Influence of Polyurethane Properties on Mechanical Performances of Magnetorheological Elastomers

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Received 23 April 2009; accepted 21 September 2009
DOI 10.1002/app.31474
Published online 10 December 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Magnetorheological elastomers (MREs) are mainly composed of magnetizable particles and elastic polymer. The polymer matrix plays an important role in mechanical performances of MREs. In this study, the polyurethane (PU), which is synthesized by using toluene diisocyanate (TDI) and poly (propylene glycol) (PPG-220), is selected as a matrix because it has better degradation stability than natural rubber and higher mechanical stability than silicone rubber. Four different MRE samples were fabricated by adjusting the reaction molar ratio of TDI to PPG to change the property of PU matrix. Structural characterization of the PU matrix was described by Fourier transform infrared analysis. The microstructures of samples were observed by using an environmental scanning electron microscope. The mechanical performances of samples, including shear modulus, magnetorheological effect (MR) effect, loss factor, and glass transition temperature \((T_g)\), were characterized with a dynamic mechanical analyzer. The results show that the shear modulus, the relative magnetic residual shear modulus and glass transition temperatures of samples increase with the increment of toluene diisocyanate, while the relative MR effects and loss factors decrease steadily. The experimental results indicate that optimal molar ratio (TDI: PPG) is 3:1. The field-induced shear modulus of sample with molar ratio 3:1 is 4.9 MPa, and the relative MR effect is 121% under an external magnetic field of 800 mT at room temperature.


Key words: magnetorheological elastomers; polyurethane (PU); mechanical performances

INTRODUCTION

Magnetorheological (MR) materials, including MR fluids, MR elastomers and MR foams, are functional and smart materials because their rheological or mechanical properties can be controlled continuously, rapidly, and reversibly by applied magnetic fields.\(^1\)–\(^6\) As an important branch of MR materials, MREs are fabricated by embedding soft magnetic particles in a matrix such as silicon rubber,\(^7\) natural rubber,\(^8\) acrylonitrile,\(^9\) and polybutadiene.\(^10\) The magnetic particles form chain-like or other complex three-dimensional structures\(^11\) in the matrix along the direction of the magnetic field before curing under a magnetic field. These structures are locked into place after the mixture is cured or crosslinked. When such prepared MREs are exposed to an applied magnetic field, the modulus of MREs can be continuously and reversely changed responding to applied magnetic field. Based on these unique characteristics, MREs have recently found many applications, including instance variable impedance surfaces, adaptive tuned vibration absorbers, and stiffness tunable mounts and suspensions.\(^1,12,13,14\)

Commonly, silicone rubber and natural rubber are used as MRE matrixes. Silicone rubber is easy for fabrication because of its liquid precursor, but their mechanical properties are poor,\(^15\) and it is not proper to most load-bearing automotive applications because of its low strength and reduced fatigue life.\(^14\) Natural rubber has many advantages such as temperature resistance\(^16\) and good mechanical performance,\(^8\) but its degradation stability is poor compared with urethane elastomers.\(^17\) The disadvantages of both silicone rubber and natural rubber have limited their practical applications. Moreover, the modulus of silicone and natural rubber matrixes are hard to change, which cannot be used for fabricating MREs with different initial modulus. It is known that polyurethane matrix plays an important role in MRE performances. Thus, it is crucial to select a suitable matrix material in fabricating high-performance MREs.

In this study, polyurethane (PU) is selected as matrix because it has better degradation stability than...
natural rubber and superior mechanical stability than silicone rubber. The different properties of polymer can be achieved by changing raw material ratio with the same composition. The PU matrixes of MREs were synthesized by using toluene diisocyanate (TDI) and poly (propylene glycol) (PPG-220), which have different properties by adjusting the molar ratio of TDI to PPG (NCO/OH). PU-based MRE samples, with different reaction molar ratios of NCO/OH, were prepared. Their mechanical performances were characterized.

**EXPERIMENTAL**

**Raw materials**

Poly (propylene glycol) (PPG-2000, Mn = 2000) (The Third Petrochemical Factory, Tianjin Petrochemical, Tianjin, China) was distilled at 110°C under vacuum for 1 h before use. Toluene diisocyanate (TDI-80; Bayer), 1,4-Butanediol (BDO, Sinopharm Chemical Reagent, Shanghai, China), tin(II) octoate (Sinopharm Chemical Reagent), and acetone (Sinopharm Chemical Reagent) were used as received. The magnetic particles were carbonyl iron bought from BASF (German, model CN) with the size distribution: d10 = 3.5 μm, d50 = 6 μm, d90 = 21 μm.

