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1. Introduction

Magnetorheological (MR) solid materials belong to a class of intelligent materials which can respond to an external magnetic field stimulus by changing their viscoelastic properties rapidly, continuously and reversibly. MR materials can be classified into MR fluids, $^{\!\!\!\!\!1,2}$ and MR solids $^{\!\!\!3,4}$ including MR elastomers,⁵⁻⁷ MR gels⁸⁻¹⁰ and MR foams.¹¹⁻¹⁷ MR fluids are the most common MR materials for commercial applications, such as vehicle seat vibration control¹⁸ and primary automotive suspensions.¹⁹ Because of the low viscosity of the fluid, its rheological properties can be changed dramatically and the magnetic particles can be aligned under magnetic field. However, the magnetic particles are easy to settle and appropriate seals are needed to prevent leakage which limits the application of MR fluids to some degrees. To overcome the shortages of MR fluids, MR solids are developed in which the solid property of matrix can solve the settlement of the magnetic particles and also the MR solid can be shaped easily. Comparing with MR fluids, the MR effect (change of shear modulus) of MR solids may be slightly faster since the particles do not have to move within the matrix in order to create the effect.³ Moreover, MR solids have a controllable, field-dependent modulus, whereas MR fluids have a field-

Smart polyurethane foam with magnetic field controlled modulus and anisotropic compression property

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A new kind of polyurethane (PU) magnetorheological (MR) foam was prepared *via in situ* polymerization and foaming for the first time. A chain-like structure of carbonyl iron particles in the liquid polyol is formed after orientation at a magnetic field and fixed in the PU foam after the *in situ* curing. The anisotropic PU MR foam possesses an anisotropic compression property. The compression strength along the magnetic chain direction reaches ~ 1053.5 KPa for the sample with 80 wt% carbonyl iron content, which is ~878 times that of the blank foam and ~57 times of that at the vertical direction of the same sample. The PU MR foam exhibits a magnetic field controlled shear modulus, *i.e.*, MR effect, which can be adjusted by changing the orientation structure and content of the carbonyl iron, test frequency and magnetic field strength. The maximum absolute and relative MR effects for the anisotropic PU MR foam are ~1.07 MPa and ~27.1%, respectively. Moreover, the introduction of carbonyl iron particles can notably improve the acoustic absorption properties in the low frequency region.

> dependent yield stress.³ The excellent and adjustable mechanical properties of MR solids make it have the potential applications in adaptive tuned variable-stiffness devices, soft actuators and artificial muscle.^{10,20}

> MR foam is one kind of MR solid materials comprised of micro-sized magnetically permeable particles into the foam matrix. Apart from the above superiority of MR solids materials, it has distinct advantages comparing with other MR materials because of the particular porous structure. The first advantage is the light weight which makes it have the potential to be used in some special fields such as aerospace. The second one is that the MR effect can be adjusted by changing the cell structures of the foam. Ju et al. fabricated isotropic porous silicone rubber MR elastomer by using the decomposition reaction of NH4HCO3 to produce the porous structure. They found that the zero-field modulus of the materials decreases sharply with increasing porosity and it has a more obvious relative MR effect than that of the MR elastomer without pores.²¹ The third advantage of MR foam is the excellent vibration and acoustic absorption performance, which is active controlled, compared with the passive feature of the conventional foam. Scarpa et al. studied the PU MR foam by immersing the PU foam with open-cell structures into the MR fluid and then drying it. They found the composite foam has a high acoustic absorption coefficient in the frequency region of 1000 to 2800 Hz.^{11,12} Zielinski et al. showed that the prepared PU MR foam containing MR fluid have different acoustic absorption properties. The peaks in the absorption curves of dual-porosity composite foam under the

