Research on synthesis and properties of room temperature curing polyurethane damping materials

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Abstract. Room temperature curing polyurethane (PU) damping materials were synthesized with PU prepolymer and self-made curing agent. The prepolymer was synthesized from poly (neopentyl adipate) with higher side methyl content and toluene diisocyanate. Effects of molecular weight of poly (neopentyl adipate) and curing agent types on mechanical properties and damping properties of PU damping materials were investigated. Results showed that tensile strength of room temperature curing PU damping materials is 22.4 MPa and the tan δmax reaches 1.10. The damping temperature range of tan δ>0.3 is more than 60℃, which is a kind of damping material with excellent comprehensive properties.

1. Introduction

PU damping material is a block polymer composed of soft and rigid segments alternately. It has become the most practical damping material because of the micro-phase separation of soft and rigid segments. Therefore, it has been widely used in aerospace, construction, bridges, locomotives, ships and other fields [1-5]. Traditionally, PU damping materials are usually mixed at high temperature with double components and then solidified at 100-120 C. Some large injection molding parts, complex shape product and special working conditions with damping properties need to be poured on site. However, the traditionally thermal curing process can’t be adopt because of the lacking of working heating environment and the guarantee of temperature conditions for product ripening. Therefore, room temperature pouring curing process becomes indispensable. In nowadays, room temperature curing PU damping material has become a new research hotspot in polyurethane industry in China [6-7]. In this research, the PU prepolymer was synthesized with poly (neopentyl adipate) with high side methyl content and toluene diisocyanate (TDI). Then the room temperature curing PU damping material was obtained after curing of PU prepolymer and self-made curing agent. What’s more, the mechanical properties and damping properties were also characterized.
2. Experimental

2.1. Materials

The raw materials are as follows: Poly (neopentyl adipate) (POL, molecular weight 1000, 2000, 3000, Qingdao xin yu tian Chemical Co., Ltd.); 2,4- toluene diisocyanate (TDI-100, GermanBayer company); 3, 3’-dichloro-4, 4’-diaminodiphenylmethane (MOCA, Suzhou special fine chemical industry Co., Ltd); 4,4’-bis-sec-butylamino diphenylmethane (MDBA, Wanhua Chemical Group Co., Ltd).

2.2. Characterization

The structure of PU damping material was tested on Fourier Transform Infrared Spectrometer (FT-IR) (5DX-B, American), tested by probe method; The mechanical properties were recorded on microcomputer control electron universal testing machine (CMT7104, China). Shaw hardness according, tensile strength/elongation at break and tear strength (right angle) are according to GB/T531.1-2008, GB/T528-2009, and GB/T529-2008, respectively. Dynamic mechanical properties were measured on Dynamic thermo mechanical analyzer (Q-800, American), and tensile method was adopted, with test frequency of 1Hz and the heating rate of 5℃/min.

2.3. Preparation of PU damping materials

(1) Synthesis of PU prepolymer (Component A)

Poly (neopentyl adipate) (POL) and liquid additives were added into the reactor at a certain mass ratio. The reaction system was heated to 120℃ for 2-3 hours of high vacuum dehydration. Then the TDI was added slowly after temperature reduced to below 60℃. The system was heated at 80±5℃ for 2-3h with vacuum degassing. The component A was obtained after cooling down to room temperature

(2) Preparation of curing agent (Component B)

Polyether and stabilizer were added into the reactor at a certain mass ratio and heated to 110℃ for 2 hours of high vacuum dehydration. Then MOCA was added after the temperature was cooled down to below 80℃. Then system was heated to 95-100℃ again. When MOCA dissolved completely and stirred continuously at high speed for 0.5h. The system was cooling down to room temperature. The MDBA was added for 1h with high speed stirring and 1h with vacuum degassing. Then component B was sealed standby.