**Synthesis of PU**

PPG and TDI were mixed in a 250-mL three-necked round-bottom flask fitted with mechanical stirrer, thermometer, and condenser. The temperature of reaction system was increased to 80°C. Then, tin (II) octoate (0.15 g) was added dropwise into the flask, and the reaction temperature was kept at 80°C for about 3 h under agitation. The mole ratio of TDI to PPG was calculated according to:

\[
\frac{n_{\text{NCO}}}{n_{\text{OH}}} = \frac{m_{\text{TDI}}}{174 g \cdot \text{mol}^{-1}} / \frac{m_{\text{PPG}}}{2000 g \cdot \text{mol}^{-1}}
\]

where \(n_{\text{NCO}}\) is the mol of NCO group, \(n_{\text{OH}}\) is the mol of OH group, \(m_{\text{TDI}}\) is the weight of TDI, and \(m_{\text{PPG}}\) is the weight of PPG.

Four categories of MRE samples with different mole ratios were prepared. The selective mole ratios for these four samples were listed in Table I.

1,4-Butanediol used as a chain extender was then added to reactor, and chain extension was performed at 60°C for the next 30 min. During the reaction, suitable amount of acetone was added to reduce the system viscosity.

**Preparation of MRE materials**

The iron particles were added to PU under stirring. In this study, four MRE samples based on PU had the same compositions (carbonyl iron particle: 80 Wt %). The mixture was put into mold. The magnetic field for the preconfiguration process was provided by a self-developed magnet-heat couple device, whose working principle and schematic structure were detailed in our previous work. During the preconfiguration stage, the MRE sample in the mold was exposed to a magnetic field of 1T for 20 min. Then, the sample was put into an oven at 35°C for 72 h to vaporize acetone.

**Characterization and measurement**

**FTIR**

Fourier Transform Infrared (FTIR) spectra of PU were collected on a Bruker FTIR (EQUINOX55) spectrometer in the range of 4000–500cm\(^{-1}\) at ambient temperature.

**Observation of microstructure**

The microstructure of MRE based on PU was observed by using an environmental scanning electron microscope (SEM, Philips of Holland, model XT30 ESEM-MP). The sample surface area was approximately 10 mm long and 5 mm wide that was covered with a thin layer of gold and then placed into the SEM. The microstructure of the sample was observed at an accelerating voltage of 15 kV.

**MRE property testing**

The properties of MRE samples were measured using a modified dynamic mechanic analyzer (DMA) (Triton Technology, UK, model Tritec 2000B) with a self-made electromagnet, which was introduced to generate a variable magnetic field from 0 to 1T.

Dynamic mechanical performances of the MREs were obtained by using a dynamic mechanical analyzer. Stress amplitude sweep mode was used to measure dynamic performance of MRE samples. Through the measurement, shear modulus and loss factor (tanδ), under various magnetic fields, were obtained. The frequency was 10Hz, and the strain amplitude was 0.3%. The magnetic flux density ranged from 0 to 800 mT at room temperature. The hysteresis loops of shear modulus were obtained when the frequency was 10 Hz and the strain amplitude was 0.2% under the magnetic flux density ranged from 0 to 600 mT at room temperature.

The glass transition temperatures of samples were obtained in tensile mode at a frequency of 1 Hz with
a strain of 0.3% and a temperature range from −40 to 50°C. The samples were approximately 20 mm × 10 mm × 1 mm.

RESULTS AND DISCUSSION

Characterization of the PU

Figure 1 shows the infrared spectrum of the PU at different reaction time. The urethane group signals, such as 3300 cm⁻¹ (―NH stretching), 1730 cm⁻¹ (―C=O stretching), and 1537 cm⁻¹ (―NH deformation vibration), can be observed. The absorption at 2274 cm⁻¹ is due to ―NCO group in Figure 1(a). This peak disappears in Figure 1(b). This result indicates that ―NCO group was reacted completely, and the formation of PU was confirmed. The asymmetric stretching of methyl (CH₃) group was observed at 2971 cm⁻¹. The symmetric stretching of methylene (CH₂) and methyl (CH₃) can be observed at 2871 cm⁻¹, respectively. A peak at 1107 cm⁻¹ is ascribed to ether (―C―O―C) group. The above results indicate that PU has been successfully prepared.