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influence of magnetic field are slightly shifted by 400-500 Hz relative to the field-free conditions or to the blank foam.¹³ Up to now, two kinds of foam matrix are mainly used for MR materials matrix: metal foam^{14,15} and polymer foam. For polymer foam matrix, polyurethane (PU) foam attracts great attention because of the flexibility in properties that can be achieved through adjusting the formulation and changing the synthesis and processing conditions.²² Carlson et al. used the PU foam as liquid carrier medium to contain the MR fluid and the materials were developed as a low cost MR fluid foam damper.^{16,17} Maranville et al. fabricated one kind of MR foam consisting of PU foam and MR fluid. They reported that the complex modulus of the materials increases from 170 kPa in 0 T to 2 MPa under an applied magnetic flux density of 0.6 T.²³ However, it should be noted that all of the MR foams at present are the combination of MR fluids with kinds of foams. The foam only acts as a supporter and the settlement of magnetic particles still exists. So far, the MR foam prepared by fixing magnetic particles into the foam matrix was not reported yet.

In this study, a new kind of MR foam with oriented carbonyl iron particles fixed in the PU foam matrix was prepared through *in situ* polymerization and foaming in the presence of magnetic field for the first time. Previously, we fabricated the MR elastomer^{24–26} and MR hydrogel,¹⁰ and it was found that the MR effect can be significantly affected by changing the carbonyl iron particles aggregation structure (isotropic or anisotropic) and contents, the test frequencies and external magnetic field. However, the high density of the bulk limits the further application in some circumstances. Herein, the structure and properties of PU MR foam were studied systematically and the difference of magnetic field controlled shear modulus between PU MR elastomer and PU MR foam were compared. This kind of MR foam material has the potential to be used as an active vibration absorber.

2. Experimental

2.1 Materials

The carbonyl iron particles (Type: OM) used in this study are supplied by BASF (Germany) with sizes of $d_{10} \sim 2 \mu m$, $d_{50} \sim 4 \mu m$, and $d_{90} \sim 9 \mu m$. Polyether triol (Type: TMN-3050) with a hydroxyl value of 56 is purchased from Tianjin Petro. Co., China. Isocyanate (PAPI, Type: PM-200) is provided by Yantai Wanhua polyurethanes Co., Ltd., China. Glycerol and dibutyltin dilaurate catalyst (DBTDL) are obtained from Chengdu Kelong Chemical Factory, China. The catalyst triethylenediamine (DABCO-33LV) is produced by Air Products and Chemicals. The foam stabilizer (Type: L-568) is the product of Momentive Company (USA) and water is used as foaming agent. All of the materials used as received without further treatment.

2.2 Preparation of isotropic and anisotropic PU MR foam

The formula for the isotropic PU MR foam is listed in Table 1. Typically, the detailed procedures of the PU MR foam with 70 Table 1 The formula for the PU MR foam

Material	Weight (g)
TMN-3050	100
Carbonyl iron	344.4
H ₂ O	2
DABCO-33LV	0.3
DBTDL	0.1
Stabilizer (L-568)	2
Glycerol	2
PAPI	42.5

wt% carbonyl iron content are as follows: TMN-3050, carbonyl iron, glycerol, DABCO-33LV, L-568 and water were mixed through ball milling at a speed of 150 r min⁻¹ for 10 min; then, DBTDL and PAPI were added to the obtained dispersion with quick stirring for 1-2 min; thirdly, the mixtures were poured into a mold coated with a layer of release agent quickly; finally, after the foaming process finished, the PU MR foam was further aged at a 70 °C oven for 1 h and after that the isotropic sample was obtained. The isotropic PU MR foam with 60, 70 and 80 wt% carbonyl iron particles were fabricated and designated as Iso-60, Iso-70 and Iso-80, respectively. The anisotropic PU MR foams were prepared by the same procedures as the isotropic one except that a magnetic field of 0.8 T was used along the thickness direction of the sample for 20 min to align the carbonyl iron particles in the foam matrix immediately after the liquid mixtures were poured into the mold. The Aniso-60, Aniso-70 and Aniso-80 were used to represent the anisotropic PU MR foam containing 60, 70 and 80 wt% carbonyl iron particles, respectively. As a contrast, the blank PU foam without carbonyl iron particles was prepared.

2.3 Characterization

2.3.1 Scanning electron microscopy (SEM). To observe the morphology of the foam and carbonyl iron particles, the fracture surface of the sample was coated with a thin gold layer prior to observation by Inspect F SEM instrument (FEI Company, USA) with an acceleration voltage of 20 kV and image-pro software was used to measure the pore size distribution quantitatively.

