Study on all water foaming of rigid polyurethane foam and design of high-performance formula

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Abstract. The foaming properties of polyurethane rigid foam were studied by using different hydroxyl value, functionality, viscosity of polyether polyols, polyisocyanates, water, catalyst, foam stabilizer and crosslinking agent as raw materials. The microstructure and macroscopic morphology of the foams were analyzed by scanning electron microscope (SEM), which provided the basis for the selection and optimization of the composition of the raw materials for the preparation of polyurethane rigid foam. The effects of polyether polyols, catalysts, water, isocyanate index, foam stabilizer and other factors on the properties of polyurethane foam plastics were emphatically analyzed. Based on this, a high-performance all water foaming rigid polyurethane foam formula was determined.

1. Introduction
The rigid polyurethane foam (RPUF) is abbreviated as rigid polyurethane foam. It is a structural material with excellent thermal insulation properties. Polyurethane rigid foam has the characteristics of light weight, high specific strength, stable mechanical properties, strong adhesion with other media. And polyurethane products have various properties and form because of its varied formula combination and the diversity of raw material structure. Therefore, it has been rapid development and is widely used in various fields of the national economy. At the same time, its consumption is in a leading position in the global synthetic materials, and it has become one of the important materials in the industry [1-3].

All water foaming rigid polyurethane foam is a kind of rigid polyurethane foam which is chemically reacted with water by using water as the sole foaming agent. In the traditional sense, many scholars only use water-soluble polyether or the polyether used in the research and preparation of all water foaming rigid polyurethane has high viscosity. Therefore, there are these problems: The diffusion rate of carbon dioxide is 10 times faster than that of air at fixed temperature, resulting in insufficient foam strength. The large amount of reaction heat can easily cause heartburn, resulting in reduced strength. There is no dilution of physical foaming agent in the foaming process, resulting in poor foam fluidity. The uncertainty of formulation causes the foam density to be inconsistent with expectations and does not meet the needs of real life. Therefore, it is urgent to design a complete water foaming rigid polyurethane foam formulation. Under the premise of solving these problems and saving cost, various performance indexes of polyurethane foam can be optimized.
Based on the above background, this article uses polyethers with different viscosities, functionalities, and hydroxyl values as the main materials. Through controlling the variable method, the amount and ratio of other additives such as catalysts and foam stabilizers are optimized. In addition, the scanning electron microscope (SEM) was used to observe and analyze the mesh structure of the rigid foam; The effects of the type and amount of each raw material on rigid foam properties including apparent density, compressive strength, milky time, gel time, and non-stick time were systematically analyzed. Based on this, a formula of high-performance all water foaming polyurethane rigid foam with a density of 35.1 g/cm³ was determined to prepare a rigid polyurethane foam.

2. Raw material research and preparation methods
Polyurethane rigid foam is prepared by reacting polyether polyol and polyisocyanate under the action of auxiliary agents such as foaming agent, catalyst and foam stabilizer. The raw material system is slightly different from other polyurethane products such as soft foam. Most of them use high functionality polyether polyols and polyisocyanates, and the reaction process is very complicated[4].

2.1 Raw material composition
The main raw materials used in the experiment are shown in Table 1, Table 2 and Table 3.

Table 1. Polyether polyols

| Name   | Hydroxyl value (mg KOH/g) | Density (g/cm³) | Viscosity (mPa·s) | Degree of functionality | Manufacturer |
|--------|---------------------------|-----------------|------------------|------------------------|--------------|
| 4110B  | 430±30                    | 1.081           | ±4500±500        | 4.2                    | Hebei Yadong Group |
| 635B   | 500±25                    | 1.080           | ±3000±500        | 4.5                    | Hebei Yadong Group |
| YD-630 | 350±50                    | 1.080           | ±1020            | 3.2                    | Hebei Yadong Group |

