calculated the dielectric constant of the elastomer under magnetic field. The magnetoresistance characteristics of MRE with graphite powder was researched by Huang et al [19, 20], and the magnetoresistance and piezoresistive properties of MRE samples with different graphite powders were tested. Meanwhile, they also discussed the feasibility of MRE displacement sensor. The test results showed that when the content of graphite powder is more than 14%, the prepared MRE has better electrical conductivity and magnetoresistance characteristics. Wen et al [21] studied the effect of different metal-filled particles on the magnetron characteristics of MRE, and prepared a flexible tactile sensor filled with nickel powder. Shabdin et al [22] studied the rheological and resistivity properties of graphite-based MRE. The results showed that the presence of graphite fractions arrangement contributes to the conductivity of MRE. Luis et al [23] studied the magnetorheological behavior of polydimethylsiloxane elastomer with iron micro/nanoparticles by experimental investigation. Aziz et al [24, 25] studied the effect of different types of multiwall carbon nanotubes on the morphological, magnetic and viscoelastic properties of MREs. The results showed that with the addition of carboxylated multiwall carbon nanotubes, the magnetic properties are improved parallel with enhancement of MR effect particularly at low strain amplitude. Later they used nanosized Ni-Mg Cobalt-Ferrites as fillers to enhance the viscoelastic and electrical properties of MRE. Zainudin et al [26] studied the rheological and resistance properties of MRE with cobalt for sensor application. The study opened new avenues for cobalt to be used as filler in MRE fabrication for future sensing applications. Hu et al [27] proposed a stretchable and magneto-sensitive strain sensitive strain sensor based on conductive MRE containing silver nanowires (AgNWs) dip-coated polyurethane sponge, carbonyl iron particles and polydimethylsiloxane (PDMS) matrix. The mechanic-electric-magnetic coupling properties of conductive MRE were investigated and they were significantly influenced by mechanical properties of PDMS matrix and the AgNWs content. Dong et al [28] used zinc dimethacrylate (ZDMA) as the dispersant to prepare MREs with carbonyl iron particles and silicone rubbers, and a quantitative method was proposed to estimate the distribution homogeneity of carbonyl iron particles in MREs. Based on the above researches, MRE with the specific structure or material proportion have a huge impact on its magnetoresistance characteristics. However, in the above studies, although the electrical properties of MRE have been studied, researchers often study only certain conductive particles, such as content of graphene, conductive carbon black, carbon nanotubes, etc. The synergistic effect between these conductive particles in MRE is rarely considered. In order to make up for the deficiencies in the above research, the impact of synergistic effect between carbon nanotubes and carbonyl iron powder on the conductive properties of MRE under the condition of magnetic field was studied in this paper. As a carbon-based conductive filler, the stability of carbon nanotubes is better than that of metal conductive fillers. At the same time, it does not affect the magnetorheological effect of MRE. Meanwhile, its excellent conductive properties and great aspect ratio can ensure that a small amount of carbon nanotubes can provide a larger conductive area, which is often used in various structural and functional polymers.

In this paper, based on the theories of effective medium and percolation, a magnetoresistance calculation model is established for the polyurethane MRE with carbon nanotubes. At the same time, a test platform that can measure the magnetoresistance characteristics of MRE was constructed, the samples of polyurethane MRE with different ratio of carbon nanotubes/carbonyl iron powder were prepared and their magnetoresistance properties were tested. Finally, based on the experimental data, the proposed theoretical model of magnetoresistance is modified to provide a new way to solve the electromagnetism problems existing in MRE.

### 2. Magnetoresistance model of MRE with carbon nanotubes

MRE has controllable magnetoresistance characteristics. When an external magnetic field is applied to the sample, the magnetic particles are magnetized by the magnetic field, and magnetic forces are generated between the magnetic particles. The force can be seen as magnetic attraction, which forces the magnetic particles to move and recombine into chains. It deforms MRE while the thickness of the polymer film between two adjacent iron particles decreases, which causes an increase in the conductive area. Therefore, a conductive path is formed
between the conductive particles, resulting in a decrease in the resistance of MRE. When a magnetic field is applied to MRE, the specific phenomenon of forming a conductive path under ideal state is shown in figure 1.

