Influences of the Ratio of Polyol and MDI on the Acoustic Parameters of Polyurethane

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Abstract. In this paper, the influence of different ratio of polyol and MDI on the absorption coefficient and acoustic parameters of polyurethane was studied. Ratio of 100:40 and 100:45 show the best sound absorption performance, and the change trend of transmission loss and sound absorption coefficient are opposite. The flow resistance increased with the increasing of the ratio of polyol and MDI, the greater the flow resistance, the worse the high frequency sound absorption property of the polyurethane. When the ratio of polyol and MDI keep 100:45, the minimum porosity of sample, the polyurethane porosity increase with the ratio of polyol and MDI increase.

1. Introduction
With the fleeting development of human society and economy, noise is more and more ruinous for human body and mind, which is becoming a worldwide problem. There are many methods to control the noise pollution, but the most radical method is to use sound absorbing materials. Polyurethane, simply called PU, is a general name for the molecular structure of the polymer containing repeated amino acid ester group (-NHCOCO-). PU foam, rubber, coating, adhesive, synthetic fiber, thermoplastic elastomer, biomedical materials and other products can be made in terms of various requirements [1-2], it used extensively in transportation, construction, machinery, electronic equipment, furniture, textile, petrochemical, water conservancy, national defense, medical and other fields [3-9].
In the 1970s and 80s, the modern multifunctional composite materials with PU foam as the main material was developed at domestic and aboard [10]. Such as the shock absorption, sound absorption, sound insulation composite material which developed by German Terson company, the thin and elastic PU film can be used to protect the foam from liquid medium, oil and dust damage, and has good sound absorption property. Japanese Takanisawa Cybernetics company developed a composite material which make the PU foam be the main material, make a double-layer and multilayer composite materials. This material has been used in various occasions such as mechanical shell, vehicle engine cover and sound room. English researchers use flame retardant PU foam to produce sound absorbing prefabricated parts [11], can be cut or molded is the advantage of this PU foam sound absorbing product. Recently, the Navy department of United States used PU foam composite with other materials.
(epoxy resin, silicone gel and carboxyl rubber), successfully developed a new type of noise barrier material, improved the ability of sound barrier 50%-100% than before. A new type 6cm thick composite material can be equal to 25.4mm thick concrete. Besides, this new type of material can be used as a sound barrier in the whole spectrum, especially have a great effect on low frequency noise. As a kind of acoustic material, PU is usually made into porous PU foam, it really have an amazing sound absorption performance, which is a popular new type of acoustic material. Compared with the normal used superfine glass wool, rock wool, slag wool and other fibrous sound-absorbing material, PU has a series of advantages such as light quality, high sound absorption coefficient, easy processing, no dust pollution, waterproof, moisture-proof, wide adaptability[12-16]. Therefore, people pay more attention to the PU acoustic material and its absorbent products, both domestic and foreign development of this new type of sound absorbing material at present. However, the main research is focused on the influence of preparation conditions on the sound absorption performance, and less acoustic characteristic parameters which determine the sound absorption performance. From this point of view, the paper studied the influence of the preparation ratio on the acoustic parameters.

2. Materials and methods

2.1. Material selection
The PU foam was fabricated by one step foaming method using polyether polyol HEP-330N, polymer polyol TPOP-36/28, deionized water, silicone oil, catalysts A33 and A-1, modified MDI (the content of –NCO group is 30%). The physical and chemical properties of polyols are shown in Table 1. The proportion of each material compared with the total mass of polyols (100 fractions in all) is displayed in Table 2. In this experiment, the total mass of raw material was 42g, and the temperature was 55℃, the ratio of polyol to modified MDI was 100:40, 100:45, 100:50, 100:55, 100:60, each experiment was repeated three times to reduce the error.

| Hydroxyl value (mg KOH/g) | Polyol330N | Polyol36/28 |
|---------------------------|------------|-------------|
| acid value (mg KOH/g)     | ≤0.1       | ≤0.05       |
| Humidity (%)              | ≤0.05      | ≤0.05       |
| pH                        | 5.0-7.0    | 6.0-9.0     |
| viscosity (mPa*s/25℃)     | 800-1000   | ≤3500       |
| molecular weight          | 5000       | 4000        |

| Raw material | mass fraction | Component |
|--------------|---------------|-----------|
| Polyol330N   | 60            | Component A |
| Polyol36/28  | 40            |           |
| Deionized water | 2             |           |
| silicone oil (8719) | 1.8          |           |
| A33          | 0.6           |           |
| Two ethanolamine | 0.5           |           |
| A-1          | 0.1           |           |
| Modified MDI | 45            | Component B |