Table 2. Polysisocyanates

| Name   | Exterior   | Density (g/cm³) | Viscosity (mPa·s) | Degree of functionality | Manufacturer |
|--------|------------|-----------------|------------------|------------------------|--------------|
| PM-200 | Brown liquid | 1.23±0.2       | 100-300           | 2.7                    | Wanhua Chemical Group Co., Ltd. |

Table 3. Other auxiliary materials and effects

| Name                             | Function                                       | Manufacturer                     |
|----------------------------------|------------------------------------------------|----------------------------------|
| PC-8, PC-46 catalyst             | Catalytic gel and foaming                      | Ruiao Additive Co., Ltd.        |
| B-3635, B-3612 foam stabilizer   | Stabilize the foam and adjust the cell nucleation effect | Zhongshan Dongjun Chemical Co., Ltd. |
| Sucrose crosslinker              | Change physical and chemical cross-linking structure | Suzhou Weiwei Chemical Co., Ltd. |
| Water                            | Chemical foaming agent                         | -                               |

Table 4. Main equipment

| Name                             | Specification | Manufacturer                                |
|----------------------------------|---------------|--------------------------------------------|
| Electronic balance              | TP-A200       | Shanghai Tingheng Weighing Apparatus Co., Ltd |
| Scanning electron microscope     | Quattro S     | American Thermo Fisher Scientific          |
| Compression test machine         | ZQ-990A-1     | Dongguan Zhizhi Precision Instrument Co., Ltd. |
| Single phase series motor        | U400/80-220   | Shanghai Beiwei Motor Co., Ltd.             |

2.3 Experimental procedures and steps
At present, most of the rigid polyurethane foams are prepared by a one-step process[5-6]. The process is as follows: Mix polyether polyol with catalyst, foam stabilizer, cross-linking agent, and foaming agent according to the formula and mix well. Put it in container as A material, and then pour isocyanate as B material quickly. Use single-phase series excitation. The motor stirs the mixture thoroughly (stirring speed is 2500 r / min) and then allows it to foam freely. The polyurethane rigid
foam is prepared in three stages of a foaming reaction (a reaction of the raw material to emit carbon dioxide), a gel reaction (forming a meridian meridian and a bubble wall), a curing reaction (a foam rise stop and a skeleton solidification). The experimental flow chart is shown in Figure 1. below:

![Figure 1. One step experiment flow chart](image)

3. Performance test

3.1 Apparent density measurement

Apparent density refers to the specific apparent density of material and the apparent volume. It represents the volume of the material bulk. According to the test standard and experience[7] of standard determination of apparent density of foam plastics and rubber, foam is made in the mould vessel of dimension $300\text{mm}\times300\text{mm}\times200\text{mm}$. After 10 minutes, the prepared all water foaming polyurethane rigid foam is treated by epidermis. Cut it into a test block size of $50\text{mm}\times50\text{mm}\times30\text{mm}$, then put it on the precision balance to weigh its mass ($m$), then add some water into the beaker and use the drainage method to get its volume of $v$. Make five samples and measure the density of each sample according to the above method, and get the average value. That is the apparent density $\rho$. The calculation formula of apparent density is as follows:

$$\rho = \frac{m}{v} \quad (1)$$

Where $\rho$ is the apparent density, g/cm$^3$; $m$ is the mass of the sample, g; $v$ is the volume of the sample, cm$^3$.

3.2 Time determination

Determination of starting time, gel time and nonstick time is an important index to measure foaming performance. The recording method is as follows: When a single-phase series motor starts mixing the mixture, the time is recorded synchronously with a stopwatch. When the mixture begins to expand the time $T_1$ is recorded as the time of initiation. The foam continued to expand and the volume increased. When the filament could be detected in the mixed material the time $T_2$ is recorded as the gel time. When the foam expands to the foam surface and touches the non-stick hand lightly the time $T_3$ is recorded as the non-stick time[8].