In order to clearly explain the relationship between the resistance value of MRE and magnetic field, the relationship between MRE resistance and magnetic field is analyzed based on dipole model. When carbon nanotubes and carbonyl iron power are added to the polyurethane MRE, they are present as conductive particles in the polyurethane matrix. When analyzing the magnetoresistance model of MRE with carbon nanotubes, carbon nanotubes can be regarded as hollow structures. Therefore, it can be regarded as tiny conductive chains from the perspective of the conductive mechanism. When it exists between the carbonyl iron powder particles, its hollow structure will play a role similar to a wire, which can be regarded as a conductive chain in the model. This conductive chain helps current flow without the influence of magnetic fields. After applying a magnetic field to MRE, the magnetic particles are magnetized into a chain. According to the dipole model, the unit structure is shown in figure 2.

McLachlan et al. [15] combined the effective medium theory with the percolation model to obtain a general effective medium model that can explain the conductive mechanism of the polymer as follows:

$$\frac{(1 - \phi)(\sigma_l^{1/t_p} - \sigma_m^{1/t_p})}{\sigma_l^{1/t_p} + [(1 - \phi_p) / \phi_p] \sigma_m^{1/t_p}} + \frac{\phi(\sigma_h^{1/t_p} - \sigma_m^{1/t_p})}{\sigma_h^{1/t_p} + [(1 - \phi_p) / \phi_p] \sigma_m^{1/t_p}} = 0$$

(1)

where $\phi$ is volume fraction of conductive particles in the polymer, $\phi_p$ is the percolation threshold of conductive particles, $\sigma_l$ is matrix conductivity, $\sigma_h$ is the conductivity of conductive particles, $\sigma_m$ is the conductivity of polymer, $t_p$ is the seepage coefficient of polymer.

Since the electrical conductivity of carbonyl iron powder is larger than the electrical conductivity of polyurethane matrix, the conductivity of polyurethane matrix can be considered to be zero ($\sigma_l = 0$). The equation (1) can be simplified as
\[ \rho_m = \rho_0 \left( \frac{1 - \phi_i}{\phi - \phi_i} \right)^{\frac{1}{2}} \]  

(2)

where \( \rho_0 = 1/\sigma_0, \rho_h = 1/\sigma_h, \rho_m \) is the resistivity of ordinary polyurethane-based MRE, \( \rho_h \) is the resistivity of carbonyl iron powder.

In the system of multi-wall carbon nanotubes/polyurethane/carbonyl iron powder (MWCNTs/PU/CIP), when studying the percolation model of polyurethane-based MRE with carbon nanotubes, the carbon nanotubes are arranged as a series of conductive chains. The previously obtained percolation model can be applied to the MRE composed of carbon nanotubes, polyurethane matrix and carbonyl iron powder to conduct research and analysis.

Based on the simplified general effective media model (assume that the conductivity of matrix is zero), the percolation model of polyurethane-based MRE with carbon nanotubes was obtained:

\[ \rho = \rho_f (1 - \phi_i)^{\frac{1}{2}} / (\phi - \phi_i)^{\frac{1}{2}} \]  

(3)

where \( \rho_f \) is the resistivity of conductive particles, \( \phi_i \) is the percolation threshold of MRE, \( t \) is the seepage coefficient of MRE.

Through the above analysis, according to the dipole model and the simplified general effective medium theory, the relationship between the resistance of polyurethane MRE with carbon nanotube and the magnetic flux density is modeled.

For polyurethane-based MRE, the Young’s modulus and Poisson’s ratio have little change with magnetic field. Near the percolation threshold, they change little with the volume fraction of carbonyl iron powder. Under the above conditions, MRE is considered to be an ideal elastomer. The change of external magnetic field causes the corresponding pressure between carbonyl iron powders, which causes the geometrical change and the resistance change of MRE.

\[ \frac{1}{\kappa} \frac{\partial \kappa}{\partial P} = -\frac{1 + 2\nu}{E} \]  

(4)

where \( \kappa \) is the geometric factors of resistance of MRE, \( E \) is the Young’s modulus of MRE, \( \nu \) is Poisson’s ratio, \( P \) is the pressure between carbonyl iron powders.

For the integral of equation (4), the resistance geometric coefficient of MRE is:

\[ \kappa = \kappa_0 \exp \left(-\frac{1 + 2\nu}{E} P \right) \]  

(5)

where \( \kappa_0 \) is the geometric factors of resistance of MRE without magnetic field.