2.2. Preparation method
The specific preparation process of PU foam is described in Figure 1. The mould was kept in baking oven for more than 30 minutes until it reached the designed foaming temperature. The mixture was stirred for 10-15 minutes at high speed of 2000 r/min with a mechanical stirrer. Poured the mixture into the mould rapidly at the cream time and postcured for 5 minutes. For the preparation of PU-RH composites, RH was weighed 2%, 5% and 8% of the total mass of all the raw materials respectively.
and then mixed with A component (all the others raw materials except modified MDI) at room temperature before mixing with B component (modified MDI).

Figure 1. The preparation process of PU foam

2.3. Sound absorption and insulation test
The main methods include standing wave tube method, transmission loss method and reverberation chamber method, in this paper, the transfer function method is used to test the sound absorption coefficient of the material. The test equipment is the SW series impedance tube and four channel acoustic analyzer from Beijing reputation Acoustic Electric Technology Co., Ltd.. Four kinds of acoustic properties was tested, acoustic impedance, sound reflection coefficient, sound absorption coefficient and transmission loss. The equipment(a) used in this test, transmission loss principle(b) and testing principle of sound absorption coefficient (c) was shown in figure 2. The impedance tube diameter is 100mm, the sampling frequency of dSPACE is 51200Hz. A wide random sound wave generated by a loudspeaker at one end of the impedance tube was transmitted to the material surface of the other end.

Figure 2. Impedance tube and its test principle
The transmission loss can be calculated as:

\[
TL = -20 \log\left(\frac{\sin[k(X_1 - X_2)]}{\sin[k(X_3 - X_4)]}\right) \times \frac{P'e^{jk(X_1 - X)} - P'e^{-jk(X_2 - X_3)}}{P_1 - P_2 e^{-jk(X_1 - X_2)}} \times e^{jk(X_1 + X_4)}
\]

The \(X_1, X_2, X_3, X_4\) is the distance between the four microphones and the surface of the test sample respectively. The \(P_1, P_2, P_3, P_4\) are corresponding position of complex sound pressure respectively. \(K\) is the complex wave number, \(Z\) is the acoustic impedance; \(r\) is the sound reflection factor; \(\alpha\) is the sound absorption coefficient; \(TL\) is the transmission loss; \(\rho_0\) and \(c_0\) are the density of air and the speed of sound respectively. The incident sound was perpendicular to the surface of the foam rise direction. Each of the tests was repeated with at least five samples to obtain consistent and representative results, and made at the temperature of \((20 \pm 2)°C\) and relative humidity of \((60 \pm 10)\%\).

2.4. Test of characteristic parameters
Using a set of experimental equipment made by myself to measure the acoustic characteristic parameters of PU. The principle and method are as follows the paper: "a method for testing of the characteristic parameters of porous materials rapidly". The main parameters of the test include flow resistance, porosity, curvature, viscous characteristic constant and thermal characteristic constant.

3. Results and discussion
3.1. Sound absorption properties of different PU
Figure 3 shows the comparison of the sound absorption coefficient of the samples prepared by different ratios of polyol and MDI. From the figure, the ratio of polyol and MDI has a significantly influence on the absorption coefficient of PU. Under the ratio of 100:40 and 100:45, the absorption performance of PU is the best, and the peak value is close to 1. More than 100:50, the sound absorption properties of PU decreased sharply, especially 100:60, the peak value was not more than 0.5. Therefore, the suitable ratio of polyol and MDI is between 100:40-100:50.
3.2. Sound insulation performance of different PU
The contrast of the transmission loss of PU with different polyol and MDI ratio was shown in Figure 4. The figure showed that the change trend of transmission loss and sound absorption coefficient are opposite.

3.3. Acoustic parameters of different PU
(1) Sound velocity test
Test characteristic parameter of polyurethane with different ratio of polyol and MDI. Table 3 shows two methods to test the values of sound speed and air density, it shows two results of sound speed difference is relatively large, in order to make the sound speed test more accurate, ensure the repeatability of the results, use two microphone method to test.