Two groups of curing agents (curing agent 1, curing agent 2) were prepared according to the above process. The formulation of the two curing agents is shown in Table 1.

| Table 1. The formulation of curing agents |
|------------------------------------------|
| Curing agent    | Curing agent 1 | Curing agent 2 |
|----------------|---------------|---------------|
| Formulation    |               |               |
| PPG            | 34wt%         | PPG           |
| MOCA           | 33wt%         | MOCA          |
| MDBA           | 33wt%         | Stabilizer    |
| Stabilizer     | certain mass  | certain mass  |

(3) Preparation of PU damping materials

Components A and B were mixed evenly in proportion and poured into the mould. The samples were placed at room temperature for 7 days and properties of the samples were tested.

3. Results and discussion

3.1. FT-IR analysis of PU damping materials
PU damping materials were prepared by curing agent 1 and curing agent 2, respectively. The FT-IR analysis of the molecular structures were shown in Fig.1
As shown in Fig.1, the hydroxyl group in POL has been completely reacted without showing vibrational absorption peak at 3580 cm$^{-1}$. Meanwhile, there is no absorption peak at 2270 cm$^{-1}$ indicating that -NCO group reacts completely. As we know, N-H has two environments in the molecular chain, either forming hydrogen bonds or not. No absorption peak near 3500-3600 cm$^{-1}$ but a weak band at 3330 cm$^{-1}$, indicating the formation of hydrogen bonds formed by N-H bond. The N-H of symmetric and asymmetric stretching bands at 1528 cm$^{-1}$ and 1610 cm$^{-1}$ respectively. The emergency of the peaks at wavenumbers at 1731 cm$^{-1}$ in the spectrum which attributed to the ―C=O stretching vibration peak of amine ester bond.

3.2. Mechanical properties of PU damping materials prepared by different curing agent

PU damping materials were prepared by prepolymer (which was synthesized with POL-2000, TDI and filler) and curing agent 1 or agent 2. The mechanical properties were shown on Table 2.

| Curing agent  | Hardness /A | Tensile strength /MPa | Tear strength /kN·m$^{-1}$ | Elongation at break/% |
|---------------|-------------|------------------------|-----------------------------|----------------------|
| Curing agent 1 | 84          | 22.4                   | 77.6                        | 532                  |
| Curing agent 2 | 79          | 18.9                   | 68.9                        | 612                  |

It can be seen from Table 2, both of PU damping materials prepared by two kind curing agent show excellent mechanical property and tensile strength is over 15 MPa.

However, the tensile strength of PU damping material prepared by curing agent 1 is higher than that of curing agent 2. The reason was that both of curing agents are alcohol-amine mixed type, and the content of diamine in curing agent 1 is higher than that in curing agent 2, which results in different phase separation between hard and soft segments of PU damping material resulting in different mechanical properties.

3.3. Damping properties of PU damping materials prepared by different curing agent

PU damping materials were prepared by prepolymer (which was synthesized with POL-2000, TDI and filler) and curing agent 1 or curing agent 2. The mechanical properties were shown on Fig.2 and Table 3.
Fig. 2 The loss factor (tanδ) of PU damping materials prepared by curing agent 1 or curing agent 2

Table 3. Damping properties of PU damping materials prepared by curing agent 1 or curing agent 2

| Curing agent | tan δ_{max} | Temperature of tan δ_{max} /℃ | damping temperature range of tan δ>0.3 /℃ | Δt /℃ |
|--------------|-------------|-------------------------------|-----------------------------------------|------|
| Curing agent 1 | 1.10        | 22.2                          | 4.7~>80                                 | >60  |
| Curing agent 2 | 1.01        | 17.9                          | 3.7~>80                                 | >60  |

Fig. 2 and Table 3 showed PU damping materials with different curing agent has good damping property. The tan δ_{max} is more than 1, and the damping temperature range of tan δ>0.3 is more than 60℃. The reason why damping properties of PU damping materials prepared by two curing agents are slightly different is mainly due to the different types and contents of diamines in curing agents.