Assuming that the carbonyl iron powder is uniformly dispersed in the polyurethane matrix. When a magnetic field is applied to MRE, the differential pressure can be obtained by the equation (5).

\[ \frac{1}{\phi} \frac{\partial \phi}{\partial P} = \frac{1}{V_h} \frac{\partial V_h}{\partial P} - \frac{1}{V_m} \frac{\partial V_m}{\partial P} \]  

(6)

where \( \phi \) is the volume fraction of carbonyl iron powder, \( \phi = V_h / V_m \). \( V_h \) is the volume of carbonyl iron powder particles, \( V_m \) is the total volume of ordinary polyurethane-based MRE.

Since the magnetic deformation of the carbonyl iron powder under the action of magnetic field is small, it is considered that its volume does not change with the magnetic field. Then equation (6) is reduced to:

\[ \frac{1}{\phi} \frac{\partial \phi}{\partial P} = -\frac{1}{V_m} \frac{\partial V_m}{\partial P} \]  

(7)

In addition, since the polyurethane MRE is an ideal elastomer, there is:

\[ \frac{1}{V_m} \frac{\partial V_m}{\partial P} = \frac{2\nu - 1}{E} \]  

(8)

Substituting equations (8) into (7):

\[ \frac{1}{\phi} \frac{\partial \phi}{\partial P} = \frac{1 - 2\nu}{E} \]  

(9)

Integrating the two sides of equation (9):

\[ \phi = \phi_0 \exp \left(\frac{1 - 2\nu}{E} P \right) \]  

(10)

where \( \phi_0 \) is the volume fraction of carbonyl iron powder without external magnetic field.
Since carbonyl iron powder is a soft magnetic material, \( \partial \rho_f / \partial P = 0 \). Substituting equations (10) into (3):

\[
\rho = \rho_f (1 - \varphi_t) \left[ \varphi_0 \exp \left( \frac{1 - 2\nu}{E} P \right) - \varphi_t \right]^{-t} \tag{11}
\]

And the relationship between resistance and resistivity can be expressed as:

\[
R = \rho k \tag{12}
\]

The geometric factors of resistance of MRE is:

\[
k = L/S \tag{13}
\]

where \( L \) is the thickness of MRE, \( S \) is the cross-sectional area of MRE.

Substituting equations (11) and (3) into (12) and (13) respectively can obtain the relationship between the resistance of MRE and the change of magnetic pressure:

\[
\frac{R}{R_0} = (\phi_0 - \phi_t)^t \left[ \phi_0 \exp \left( \frac{1 - 2\nu}{E} P \right) - \phi_t \right]^{-t} \times \exp \left( \frac{1 + 2\nu}{E} P \right) \tag{14}
\]

where \( R_0 \) is the resistance of MRE without magnetic field, \( R_0 = \rho_f (1 - \phi_t) (\phi_0 - \phi_t)^{-t} \kappa_0 \).

The action of the iron powder particles by the magnetic field is called as the magnetic attraction. The magnetic field force, which is experienced by MRE, can be solved by applying a Maxwell electromagnetic stress tensor to the boundary of the ferromagnetic particles. Due to the complexity of the distribution of magnetic field, the calculation of the magnetic attractive force is complicated. In practical applications, assuming that the magnetic field is uniformly distributed in the area where the magnetically permeable material is located. Besides, the relative magnetic permeability \( \mu_r \) is large (\( \mu_r \gg 1 \)). According to the magnetic circuit design and calculation, the formula for solving the magnetic field force can be expressed as:

\[
F = \frac{\mu_r - 1}{2\mu_0\mu_r} B^2 S = \frac{1}{2\mu_0} B^2 S \tag{15}
\]

where \( B \) is magnetic flux density, \( \mu_0 \) is vacuum permeability (\( \mu_0 = 4\pi \times 10^{-7} \text{ Wb/A · m} \)).