Table 3. The sound speed and air density of PU with different ratios

| Sample     | Air density (g/cm³) | Sound speed (m/s method 1) | Sound speed (m/s method 2) | Sound velocity difference(m/s) |
|------------|---------------------|----------------------------|---------------------------|-------------------------------|
| 100:40     | 1.2100              | 337.0247                   | 344.3000                  | 7.2753                        |
| 100:45     | 1.1944              | 338.9808                   | 345.000                   | 6.0192                        |
| 100:50     | 1.1960              | 338.2439                   | 346.9000                  | 8.6561                        |
| 100:55     | 1.1811              | 340.2290                   | 343.4000                  | 3.171                         |
| 100:60     | 1.1736              | 341.2543                   | 344.6000                  | 3.3457                        |

(2) Sound absorption performance test of self-made equipment
Figure 5 shows the sound absorption coefficient of PU with different ratio of polyol and MDI. Compare with the test results with equipment of BSWA in figure 3, the influence trend is completely consistent, sound absorption are best at ratio of 100:40 and 100:45. The sound absorption properties of PU decreased sharply when the ratio is larger than 100:50. The results show that the self-made equipment is reliable and effective.
(3) Characteristic parameter test

Characteristic parameter of each sample material obtained by MATLAB calculation are shown in table 4, the table showed that the flow resistance increases with the ratio increase, the greater the flow resistance, the worse the high frequency sound absorption property of PU. And low frequency sound absorption performance is better, but the change of the high frequency sound absorption coefficient is larger, that the best flow resistance of PU porous material is about 1000 Pa • s, the porosity is relatively stable, more than 0.9.

| Sample | Flow resistance (rayls/m) | Porosity | Curvature | Viscous shape factor | Thermal shape factor | $M^*$ |
|--------|--------------------------|----------|-----------|----------------------|---------------------|-------|
| 100:40 | 10988                    | 0.9251   | 1         | 0.2992               | 1.7451              | 2.1374|
| 100:45 | 9682.2                   | 0.9106   | 1         | 0.3018               | 2.0122              | 1.0007|
| 100:50 | 18097                    | 0.9413   | 1.4       | 0.2455               | 2.7639              | 1.0024|
| 100:55 | 39446                    | 0.9843   | 1.1       | 0.3959               | 1.9234              | 1.0002|
| 100:60 | 45279                    | 0.99613  | 1.5       | 0.3428               | 2.3921              | 1.0013|

The measured flow resistance and porosity of the samples are shown in Figure 6, the change of flow resistance with the ratio of polyol and MDI in the first decreased and then increased. Minimum sample flow resistance when the ratio of polyol and MDI keep 100:45, and then with the increasing of proportion, the flow resistance of the samples showed an upward trend. The trend of porosity is the same as flow resistance, minimum porosity of sample when The ratio of polyol and MDI keep 100:45, minimum porosity of sample, and then the proportion increased, PU porosity increasing. The increase of porosity is due to the reaction of polyol and MDI more completely, create more small and dense holes.

![Figure 6](image)

Figure 6. The effect of the ratio of polyol and MDI on the flow resistance (a) and porosity (b) of PU

(4) Comparison of predicted and experimental values

In condition of 30mm of back cavity, predict the sound absorption coefficient of samples with different ratios of polyol and MDI, compare with the obtain values and the test values, the results are shown in Figure 7, the predicted values are in almost same with the experimental values in addition to 100:55, especially in the middle and high frequency of 500Hz, maximum less than 5%. For the 100:55 samples, the predictive value and the test value have a large difference, some frequencies node even reach 16%. This is due to an excess of isocyanate, the formation of the foam inner hole is different from the ideal, make the test curve of the sound absorption coefficient is not smooth enough, and predict use the Johnson-Allard model and Lafarge-Allard model will derive a huge error.
Figure 7. Comparison of the predicted and experimental values of the sound absorption coefficient of PU with different ratios

4. Conclusion
The study prepared kinds of PU with different ratio of polyol and MDI, tested the effect of the ratio on sound absorption and acoustic characteristic parameters of PU foam. Compare of the test results, although the impedance tube cross-section is different, the sound absorption coefficient curve of the same sample is different, but the proportion of polyol and MDI on sound absorption properties of PU trend is completely consistent. The proportion of polyol and MDI had significant influence on the sound absorption performance of PU. Analyze the effects of ratio of polyol and MDI of the flow resistance and porosity of PU foam, the characteristic parameters were obtained through Johnson-Allard model and Lafarge-Allard model, the sound absorption coefficient of the sample backed with 30mm cavity is compared with the test values, except for a few samples, the predicted values are highly consistent with the test values, especially in the middle and high frequency of 500Hz.

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