2.3.2 Apparent density. The blank foam, isotropic and anisotropic PU MR foam were cut into a cube with dimensions of $2.5 \times 2.5 \times 2.5$ cm. The mass of the specimen was measured and the density was calculated. All of the data were the average of three samples.

2.3.3 Compression properties measurement. The measurement of compression properties was conducted on a universal testing machine (Instron 5567, USA) with the dimensions of $2.5 \times 2.5 \times 2.5$ cm. The maximum strain was 25% and the compression rate was 10 mm min⁻¹. For blank PU foam and isotropic PU MR foam, the compression direction have no effect on the compressive stress. However, for the anisotropic PU MR foam, it has two kinds of compressive models. The first one is the applied compressive force along the direction of the carbonyl iron chain (Fig. 1, Aniso-*xx*-1); the second one is the applied compressive force vertical to the direction of the



Fig. 1 Two kinds of compressive model for anisotropic PU MR foam.

carbonyl iron chain (Fig. 1, Aniso-*xx*-2). The *xx* represents the content of carbonyl iron particles.

2.3.4 The MR effect analysis. The MR effect test was performed on a modified dynamic mechanical analyzer^{10,24–26} with a shear mode under magnetic field (Triton Technology Ltd., model Tritec 2000B, UK) at room temperature. A shaft connects the sample and the motor in DMA. The motor drives the shaft and the sample moves at a given amplitude and frequency. The stress in the sample was measured with the sensor and the strain was taken as the displacement amplitude. The shear modulus was calculated from the data of strain-stress curve. During the test, a magnetic field which can vary from 0 to 1.0 T was applied to the sample. The dimensions of the sample were $10 \times 10 \times 3$ mm. The dynamic strain amplitude was set as 0.3%. The MR effect was tested at three different frequencies, *i.e.*, 1, 5 and 10 Hz.

2.3.5 Acoustic absorption properties measurement. The acoustic absorption property of blank foam, isotropic and anisotropic PU MR foam was conducted on a noise and vibration test system (Bswa Technology Co., Ltd., China) with the dimensions of 30 mm in diameter and 10 mm in height.

2.3.6 Thermogravimetric analysis (TGA). The thermal stability of anisotropic PU MR foam sample with different carbonyl iron particles content were carried out on a Q 600 equipment (TA Instrument, USA) in a nitrogen atmosphere with a heating rate of 10 $^{\circ}$ C min⁻¹ from 40 to 600 $^{\circ}$ C.

3. Results and discussion

3.1 The morphology of PU MR foam

The surface morphology of the fractured blank foam and isotropic PU MR foam with different carbonyl iron particles contents are shown in Fig. 2. The blank foam (Fig. 2(a, b)) has a pore structure with an average diameter about 1 mm. Fig. 2(c, d), Fig. 2(e, f) and Fig. 2(g, h) are the SEM images of pore morphology of isotropic PU MR foam with 60, 70 and 80 wt% carbonyl iron particles, respectively. A large amount of carbonyl iron particles are dispersed randomly in the wall of the pores. After incorporating the carbonyl iron particles, the pore morphology of isotropic PU foam is changed and the pore size becomes smaller. The average pore sizes are 0.54, 0.33 and 0.23 mm for the samples with the iron content of 60, 70 and 80 wt%, respectively. The reason for the reduction in the pore size



Fig. 2 SEM of fractured surface for blank PU foam (a, b) and isotropic PU MR foam with different carbonyl iron contents: (c, d) 60 wt%, (e, f) 70 wt%, (g, h) 80 wt%.

may be that increasing the carbonyl iron particles content would increase the nucleating points and reduce the coalescence of the cellular structure formed in the foam. It seems that the open-cell structure turns to close-cell structure when the iron amount is higher. The reason is that the high iron content increases the viscosity of the mixture and the CO_2 generated by reacting isocyanate with water is hard to diffuse out of the highly viscous matrix.