3.4. Mechanical properties of PU damping materials prepared by POL with different molecular weight

PU damping materials were prepared by prepolymer (which was synthesized with POL-1000 (POL-2000, POL-3000), TDI and filler) and curing agent 1. The mechanical properties were shown on Table 4.

Table 4. Mechanical properties of PU damping materials prepared by POL with different molecular weight

| Molecular weight (POL) | Hardness/ A | Tensile strength /MPa | Tear strength /kN·m⁻¹ | Elongation at break /% |
|------------------------|-------------|-----------------------|-----------------------|-----------------------|
| 1000                   | 92          | 33.1                  | 112                   | 444                   |
| 2000                   | 84          | 22.4                  | 77.6                  | 532                   |
| 3000                   | 69          | 12.7                  | 47.6                  | 689                   |

As can be seen from Table 4, With the increasing of the molecular weight of POL, the hardness, tensile strength and tear strength of PU damping materials decrease obviously, while the elongation at break increases obviously. The reason is that the content of soft segment increases with the increasing of molecular weight of POL, while the content of hard segment decreases relatively. The content of amino ester group and urea group in polyurethane macromolecule decreases, and the number of hydrogen bonds decreases, which destroys the aggregation of hard phase. At the same time, side methyl content of main chain increases with the increasing of the molecular of POL, resulting in the decreasing
of intermolecular force. Thus, the mechanical properties of PU damping materials decreases. Therefore, with the increasing of molecular weight of polyester increases, the mechanical properties of PU damping materials decrease.

3.5. Damping properties of PU damping materials prepared by POL with different molecular weight

PU damping materials were prepared by prepolymers (which was synthesized with POL-1000 (POL-2000, POL-3000), TDI and filler) and curing agent 1. The mechanical properties were shown on Fig.3 and Table 5.

![Fig. 3 The loss factor (tanδ) of PU damping materials prepared by POL-1000, POL-2000,POL-3000](image)

**Table. 5 Damping properties of PU damping materials prepared by POL with different molecular weight**

| Molecular weight (POL) | tan δ<sub>max</sub> | Temperature of tan δ<sub>max</sub> /°C | damping temperature range of tanδ>0.3 /°C | Δt /°C |
|------------------------|---------------------|----------------------------------------|------------------------------------------|-------|
| 1000                   | 0.83                | 34.4                                   | 20.1~>80                                 | >60   |
| 2000                   | 1.10                | 22.2                                   | 4.7~>80                                  | >60   |
| 3000                   | 1.19                | 6.5                                    | -7.5~>80                                 | >60   |

It can be seen from Fig. 3 and Table 5 that PU damping materials prepared by POL with different molecular weight all have good damping properties. The tan δ<sub>max</sub> is more than 0.8, and the damping temperature range of tanδ>0.3 is more than 60°C. Value of Tanδ<sub>max</sub> increased significantly with the increasing of molecular weight. The reason is that the content of soft segment increases with the increasing of molecular weight of POL, while the content of hard segment decreases relatively. There are a lot of side methyl and ester groups in the soft segment, which increase the friction between molecules when the segment moves, so the Tanδ<sub>max</sub> value increases with the increase of the molecular weight of polyester.

4. Conclusion

In this research, Room temperature curing PU daming materials were prepared by curing PU prepolymer and self-made curing agent at room Temperature. And the PU prepolymer was synthesized of
polyneopentanediol adipate with higher side methyl content and toluene diisocyanate. Moreover, effects of curing agent on the mechanical properties and damping properties of PU damping materials have been studied. The mechanical properties of PU damping materials prepared by curing agents with higher diamine content and similar curing agent systems are better. Tan δmax and its corresponding temperature is also higher. The effects of different molecular weight soft segments on the mechanical properties and damping properties of PU damping materials were also studied. The mechanical properties of PU damping materials decrease with the increasing of molecular weight of soft segment, while the damping properties increase.

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