The magnetic pressure generated by the applied magnetic field on the magnetic particles is:

\[
P = \frac{1}{2\mu_0} B^2 \tag{16}
\]

Substituting equations (16) into (14), the relationship between the resistance of MRE and the magnetic flux density is obtained.

\[
\frac{R}{R_0} = (\phi_0 - \phi_t)^t \left[ \phi_0 \exp \left( \frac{1 - 2\nu}{E} \frac{1}{2\mu_0} B^2 \right) - \phi_t \right]^{-t} \times \exp \left( \frac{1 + 2\nu}{E} \frac{1}{2\mu_0} B^2 \right) \tag{17}
\]

When carbon nanotubes are added to the MRE, the coefficient \( \lambda \) is introduced to represent the effect of carbon nanotubes on MRE resistance. Meanwhile, considering the influence of adding carbon nanotubes on the percolation characteristics of MRE, the obtained percolation value has a certain deviation. Therefore, it is necessary to introduce correction coefficients \( \alpha \) and \( \beta \) to correct \( \phi_t \) and \( t \). So, the relationship between the resistance of polyurethane-based MRE with carbon nanotubes and the magnetic flux density is:

\[
\frac{R}{R_0} = \lambda (\phi_0 - \alpha \phi_t)^{\beta t} \left[ \phi_0 \exp \left( \frac{1 - 2\nu}{E} \frac{1}{2\mu_0} B^2 \right) - \alpha \phi_t \right]^{-\beta t} \times \exp \left( \frac{1 + 2\nu}{E} \frac{1}{2\mu_0} B^2 \right) \tag{18}
\]

where \( \phi_t \) is volume fraction of conductive filler in polyurethane-based MRE material system with carbon nanotubes added under no external magnetic field, \( \phi_t \) is the percolation threshold of polyurethane-based MRE with carbon nanotubes, \( t \) is the percolation coefficient of polyurethane-based MRE with carbon nanotubes.

3. Samples preparation and test device construction

3.1. Samples preparation

Polyurethane elastomer is used as the matrix of MRE while soft magnetic carbonyl iron powder is used as magnetic particles (particle size 5 ~ 8 mm). Besides, dibutyl phthalate can be used as plasticizer. In addition, based on the excellent electrical properties of multi-walled carbon nanotubes, functional multi-walled carbon nanotubes are added to MRE to modify it.

The specific process is as follows. Firstly, MWCNTs are treated while 0.4 g of MWCNTs and 8 g of KOH are mixed, and they are placed in a ball mill jar. Then put them into a ball mill jar and add balls with diameters of
15 mm, 10 mm and 5 mm for ball milling. Adjust the rotation speed of the ball mill to 250 \text{ r} \text{ min}^{-1}, mill for 15 h, wash the reactants to neutral with deionized water, and finally dry the treated MWCNTs in a vacuum oven at 100 °C for 12 h to obtain hydroxylated MWCNTs. Besides, weigh the appropriate amount of castor oil, put it in a vacuum drying oven, dilute and dry at 100 °C for 2 h, then drop to 75 °C, react castor oil with polyurethane (MDI-50). Stir it well with an electronic stirrer, then add appropriate amount of carbon nanotubes, stir for about 10 min and mix, put it in a vacuum drying oven, heat at 75 °C for 1 h, then take it out and let it at room temperature. Finally, add appropriate amount of carbonyl iron powder, plasticizer and catalyst, stir with a glass rod and put it into a vacuum drying oven for bubble treatment. After the stir reaches the ideal state, the reactant is taken out and placed in a preheated mold for vulcanization treatment, and the vulcanization treatment is taken out for 24 h. Through this way, the isotropic polyurethane-based MRE samples can be obtained. The content of each component of samples are shown in table 1.