For anisotropic PU MR foam, a magnetic field with 0.8 T was applied to align the carbonyl iron particles during the fabrication procedures. The SEM images of fractured surface of anisotropic PU MR foam at different contents of carbonyl iron particles are shown in Fig. 3. It can be seen that the oriented chain-like structure of carbonyl iron particles is formed and fixed in the matrix of the foam. When the iron content is 60 wt%, the pore size and the gap between the adjacent chains are relatively wide, and the chain structure is a little bit discontinuous. With increasing the amount of carbonyl iron particles, the pore size and the distance between



Fig. 3 SEM of fractured surface for anisotropic PU MR foam with different carbonyl iron contents: (a, b) 60 wt%, (c, d) 70 wt%, (e, f) 80 wt%.

the adjacent magnetic chains decrease and the oriented magnetic chains become denser.

3.2 Apparent density

Fig. 4 reveals the apparent density of blank foam, isotropic and anisotropic PU MR foam with different iron contents. The blank foam has a low density of 94.7 Kg m⁻³, after incorporating 80 wt% carbonyl iron into the matrix, the density of isotropic PU MR foam increases to 864.7 Kg m⁻³. The reason for the remarkable increase in the density are: (1) the carbonyl iron particles have a much higher density than



Fig. 4 The density of blank PU foam, isotropic and anisotropic PU MR foam with different iron contents.

the matrix, (2) the high content of iron can decrease the pore size and change the pore structure from open-cell to close-cell structure. Comparing with the isotropic samples, it can be found that the anisotropic one has a higher density, for example, the Aniso-80 sample has a density of 1060.8 Kg m⁻³, while the Iso-80 one only has 864.7 Kg m⁻³. When the magnetic field is applied, the formed magnetic chains of iron particles can compress the cell. The wall of the cell has a certain extent of degeneration and the coalescence may occur, which reduces the cell structure and results in a higher density.

3.3 Compression properties

For MR materials, a high weight filling content of iron particles is needed to obtain an excellent MR effect. But in such a case, the mechanical properties usually become worse and may restrict the practical applications. The compression properties of blank PU foam, isotropic and anisotropic PU MR foam with different amounts of carbonyl iron were studied. The results are shown in Fig. 5 and the compression stress at 3.9% and 10% strains are listed in Table 2. It can be seen that the blank PU foam is flexible with a low compression stress of 1.2 and 2.6 KPa at 3.9% and 10% strains, respectively. The compression properties are notably improved with increasing the iron content. Moreover, the aggregate structure of carbonyl iron particles can significantly affect the compression strength. It is interesting that the anisotropic PU MR foam presents an anisotropic compression property. When the compression direction is parallel to the magnetic chain structure, the compression stress increases at first until the strain reaches \sim 3.9%, and then, a dramatic decrease occurs with increasing the strain continually, as the aligned chains of iron particles will be destroyed. Further increasing the strain would destroy the cell structure of foam and lead to the decrease of stress. It can be noted that the orientation of the carbonyl iron particles can notably improve the compression stress along the aligned direction. For example, the compression strength of Aniso-80 sample along the magnetic chain direction reaches 1053.5 KPa at 3.9% strain, it is \sim 57 times that at the vertical direction of the same sample (18.5 KPa) and \sim 878 times that of the blank PU foam (1.2 KPa). Sorrentino et al. prepared PU/iron particles composite foam without MR effect and showed that the maximum stress along the chainlike direction is 33.1 KPa for anisotropic sample at an iron content of 15 wt%, which is ~2.4 times and ~3.3 times that at the vertical direction of the same sample (14 KPa) and the blank foam (10.1 KPa), respectively.^{27,28} The PU MR foam we prepared has an outstanding anti-compression property for both isotropic and anisotropic samples.

3.4 The MR effect of PU MR foam

The MR effect originates from the interaction of magnetic particles. When MR foam is subjected to an external magnetic field, the ferrous particles can be magnetized easily and tend to align along the direction of the magnetic field. The fieldinduced magnetic force between the magnetic particles provides an ability of anti-deformation, resulting in the change of shear modulus. The change of relative and absolute shear modulus can be used to characterize the relative and absolute



Fig. 5 The compressive stress-strain curves of isotropic (a) and anisotropic (b) PU MR foam with different iron contents.