Microstructure of the MRE based on PU

The microstructures of MRE based on PU samples were investigated by the SEM, as shown in Figure 2. The orientation of particles is apparently observed, and the aligned particle chains can be formed by preparation under the magnetic field during curing, which are along the direction of the magnetic field. It can be observed that the agglomeration of carbonyl iron particles increased with the NCO/OH ratio increment. This may be explained by the different viscosity of PU matrix. The hard segments of PU are composed of TDI, and the soft segments are composed of PPG. The hard segments (TDI) are available to aid in the construction of physical crosslinking, and the amount of hard segments (TDI) is related to the viscosity conditions. Thus, carbonyl iron particles in high viscosity matrix agglomerate with the particles around them during curing under the magnetic field. The filamentary structure of the matrix is obviously observed in Figure 2(c,d), which may be as a result of tension among the magnetic particles in the matrix when the sample is exposed to the magnetic field. But the filamentary structure is not clearly observed in Figure 2(a,b). This result indicates that the more the agglomeration of carbonyl iron particles are, the stronger interaction between agglomeration of carbonyl iron particles is. This result agrees with the report from Wu et al.²⁰

Dynamic Performances

MR effect

Figure 3 shows the shear modulus of the PU MREs with different NCO/OH ratio, which were measured under various magnetic fields from 0 to 800 mT at the frequency of 10 Hz. As can be observed from this figure, the PU MREs have high shear modulus without the magnetic field, and the zero-field shear modulus of samples increase from 4.1 to 20.9 MPa. This result suggests that the modulus of PU MREs can be controlled by adjusting molar ratio of TDI to PPG. The shear modulus of samples 1–4 shows an increasing trend with magnetic field before they reach magnetic saturation at high field strength. The shear modulus of samples increases steadily with the addition of TDI.

On one hand, this result is due to the change of PU matrix as the NCO/OH ratio increased. The hard segments (TDI) are available to aid in the construction of physical crosslinking, and the amount

<table>
<thead>
<tr>
<th>Sample</th>
<th>nNCO : nOH</th>
<th>Tg(°C)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>3 : 1</td>
<td>−16.8</td>
</tr>
<tr>
<td>2</td>
<td>4 : 1</td>
<td>−7.3</td>
</tr>
<tr>
<td>3</td>
<td>5 : 1</td>
<td>8.6</td>
</tr>
<tr>
<td>4</td>
<td>6 : 1</td>
<td>11.5</td>
</tr>
</tbody>
</table>

TABLE I
Four Samples Classified from Different Reaction Molar Ratios of TDI to PPG and the Glass Transition Temperature of Each MRE Sample

Figure 1 FTIR spectra of the PU at different reaction time in the range 500–4000cm⁻¹: (a) 30 min after reaction, (b) 3.5 h after reaction.
and size of physical crosslinks increase in the matrix with the NCO/OH ratio increment, which can not move as easily as soft segments (PPG). When shear stress is used, the soft segment chains are better able to move for responding to shear stress than hard segments. Thus, with the increase of NCO/OH ratio in the PU matrix, amount and size of physical crosslinks increase, and it is harder for soft segments to move under the same shear stress, which results in the increase of PU matrix stiffness and the increase of shear modulus.

On the other hand, as can be observed in Figure 2, the microstructure of carbonyl iron particles also influences the shear modulus of the PU MREs. The agglomerations of carbonyl iron particles have large volume as the NCO/OH ratio is increased, and the iron particles can not move easily due to restriction of interaction between each other and the matrix under the magnetic field. As a result of the change of iron particle microstructure, the composite material becomes rigid, and the shear modulus of samples increases with the increase of NCO/OH ratio under the same magnetic field.

The shear modulus of samples is influenced by both the NCO/OH ratio of PU matrix and the microstructure of carbonyl iron particles under the magnetic field; therefore, the shear modulus of samples is not in linear relation with the NCO/OH ratio.

The field-induced shear modulus of the samples with different molar ratios of TDI to PPG is shown in Figure 4. It can be observed from this figure that

Figure 2 The microstructure of the MRE based on polyurethane observed by SEM: (a) sample 1, (b) sample 2, (c) sample 3, and (d) sample 4.