### Table 1. The content of each component of MRE samples.

| Volume fraction | Different ratio | Castor oil content (g) | MDI content (g) | MOCA content (g) | Carbon nanotube (g) | Carbonyl iron powder (g) |
|-----------------|-----------------|------------------------|-----------------|------------------|---------------------|------------------------|
| 24%             | 1:4             | 15                     | 4               | 1                | 1.93                | 29.23                  |
|                 | 2:3             | 15                     | 4               | 1                | 3.86                | 21.8                   |
|                 | 1:1             | 15                     | 4               | 1                | 4.83                | 18.17                  |
| 26%             | 1:4             | 15                     | 4               | 1                | 2.14                | 32.23                  |
|                 | 2:3             | 15                     | 4               | 1                | 4.28                | 27.17                  |
|                 | 1:1             | 15                     | 4               | 1                | 5.35                | 20.14                  |
| 28%             | 1:4             | 15                     | 4               | 1                | 2.35                | 35.40                  |
|                 | 2:3             | 15                     | 4               | 1                | 4.70                | 26.50                  |
|                 | 1:1             | 15                     | 4               | 1                | 5.88                | 22.12                  |
| 30%             | 1:4             | 15                     | 4               | 1                | 2.60                | 39.26                  |
|                 | 2:3             | 15                     | 4               | 1                | 5.22                | 29.43                  |
|                 | 1:1             | 15                     | 4               | 1                | 6.52                | 24.53                  |
| 32%             | 1:4             | 15                     | 4               | 1                | 2.86                | 43.00                  |
|                 | 2:3             | 15                     | 4               | 1                | 5.71                | 32.00                  |
|                 | 1:1             | 15                     | 4               | 1                | 7.14                | 26.86                  |
| 34%             | 1:4             | 15                     | 4               | 1                | 3.12                | 47.16                  |
|                 | 2:3             | 15                     | 4               | 1                | 6.27                | 35.41                  |
|                 | 1:1             | 15                     | 4               | 1                | 7.84                | 29.51                  |
| 36%             | 1:4             | 15                     | 4               | 1                | 3.44                | 51.8                   |
|                 | 2:3             | 15                     | 4               | 1                | 6.93                | 38.90                  |
|                 | 1:1             | 15                     | 4               | 1                | 8.61                | 32.40                  |
| 38%             | 1:4             | 15                     | 4               | 1                | 3.73                | 56.12                  |
|                 | 2:3             | 15                     | 4               | 1                | 7.45                | 42.09                  |
|                 | 1:1             | 15                     | 4               | 1                | 9.32                | 35.07                  |

3.2. Test device construction

In this paper, the low carbon steel Q235 is selected as the material of test device. Through the design of the magnetic circuit and the calculation of the number of turns, the current variation range is determined to be 0 ~ 2 A, the number of turns of coil is 1700, and the diameter of wire is 0.8 mm. According to the calculation result, the coil on the test mold is wound, and the insulating coil is wrapped on the wound coil to prevent the external enameled wire of the copper wire from being damaged and short-circuited. The test device is shown in figure 3.

The test principle of this experiment is that when a current is input to the coil, the electromagnet generates a magnetic field, and as the current value changes, the magnitude of the magnetic field also changes. In this paper, the Tesla meter is used to calibrate the magnetic field. Meanwhile, the conductive magnet piece is adhered to the upper and lower surfaces of the polyurethane MRE, which is beneficial to the wire soldering on the elastomer, and the elastic body is covered with insulating paper to prevent short circuit during measurement. For measuring the resistance, the wire is connected to a multimeter. The experimental principle is shown in figure 4.
4. Experimental on the resistance characteristics of MRE with carbon nanotubes

4.1. Seepage phenomenon of MRE with carbon nanotubes

Conductive polymers are synthesized from a matrix and conductive particles. In general, tunneling and conductive channel theory can be used to analyze the conductive mechanism \[11\]. When the volume fraction of conductive filler is low, the conductive paths cannot be formed between the particles, and the tunneling effect is used to indicate the conductive mechanism of materials. When the volume fraction of conductive filler reaches a certain level, the conductive channel is formed by the mutual contact between the particles, and the resistance value of the composite material is rapidly decreased. At this time, the conduction channel theory is the main one while the tunneling effect is the aid used to analyze its conduction mechanism.

The volume fraction of conductive particles selected in this paper is 24%, 26%, 28%, 30%, 32%, 34%, 36% and 38%. And the volume ratio of carbon nanotubes and carbonyl iron powder is set to 1:4, 2:3 and 1:1, so as to study the conductive percolation characteristics of MRE. The parameters of carbon nanotubes are as follows: length is 12 $\mu$m; outer diameter is 10 nm; inner diameter is 4 nm.

Among them, 1:4 is equivalent to increasing the specific gravity of carbonyl iron powder in the ratio compared with 2:3, and 1:1 is equivalent to increasing the proportion of carbon nanotubes in the ratio compared with 2:3. According to the resistivity of MRE with 28%, 32% and 36% volume fraction of the conductive filler, the values of $\rho_f$, $\phi$, and $t$ are calculated under the three ratios. Then, the conductive percolation curve of MRE with carbon nanotube can be obtained by substituting the numerical value into equation (3).