MR effect. For relative MR effect, it is defined as $\Delta G/G_0 \times 100\%$, which G_0 is the zero-field shear modulus and ΔG is the increment of field-deduced shear modulus, the ΔG is also called as absolute MR effect. The influencing factors of the MR effect include polymer matrix, magnetic particles type and content, aggregate structure, testing frequency, external magnetic field intensity, *etc.*⁶ In this study, the MR effect of PU MR foam was investigated in detail.

Fig. 6 illustrates the change of shear modulus for isotropic and anisotropic PU MR foam with different contents of carbonyl iron particles and different external magnetic field strengths. The zero-field modulus, relative and absolute MR effects are listed in Table 3. The isotropic PU MR foam has a low zero-field modulus which increases with the addition of the iron particles. The zero-field modulus of anisotropic samples is higher than that of the isotropic one at the same iron content. For example, the zero-field modulus of Iso-80 and Aniso-80 samples are 0.58 MPa and 3.95 MPa, respectively, the orientation of iron particles results in an increase of the zero-field modulus by 580% as the orientation of iron particles further enhances the rigidity of the composite. The absolute and relative MR effects of both kinds of MR foams increase with increasing the iron content. For Iso-80 sample, it has a low absolute MR effect of only 0.29 MPa, while for Aniso-80 sample the absolute MR effect is 1.07 MPa which is ~ 3.7 times of that for Iso-80 one. This is attributed to the orientation of carbonyl iron reducing the distance between particles and subsequently enhances the interaction of iron particles under a magnetic field. The chain-like structure in the PU MR foam with 80 wt% iron is the densest, so the interaction between iron particles under the magnetic field and the absolute MR effect are the strongest. However, the

Table 2 Compression stress of PU MR foam at 3.9% and 10% strains							
	Stress at 3.9% strain (KPa)			Stress at 10% strain (KPa)			
	Iso-xx	Aniso-xx-1	Aniso-xx-2	Iso-xx	Aniso-xx-1	Aniso-xx-2	
Blank foam	1.2			2.6			
60 wt% iron	1.9	259.0	11.1	7.0	174.8	34.1	
70 wt% iron	20.0	408.9	16.8	46.9	220.3	54.2	
80 wt% iron	45.7	1053.5	18.5	182.1	732.1	54.7	

relative MR effect of anisotropic samples with aligned chainlike structure of iron particles are lower than that of isotropic samples due to a higher zero-field modulus for anisotropic PU MR foam.

The motion of polymer molecular chain is frequency dependent, so the frequency dependence of the MR effect of the PU MR foam was also investigated. The shear modulus change (MR effect) of isotropic and anisotropic PU MR foam with 80 wt% iron at 1, 5, 10 Hz are shown in Fig. 7. The zerofield modulus for both the isotropic and anisotropic samples increases with increasing the test frequency, which attributes to the frequency dependence of the polymer matrix. With



Fig. 6 Magnetic field induced shear modulus increment of isotropic (a) and anisotropic (b) PU MR foam with different iron contents.

Iron content (wt%)	Zero-field modulus (MPa)		Absolute MR effect (MPa)		Relative MR effect (%)	
	Isotropic	Anisotropic	Isotropic	Anisotropic	Isotropic	Anisotropic
60	0.072	1.47	0.021	0.10	29.2	6.8
70	0.22	2.40	0.13	0.36	59.1	15.0
80	0.58	3.95	0.29	1.07	50.0	27.1

Table 3 The zero-field modulus and the MR effect of PU MR foam with different iron contents

increasing the test frequency, the mobility of PU molecular chains cannot keep up with the external stimuli and the molecular chains tend to be rigid which leads to the enhancement of zero-field modulus. From Fig. 7(a, b), the absolute MR effect of this two kinds of MR foam changes little with increasing the frequency, but the relative MR effect decreases. According to this result, the operating frequency is important to be considered in practical applications.