Figure 3 The shear modulus of the samples for different reaction molar ratio PU MREs.
the maximum field-induced shear modulus of PU MREs is 6.7 MPa (sample 2, under the magnetic field of 800 mT), this result has exceeded the MREs based on nature rubber (3.6 MPa, carbonyl iron particle content of 80 Wt % under the same magnetic field strength). This result is due to the change of PU stiffness and the microstructure of iron particle chains. It was confirmed by SEM that the carbonyl iron particles tend to agglomerate as the NCO/OH ratio is increased. Comparing Figure 2(b) with Figure 2(a), it can be observed that the extent of iron particles agglomeration is large in Figure 2(b), and the interaction between iron particles along the liner chain is strong in sample 2. Thus, the field-induced shear modulus of the sample 2 is higher than that of sample 1. Comparing Figure 2(b) with Figure 2(c,d), it can be observed that the distance between particle chains decreases with the agglomerations of carbonyl iron particles. When the distance between particle chains decreases, the magnetic interaction between particles from neighboring chains occurs. The interaction of the same chain particles decreases by the influence of the particles in neighboring chains, and the field-induced shear modulus of the samples decreases. The matrix of sample 2 is neither as soft as sample 1 nor as hard as sample 3 and sample 4 due to proper NCO/OH ratio. Compared with sample 2, the motion of iron particles is hard by the restrain of rigidity matrix in sample 3 and sample 4. Therefore, the proper proportion between hard and soft segments in the PU is favorable for improving the field-induced shear modulus of sample due to the influence of the microstructure of iron particle chains and the property of matrix.

The results of relative MR effect for different molar ratios of TDI to PPG samples with the same iron particle content are shown in Figure 5. As can be seen from this figure, the maximum value of relative MR effect is 121% under an external magnetic field of 800 mT at room temperature, which attributed to sample 1. Along with the increase of hard-to-soft segment (NCO/OH) ratio in the PU, the relative MR effect obviously shows a decreasing trend. The relative MR effect of sample is extraordinarily influenced by the structure of carbonyl iron particle chains and the stiffness of matrix.

The viscosity of PU matrix increases with the NCO/OH ratio increment during curing under the magnetic field. Lower viscosity of the reactive mixture makes alignment of the iron particles with the magnetic field lines easily. The carbonyl iron particles are difficult to be arranged to line under the magnetic field due to the increase of PU matrix viscosity.

Figure 4 Relationship between field-induced shear modulus and magnetic field for different reaction molar ratio PU MREs.

Figure 5 Relationship between relative MR effect and magnetic field for different reaction molar ratio PU MREs.

Figure 6 Hysteresis loops of different NCO/OH ratio PU MREs under the magnetic field ranged from 0 to 600 mT.
Table II

<table>
<thead>
<tr>
<th>No. of samples</th>
<th>Shear modulus (MPa): $G'_0$</th>
<th>$G'_0$load</th>
<th>$G'_0$up load</th>
<th>$\Delta G'_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.04</td>
<td>3.86</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>15.14</td>
<td>17.19</td>
<td>2.05</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>35.22</td>
<td>38.83</td>
<td>3.61</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>38.79</td>
<td>43.61</td>
<td>4.82</td>
<td></td>
</tr>
</tbody>
</table>

where: $\Delta G'_0 = G'_0$up load $- G'_0$load.

$G'_0$load is the shear modulus on the load process with magnetic field of 0 mT, and $G'_0$up load is the shear modulus on the upload process with magnetic field of 0 mT. $\Delta G'_0$ is the relative magnetic residual shear modulus of samples.

viscosity, and the relative MR effect decreases with the increase of NCO/OH ratio. On the other hand, the concentration of the hard segment, which is mainly composed of diisocyanate, increased. This results in final stiff PU. As can be observed in Figure 3, the zero-field shear modulus of samples increases immensely due to the increase of NCO/OH ratio. This also results in the decrease of the relative MR effect.

Figure 6 represents the hysteresis loops of different NCO/OH ratio PU MREs under the magnetic field ranging from 0 to 600 mT when the frequency was 10 Hz and the strain amplitude was 0.2%. Table II shows the relative magnetic residual shear modulus of samples. Comparing the hysteresis loops of four samples in Figure 6, it can be observed that the area enclosed by the hysteresis loop and the relative magnetic residual shear modulus ($\Delta G'_0$) after switching off the field increases as the NCO/OH ratio increases. It can also be observed that as the NCO/OH ratio increased, the upload curves tend to level. This phenomenon may result from microstructure of carbonyl iron particle chains in different NCO/OH ratio PU matrix. As can be observed from SEM, the agglomeration of carbonyl iron particles and interaction between them increase with the NCO/OH ratio increment. The motion of carbonyl iron particles may be constrained by the interaction force between each other and the matrix. The change of chain microstructure in high NCO/OH ratio PU matrix decreases slowly in the process of uploading magnetic field. Thus, the area of the hysteresis loop and the relative magnetic residual shear modulus ($\Delta G'_0$) increase with the increment of NCO/OH ratio in PU matrix. This result indicates that the stability of PU MREs is not so good compared with the magnetorheological elastomers based on silicone rubber during the process of loaded and uploaded magnetic field. Comparing four samples, it is observed that the sample 1 has the best stability in the test.