The experimental curves of the relationship between MRE resistivity and volume fraction of filler under ratios are shown in figure 5. It can be seen from it that when the MWCNTs/CIP ratios are 2:3, 1:4 and 1:1, the curves show turning points at 26%, 28% and 30% of the volume fraction. The resistivity of MRE still decreases after the turning point, but the downward trend is significantly slower than before the turning point. Within the range selected by experiment, when the volume fraction of conductive filler is near the percolation threshold, the resistivity of MRE will sharply change, and the small change of the volume fraction has an obvious effect on the resistivity of MRE.
The theoretical model proposed above is modified and identified by parameter based on experimental data. With the help of MATLAB’s powerful scientific calculation function, the paper used the nonlinear least square method based on trust region algorithm (NLLS-TRA) to identify parameters in the model. The flowchart based on the parameter identification process as shown in figure 6, and the parameter identification steps are as follows:

1. In Simulink, set up the magnetoresistance model proposed above. The input and output of the model must be in and out modules.

![Flowchart of parameter identification](image)

**Figure 5.** Experimental curve between volume fraction of conductive filler and resistivity of samples.

**Figure 6.** Flowchart of parameter identification.
(2) Introduce experimental data of different pieces into MATLAB, and give initial values of parameters based on past experience. \( f_c = 0.26, t = 2.31, \rho_f = 0.876 \).

(3) Create a new data set in Parameter Estimation, import the experimental data in the workspace, enter the volume fraction of the conductive filler and output the logarithmic value of the resistance.

(4) Create fitting parameters and set the value ranges of them. The parameters of the model are all positive values, so the value range of the parameter is set to \( 0 \sim +\infty \).

(5) Create a new fitting project. After adding fitting data and parameters, set the fitting algorithm and algorithm operation parameters.

(6) After running the fitting project, the parameter values of the model can be obtained, and evaluate whether the fit meets the requirements by analyzing the parameter trajectory, parameter sensitivity, experimental comparison and residual error in the analysis result display.

Figure 7 is a comparison of the experimental curve and the model calculation curve when the volume ratio of carbon nanotubes and carbonyl iron powder is set to 1:4, 2:3 and 1:1. According to the research results of Jang et al [29], when carbon nanotubes are not added to the MRE, the order of magnitude of resistivity is \( 10^{13} \). It can be seen from figure 7 that after adding carbon nanotubes, the order of magnitude of resistivity can be as low as \( 10^{2.6} \sim 10^4 \). It is much smaller than the resistivity of MRE without carbon nanotubes. Therefore, the addition of carbon nanotubes can improve the conductivity of MRE. It can be seen from figure 7 that the resistivity of MRE decreases with the increase of the volume fraction of conductive filler. When the ratio of MWCNTs/CIP is 2:3, the theoretical seepage curve agrees well with the experimental data and the conductivity is better. However, at 1:4, the experimental results fluctuate greatly near the theoretical curve, and MRE has poor conductivity. When the ratio is 1:1, the resistivity of MRE is much larger than the resistivity when the ratio is 2:3. The main reason for the above phenomenon is that carbon nanotubes are carbon based conductive materials, which can act as a ‘conductive bridge’ between carbonyl iron powder particles. The proper ratio of carbon nanotubes and carbonyl iron powder can effectively improve the conductivity of MRE. However, the aspect ratio of carbon nanotubes is relatively large, and the excessive content of carbon nanotubes will lead to agglomeration of itself, which cannot be evenly dispersed in the matrix of magnetorheological elastomer to act as a ‘conductive bridge’ between carbonyl iron particles. It will greatly reduce the conductivity of MRE. Therefore, when the ratio of MWCNTs/CIP is 1:1, the resistivity of MRE is much higher than that of 2:3. When the ratio of carbon nanotubes to carbonyl iron powder is 1:4, compared with carbonyl iron powder, the content of carbon nanotubes is too small to fully fill in a large number of carbonyl iron powder particles. It has little effect on improving the conductivity of MRE. When the ratio reaches 2:3, the content of carbon nanotubes is slightly less than that of carbonyl iron powder,
which can be evenly filled between carbonyl iron powder particles to fully play the role of ‘conductive bridge’, so the resistivity of MRE is smaller than that of 1:4.

The error values between the experimental data and the theoretical calculation value are shown in table 2. It can be seen that the average and maximum errors of different ratios are controlled within 10%, which is within a reasonable range. Therefore, it can be considered that the magnetoresistance correction model proposed above has good accuracy and effectiveness. There are two main reasons for the error. The first point is that the samples used in the experiment are self-made in laboratory, it cannot be guaranteed that they are exactly the same as the ideal samples, so it will affect the final experimental results. The second point is that during the derivation of the theoretical model, the interaction between the conductive chains is not considered. Therefore, there is deviation between the final theoretical calculation result and the experiment.