The absolute MR effect of the anisotropic PU MR foam at a content of 70 wt% carbonyl iron particles is 0.36 MPa in this study, which is lower than that of the anisotropic PU MR elastomer (1.3 MPa) we prepared previously at the same iron content of 70 wt%.²⁵ A mechanism is proposed to explain the phenomenon, which is shown in Fig. 8. For MR elastomer (Fig. 8(a)), the formed chain-like structure of carbonyl iron particles is dispersed continuously in the whole elastomer matrix but for MR foam (Fig. 8(b)), the chain-like structure is only dispersed in the wall of the pore and it becomes somewhat discontinuous which is divided by pore junctions.



Fig. 7 The effect of test frequency on the magnetic field induced shear modulus increment of isotropic (a) and anisotropic (b) PU MR foam with 70 wt% carbonyl iron.

According to the dipole model,²⁹ the magnetic-induced shear modulus (absolute MR effect) can be calculated as: $\Delta G = \phi J_s^2 d^3/2\mu_1\mu_0 r_0^3$ where ϕ is the volume fraction of particles, J_s is the dipole moment magnitude per unit particle volume as magnetically saturated, *d* is the diameter of the magnetic particles, μ_1 is the relative permeability of the matrix, μ_0 is a constant, r_0 is the distance between magnetic particles. Therefore, the pore wall of PU foam will increase the average gap (r_0) between the magnetic particles and thus make the absolute MR effect decrease.

3.5 The acoustic absorption properties of PU MR foam

Foam is one kind of material which has excellent acoustic absorption properties. Fig. 9 shows the acoustic absorption properties of blank PU foam, isotropic and anisotropic PU MR foam with three different carbonyl iron particle contents. The acoustic absorption coefficient of blank foam is low in the area from 800 to 2000 Hz, but it is extremely high in the high frequency especially around 5000 Hz. For blank foam, the existed open-cell structure makes the acoustic wave easily flow into the interior of the foam and leads to the vibration of the air. Owing to the viscous resistance, the friction between air and pore wall, and heat conduction, one part of the acoustic energy can be transformed into thermal energy and dissipated which produces the effect of acoustic absorption.³⁰ In Fig. 9(a), we find that the incorporation of carbonyl iron particles can increase the acoustic absorption coefficient at the low frequency range between 800 to 2000 Hz to a certain extent.



Fig. 8 A comparison of mechanism of anisotropic MR elastomer (a) and MR foam (b).



Fig. 9 The acoustic absorption coefficient of isotropic (a) and anisotropic (b) PU MR foam with different carbonyl iron contents

The acoustic absorption coefficient of Iso-70 sample is 0.52 at 1280 Hz while it is only 0.22 for the blank foam. However, as the frequency is higher than 2000 Hz, the acoustic absorption coefficient of isotropic PU MR foam becomes much lower comparing with the blank foam. The possible reason is that some open-cell structures for blank foam change into closecell structures for PU MR foam containing carbonyl iron particles which is confirmed by the SEM results. From Fig. 9(b), the anisotropic PU MR foam has a higher acoustic absorption coefficient in the low frequency region. Also the low frequency range becomes wider when the iron content increases. Comparing with blank foam, especially for Aniso-80 sample, the acoustic absorption coefficient in the region from 800 to 3500 Hz is greatly improved with a maximum coefficient as high as 0.85. This is in agreement with Scarpa's results which was shown that the acoustic absorption coefficient at the low frequency region is improved for the PU foam immersed in the MR fluid.^{11,12} Comparing with the isotropic sample, the anisotropic one has a higher acoustic absorption coefficient overall and a wider frequency range of acoustic absorption coefficient. According to the modern acoustic theory for acoustic absorption, the functional particles (micro-resonance unit) regularly dispersed in the polymer matrix can dissipate the energy of the acoustic wave at a special frequency range through resonance.31,32 With the incorporation of the carbonyl iron particles into the PU foam, it acts as a micro-resonance unit which increases the acoustic absorption coefficient at the low frequency range. Additionally, the aggregate structure of carbonyl iron particles can produce different micro-resonance units and result in the difference in the intensity and location for acoustic absorption.

