Research of synthesis and properties of polyurethane damping materials with multiple side methyl structures

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Abstract. In this paper, the poly 3,3'-dimethylglutaric acid neopentane diol ester and poly (3,3'-dimethyl glutaric acid 1115 ester) were synthesized. The PU damping material was obtained by preparing prepolymer synthesized with above materials and 2,4-toluene diisocyanate or isophorone diisocyanate, and taking 3,3'-di chlorine-4,4'-diamino double phenyl methane as chain extender. The effects of various soft and hard segments on the mechanical properties and damping capacity of PU damping materials were investigated. The results showed that the tensile strength of the prepared PU damping material is above 15MPa, and the tan δ max reaches more than 0.95. The damping temperature range of tan delta >0.3 is more than 70℃, which is a kind of damping material with excellent comprehensive properties.

1. Introduction

With the rapid development of modern industry, polyurethane (PU) damping materials are not only widely used in vibration and noise reduction technology, but also in aerospace, architecture, bridge, locomotive, ship and other fields[1]. PU is a alternating block copolymer consisting of soft and rigid segments., with the special structure making microphase separation in soft and hard segments, which lead to be the most concerned and the most practical damping materials [2-3]. As a damping material, PU could adjust the degree of microphase separation by changing the structure and proportion of the soft and rigid segments, in order to change the damping temperature and loss factor [4-6]. Based on the group contribution method [7-8], polyester diol with multiple side methyl structures was taking as the soft segment in the prepare of PU in this research, which was synthesized with 3,3'-double methylglututaric acid, NPG, and hydroxydivalerate monoester (1115 ester) with the same carbon side methyl structure. Moreover, the PU damping material was prepared and PU was prepared. The mechanical properties and damping properties are characterized.
2. Experimental

2.1. Materials
The raw materials are as follows: 3,3-Dimethylglutaric acid was supplied by WuHan Jiakailong Technology Development Co., Ltd. Neopentyl glycol was obtained from LG chemical Ltd. Hydroxy pivalate neopentyl glycol monoester were bought from Linzi Organic Chemical Co., Ltd., and Isophorone diisocyanate (IPDI) and 2,4- toluene diisocyanate (TDI-100) were all donated by German Bayer company. 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) was supplied from Suzhou special fine chemical industry Co., Ltd and Titanium (IV) isopropoxide was bought from Zibo Linzi Yitong chemical plant.

2.2. Synthesis of polyester diol with multiple side methyl
The 3,3-Dimethylglutaric acid and partial diol (NPG or 1115 ester) were charged into a round bottom flask equipped with a mechanical stirrer, thermometer, and water separator under nitrogen atmosphere. The mixture was heated at 200 ± 5 °C for 4h after the water was fractionated. Then other partial diol was added into the reaction when the temperature of the system is reduced to 170 °C. Moreover, the system was heated to 200 ± 5 °C for 4h again. In the end, the other diol mixed with catalyst were added. The reaction system was cooling down when acid value of the system falls below 0.7. The system was evacuated for 0.5-1 hours while cooling down to 160 °C. Then poly 3,3'-dimethylglutaric acid neopentane diol ester (JZ-1) and poly (3,3'-dimethyl glutaric acid 1115 ester) (JZ-2) were obtained.

2.3. Preparation of PU damping materials
The polyester diol and fillers were mixed evenly in three round bottomed flask equipped with agitator and thermometer, and the mixture was evaporated at about 120 °C for 3h. The PU prepolymer was obtained by adding diisocyanate (NCO / OH=2:1) into the mixture and keeping the system at 80 °C. The chain extender was heated and melted, and the dry packing and auxiliaries were added to the prepolymer at 80 °C to mix evenly, and then pouring into a ready mold or structural part, vulcanizing at 100 °C for 4h or curing at room temperature for 7 days. Moreover, the polyurethane damping materials were prepared and named as PU-1, PU-2, PU-3, respectively.

2.4. Characterization
The molecular structure of polyurethane was analyzed by Fourier Transform Infrared Spectrometer(FT-IR). Dynamic mechanical properties were recorded on the Dynamic thermo mechanical analyzer(Q-800). The mechanical properties were measured via the microcomputer control electron universal testing machine. And the hardness of polyurethane damping materials were tested on the Shore hardness tester.