Based on the above analysis, in order to obtain a MRE with excellent conductivity and stability, it is particularly important to select a suitable ratio.

4.2. Response hysteresis effect of MRE with carbon nanotubes

After applying a magnetic field to MRE, the phenomenon that its resistivity changes with time is called the response hysteresis effect. This effect is mainly caused by the large viscosity matrix and the recombination of the magnetic particles present in MRE under the action of magnetic field.

In this paper, the volume fraction of conductive filler is 24%, 28%, 32% and 36%, and the volume ratio of carbon nanotubes and carbonyl iron powder is 1:4, 2:3 and 1:1. Put it in a zero magnetic field, and then apply the external magnetic field with magnetic flux density of 500 mT. As shown in figure 8, the time-dependent changes of MRE with different proportion of carbon nanotubes and carbonyl iron powder after applying magnetic field were tested.

It can be seen from figure 8 that after applying a magnetic induction intensity of 500 mT, the resistivity of MRE with different ratios decreases rapidly and gradually stabilizes with time. In contrast, when the volume fraction of the conductive filler contained is the same, the time for the resistivity of MRE with the ratio of 2:3 to

| Proportion of filler | 1:1 | 1:4 | 2:3 |
|---------------------|-----|-----|-----|
| Average error       | 4.1%| 5.7%| 2.4%|
| Maximum error       | 6.2%| 9.1%| 6.4%|
reach stability under magnetic field is shorter. It is mainly because the addition of MWCNTs reduces the viscosity of the matrix and increases the conductive area between the carbonyl iron powders, which can make the resistivity of MRE stable faster under the magnetic field.

4.3. Magnetoresistance characteristics of MRE with carbon nanotubes

MRE has the magnetoresistance characteristic, the resistance value varies with the change of the applied magnetic field. According to the previous analysis, when the ratio of MWCNTs/CIP is 2:3, the samples of MRE with volume fractions of 24%, 28%, 32% and 36% are tested on the relationship between resistance and magnetic flux density. After that, use the equation (18) to perform the least squares fitting on the measured experimental results. The relationship at different volume fractions is shown in figure 9.

It can be seen from figure 9 that as the magnetic flux density increases, the resistance of polyurethane MRE decreases, and the resistance changes greatly in the small range of magnetic flux density. In the range of 0 ~ 0.1 T, the resistance ratio of MRE with a conductive particle volume fraction of 36% is reduced from 1 to 0.6. When the magnetic flux density continues increasing, the resistance changes slowly and gradually becomes stable. Because the iron powder content is small, and MRE can reach magnetic saturation under a small magnetic flux density. It can also be clearly seen from the figure that under different magnetic flux density, the resistance changes of conductive particles with different volume fractions have significant differences. When the volume fraction of conductive particles is larger, the content of the carbonyl iron powder becomes higher, the more the resistance decreases as the magnetic flux density increases. The reason for the above phenomenon is that the higher the content of iron powder, the more the magnetic particles are chained at the same magnetic induction intensity, the easier the conductive path is formed, and the greater the decrease in the value.

5. Conclusion

In this paper, for the problem of poor conductivity, long response time and instability of MRE, a carbon nanotube-added polyurethane MRE was proposed while its magnetoresistance properties were studied. Main conclusions are as follows.

(1) A carbon nanotube-added polyurethane MRE was prepared, and the response time of the resistivity of samples with different ratios of carbon nanotube/carbonyl iron powder in magnetic field was tested. The test results showed that when the ratio is 2:3, the resistivity is the smallest and the response time is the shortest.

(2) The magnetoresistance properties of polyurethane MRE with different volume fractions at ratio of 2:3 was tested. The test results showed that the resistance of MRE with carbon nanotube decreases with the increase
of the applied magnetic field strength, and the larger the volume fraction of conductive particles, the more obvious the resistance drop.

(3) Based on the theory of magnetic medium and percolation, a theoretical model of magnetoresistance of polyurethane MRE with carbon nanotubes added was proposed. This model and the experimental test results are compared and analyzed, which proves the accuracy and effectiveness of the model, and provides a research basis for the preparation of MRE with excellent conductivity and sensitivity.

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