Loss factor

Figure 7 shows the relationship between the loss factor (tan$\delta$) and magnetic field for different reaction molar ratio PU MREs. The loss factors of these four samples decrease steadily with the increase of magnetic field. When the magnetic field is applied to the MRE sample, carbonyl iron particles transfer to respond to external magnetic field, and the interaction force between the particles and the matrix is enhanced. In this condition, relative motion between carbonyl iron particles and matrix results in friction, which causes energy dissipation. Hence, the MRE sample’s loss factor is high when exposed to low magnetic field. With the increase of applied magnetic field, the relative motion displacement was decreased by the strong interaction force.

Figure 8 Relationship between loss factor and temperature for different reaction molar ratio PU MREs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
between the particles and the matrix. As a result, the energy dissipation is reduced and the loss factor decreased when the magnetic field further increased.

These results also indicate that the loss factors decrease steadily with the increment of NCO/OH ratio. It is noted that the loss factor of sample 1 is higher than other samples. This may result from the structure of carbonyl iron particles in PU matrix. As shown in the Figure 2, the large iron particle agglomerations cannot transfer easy by the restraint of interaction between particles and matrix. The final PU becomes stiff when the concentration of the hard segment increases. On this condition, the relative motion between particles and matrix is easy, and the relative motion displacement on the interface is increased under the external magnetic field with the decrease of NCO/OH ratio. This result leads to more energy dissipated on the interface and higher loss factor of the MR elastomers.

The glass transition temperature

The relationship between the loss factor (tanδ) and the temperature for different hard-to-soft segment (NCO/OH) ratio PU MREs, where the iron particle contents are same, are shown in Figure 8. The temperature corresponding to the peak loss factor can be approximately regarded as the glass transition temperature (Tg). The Tg of samples is shown in the Table I. The Tg increase from −16.8 to 11.3°C with the increase of NCO/OH ratio. This result is in agreement with Fuchs et al. Transition from glassy to rubbery phase contributes to mobility of the soft segments in PU matrix at low temperature. In the PU, the increasing amount of isocyanate groups can hinder the movement of the soft segments. With the increase of NCO/OH ratio, the interaction between hard segments and soft segments become strong. The motion of soft segment is confined due to the obstruction of hard segment. Thus, the glass transition temperatures of samples increase with the increment of NCO/OH ratio.

CONCLUSIONS

The MREs based on PU matrix were prepared and experimentally studied in this article. By adjusting the molar ratio of hard segment (TDI) to soft segment (PPG), MREs with high MR effect were prepared.

1. By adjusting the molar ratio of hard segment (TDI) to soft segment (PPG), the microstructures of PU MRE are changed as the SEM results shown. The agglomeration of carbonyl iron particles and the interaction between agglomerations of carbonyl iron particles increase with the NCO/OH ratio increment.

2. The shear modulus of samples increase with the increment of NCO/OH ratio. This result indicates that the modulus of PU MREs can be controlled by adjusting molar ratio of TDI to PPG, and PU MREs can satisfy different applications by the adjustment of NCO/OH ratio.

3. The maximum field-induced shear modulus of PU MREs reaches as high as 6.7 MPa, and this result has exceeded the MREs based on nature rubber (3.6 MPa, carbonyl iron particle content of 80 Wt % under the same magnetic field strength). The proper proportion between hard segments to soft segments in the PU matrix contributes immensely to the progress of the field-induced shear modulus of samples.

4. The relative MR effects of the PU MREs decrease with the increment of NCO/OH ratio. This results from the influence of the structure of carbonyl iron particle chains and the stiffness of matrix.

5. The hysteresis phenomenon of PU MREs increases as the NCO/OH ratio increased. This may result from microstructure of carbonyl iron particle chains in different NCO/OH ratio PU matrix. This result also indicates that the stability of PU MREs is not so good compared with the magnetorheological elastomers based on silicone rubber during the process of loaded and uploaded magnetic field. The sample 1 (TDI : PPG is 3 : 1) has the best stability in the test.

6. The loss factor increases with the addition of soft segment. The glass transition temperature for the PU MREs increases from −16.8 to 11.3°C with the increment of NCO/OH ratio. This results from that the interaction between hard segment and soft segment becomes strong and the motion of soft segment is confined due to the obstruction of hard segment.

7. The experimental results indicate that the optimal molar ratio (TDI : PPG) is 3 : 1 because of high relative MR effect (121%) and the best stability. And the field-induced shear modulus of optimal molar ratio sample is 4.9 MPa.

References