3. Results and Discussion

3.1. Characterization of the structure of PU damping material
The infrared spectrum can be used to detect the chemical bonds and functional groups of a substance. Fig.1 shows the IR spectra of PU-1 damping material. As it can be seen, the PU damping material exhibited the ammonia ester (urea) bond - NH at 3353 cm⁻¹. The C-H of symmetric and asymmetric stretching bands at 2889cm⁻¹ and 2967cm⁻¹ respectively. The emergency of the peaks at wavenumbers at 1724cm⁻¹ and 1147cm⁻¹ in the spectrum which attributed to the \(-\text{C}=\text{O}\) and \(-\text{C} \cdots \text{O} - \text{C} \cdots\) stretching vibration bands. What’s more, the 3580 cm⁻¹ and 2270 cm⁻¹ corresponding to the -OH of the telescopic vibration absorption peak of the polyester glycol and -NCO of the telescopic vibration absorption peak of the TDI were disappear. These results suggest that PU damping material was successfully prepared.
Figure 1. FT-IR spectra of the PU-1

3.2. Influence of various soft and hard segment structure on the mechanical properties for PU damping materials

The mechanical properties of PU-1, PU-2 and PU-3 were tested according to the testing method. Table 1 showed the influence of various soft and hard segment structure on the mechanical properties for PU damping materials.

Table 1. The mechanical properties of PU-1, PU-2 and PU-3

| Type of material | Hardness /A | Elongation at break /% | Tensile strength /MPa | Tear strength /kN·m⁻¹ | permanent deformation % |
|------------------|-------------|------------------------|-----------------------|------------------------|-------------------------|
| PU-1             | 72          | 676                    | 27.3                  | 45.8                   | 19.1                    |
| PU-2             | 66          | 779                    | 19.6                  | 40.1                   | 23.2                    |
| PU-3             | 77          | 983                    | 17.5                  | 36.6                   | 25.6                    |

As can be seen, the properties of tensile strength, tear strength and permanent deformation of PU-1 material of TDI system are better than those of PU-2 material of IPDI system while the elongation at break is slightly reduced. This is because the hard segment of TDI take regular structure and the hydrogen bonds are easily formed between macromolecules. Therefore, the hard segment cohesion of this PU damping material is large, the number of physical crosslinking points is increased and the phase separation of the soft and hard segment is serious, so that the hardness, tensile strength and tear strength of the PU material are higher than that of IPDI. It is obvious that the PU-1 is superior to PU-3 in tensile strength, tear strength and permanent deformation. The reason was that the content of the side mmethyl of the PU-3 is higher than that of PU-1, resulting in the distance between molecules increase and the intermolecular force decreases, which makes the tensile strength and tear strength of the PU-3 material lower, while the permanent deformation, the elongation at break, and the shore hardness increase.

3.3. Influence of various soft and hard segment structure on the damping properties for PU damping materials

The loss factor (tan δ) of various soft and hard segment structure of PU damping materials are shown in figure 2. The maximum tan δ of PU-1 and PU-2 were 1.03 and 1.17 corresponding to the temperature was 16.9°C and 20.6°C. The effective damping temperature domain were -11.6~57.4°C.
and -2.5°C~ above 60°C, respectively. It’s obvious that the tan δ and its corresponding temperature of PU-2 was higher than that of PU-1, the reason was that their soft segment structure are different. The soft segment structure of PU-3 was poly (3,3’-dimethyl glutaric acid 1115 ester), while PU-1 was poly 3,3’-dimethylglutaric acid neopentane diol ester. The side methyl content of the former was higher than that of the latter, while the content of the methylene decreases, the internal friction resistance of the motion needs to be increased, the rotation barrier between the methylene is increased and the intermolecular force decreases, resulting in the increase of tan δ and its corresponding temperature.

The maximum of tan δ max of PU-2 prepared by IPDI system was 0.97 corresponding to temperature of 10.1°C and its effective damping temperature domain was -16.4°C~ above 60°C. We can conclude that its effective damping temperature range is wider, and the initial temperature is reduced by 4.7°C comparing with PU-1 material. This is because IPDI is aliphatic isocyanate while TDI is aromatic isocyanate. Thus the hard segment structure of the PU material prepared by IPDI is poor, and some types of chain segments can be moved at lower temperature, so that the hard segments are better dispersed in the soft phase, and the contact area of the soft and hard segments is relatively increased. When the material vibrates, more kinetic energy will be transformed into thermal energy dissipation.

![Figure 2. The loss factor (tanδ) of PU-1, PU-2 and PU-3](image)

4. Conclusion
In this paper, the PU damping materials with multiple side methyl structures containing various soft and hard segments were synthesized successfully. The effects of various soft and hard segments on the mechanical properties and damping capacity of PU damping materials were investigated. The experimental results showed that The tensile strength and tear strength decrease with the increase of the lateral methylation of the soft segment structure, while the permanent deformation and elongation at break increase. The tan δ max and its corresponding temperature increase, and the damping temperature range of tan δ >0.3 is widened. Moreover, The tensile strength, tearing strength and permanent deformation of the TDI system materials are better than those of the IPDI system. The tan delta max of the TDI system material is higher and its corresponding temperature is higher, and the damping temperature range of the IPDI system material tan δ >0.3 is wider.
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