3.6 The thermal properties of PU MR foam

The thermal properties of anisotropic PU MR foam with different amounts of carbonyl iron particles in nitrogen atmosphere and the characteristic thermal decomposition temperature are presented in Fig. 10 and Table 4, respectively. The weight of the carbonyl iron is nearly unchanged from room temperature to 600 $^{\circ}$ C, so it can be deduced that the mass loss of PU MR foam is almost due to the thermal degradation of PU foam. For the blank PU foam in the Fig. 10, it can be seen that there is two degradation stages which range from 250 $^{\circ}$ C to 350 $^{\circ}$ C and 350 $^{\circ}$ C to 400 $^{\circ}$ C. After incorporation the carbonyl iron particles into the PU foam, the temperature

of the two stages increase to high temperature. In general, the thermal degradation of polyurethane occurs in two stages: the initial degradation stage I occurs from 40 to 350 °C and is primarily the decomposition of the hard segment, which includes the dissociation of urethane to the original polyol and isocyanate, which then forms a primary amine, alkene, and carbon dioxide. Stage II occurs from 350 to 600 °C and proceeds by the depolycondensation and polyol degradation mechanisms and is influenced by the soft segment content.³³ In Table 4, T_{onset} and T_{end} represent the temperature at which the degradation of the PU foam starts and ends, $T_{\text{max 1}}$ and $T_{\text{max} 2}$ are the temperature with the maximal thermal degradation rate in stage I and stage II, respectively. With the incorporation of carbonyl iron particles, the T_{onset} and $T_{\text{max 1}}$ increases but the T_{end} and $T_{\text{max 2}}$ nearly do not change. Taking the temperature with the mass loss of 10% as a criterion, it can be seen clearly that the temperature increases from 316 °C to 381 °C for Aniso-80 sample. This is because the carbonyl iron particles restrain the mobility of PU molecular chain which delays the degradation under a nitrogen atmosphere. This is in agreement with the results of the thermal stability of polyurethane/carbonyl iron particles magnetic foam reported by Zhang et al.34



Fig. 10 TGA curves of anisotropic PU MR foam with different iron contents in a nitrogen atmosphere.

Sample	$T_{\text{onset}} (^{\circ}\text{C})$	$T_{\max 1}$ (°C)	$T_{\max 2}$ (°C)	$T_{\rm end}$ (°C)	10 wt% loss $T(^{\circ}C)$	Residue at 600 $^{\circ}$ C (%)
Blank PU	225	289	386	405	316	4.7
Aniso-60	264	317	386	401	362	63.7
Aniso-70	265	321	382	399	370	73.1
Aniso-80	269	319	382	399	381	82.1

Table 4 The thermal decomposition temperature of PU MR foam in a nitrogen atmosphere

4. Conclusions

The isotropic and anisotropic PU MR foam with good MR effect were prepared through in situ polymerization and foaming for the first time. The microstructure and properties of the MR foam were characterized in detail. The carbonyl iron particles can form a chain-like structure in the liquid polyol after orientation under a magnetic field, which can be fixed in solid PU foam after curing and foaming. The anisotropic PU MR foam shows an anisotropic mechanical property. The compressive strength along the orientation direction of the magnetic chain structure of the composite is greatly improved. The maximum compression stress parallel to the magnetic chain direction reaches 1053.5 KPa at 3.9% strain for Aniso-80 sample, which is ~ 878 times that of the blank PU foam and \sim 57 times of that at the vertical direction of the same sample. The MR effect of the PU MR foam can be adjusted by changing the aggregate structure and content of carbonyl iron particles, testing frequency and external magnetic field strength. When the iron content is 80 wt%, the maximum absolute and relative MR effect of anisotropic PU MR foam are 1.07 MPa and 27.1%, respectively. The PU MR foam also can improve the acoustic absorption coefficient at the low frequency region comparing with the blank PU foam. The PU MR foam is a new kind of MR material with magnetic field-controlled modulus function, which can extend the function of vibration and acoustic absorption of PU foam from a passive mode to an active mode.

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