3.3 Compression performance and strength test

According to GB/T8813-2008 determination of compression performance of rigid foam plastics national standard [7], the samples were made and placed for strength test after 3 days. First, the foam surface is peeled and then processed into a size of $40\text{mm}\times40\text{mm}\times160\text{mm}$. The test block is placed in the middle of the two parallel plates of the compression machine and compressed at a rate of 10% of the original height of the sample per minute. When the sample is compressed to 85% of the original height, the compression stress is recorded when the relative shape variable is 10%. Each sample shall be tested at least 5 times and the average value shall be obtained.

$$\sigma_m = \frac{F}{A} \times 10^{-3} \quad (2)$$

Where $\sigma_m$ is the compressive strength, KPa; $F$ is the compression force when the relative shape variable is 10%, N; $A$ is the cross-sectional area of the sample, $mm^2$. 
4. Formula selection and influence of various factors on rigid polyurethane foam

4.1 Analysis of the influence of single and compound polyether polyols on the mechanical properties of rigid foam

The control variable method was used to set up a control group to study the effect of different polyether polyol ratios on rigid foam performance. The specific ratio is shown in Table 5 below:

| Compound ratio (4110B/635B/YD-630) | Mass (g) | Compressive strength (KPa) |
|-------------------------------------|----------|---------------------------|
| 1: 0: 0                             | 100      | 214                       |
| 0: 1: 0                             | 100      | 211                       |
| 0: 0: 1                             | 100      | 177                       |
| 0.5: 0.5: 0                         | 100      | 212                       |
| 0.4: 0.6: 0                         | 100      | 211                       |
| 0.3: 0.7: 0                         | 100      | 211                       |
| 0.7: 0.3: 0                         | 100      | 213                       |
| 0.6: 0.4: 0                         | 100      | 212                       |
| 0.5: 0: 0.5                         | 100      | 196                       |
| 0.4: 0: 0.6                         | 100      | 188                       |
| 0.3: 0: 0.7                         | 100      | 185                       |
| 0.6: 0: 0.4                         | 100      | 198                       |
| 0.7: 0: 0.3                         | 100      | 203                       |
| 0: 0.5: 0.5                         | 100      | 195                       |
| 0: 0.4: 0.6                         | 100      | 189                       |
| 0: 0.3: 0.7                         | 100      | 186                       |
| 0: 0.7: 0.3                         | 100      | 204                       |
| 0: 0.6: 0.4                         | 100      | 199                       |
| 0.45: 0.45: 0.1                     | 100      | 205                       |
| 0.4: 0.4: 0.2                       | 100      | 204                       |
| 0.35: 0.35: 0.3                     | 100      | 203                       |
| 0.3: 0.3: 0.4                       | 100      | 200                       |
| 0.25: 0.25: 0.5                     | 100      | 196                       |
| 0.2: 0.2: 0.6                       | 100      | 190                       |
| 0.15: 0.15: 0.7                     | 100      | 187                       |
| 0.1: 0.1: 0.8                       | 100      | 180                       |
| 0.05: 0.05: 0.9                     | 100      | 178                       |

All water foaming polyurethane uses only a single-ether polyether. Although the obtained polyurethane has relatively good fluidity, it has greater brittleness and lower strength. Only with high hydroxyl value and high official energy polyether foaming, although the foam strength is higher, its fluidity and viscosity are too high to be conducive to practical application. Therefore, in practical production, it is necessary to mix 4110B and other high hydroxyl value and high official energy polyether with low hydroxyl value and low viscosity polyether to adjust the foam brittleness and fluidity, so as to realize high fluidity and high stability while improving fluidity. The influence of different proportion of polyether polyols on the compressive strength is shown in Figure 2. The compressive strength of rigid polyurethane foam increased with the increase of high hydroxyl value and high functional polyether 4110B and 635B. The high functionality of 4110B and 635B leads to the formation of cross-linked network structure in rigid polyurethane foam, while the low functionality of YD-630 leads to the formation of linear structure. When the two polyether of 4110B and 635B were 30% and YD-630 polyether content was about 40%, the foam showed good fluidity and viscosity. And when the YD-630 polyether content exceeded 40%, the foam compressive strength value tended to be
stable. To obtain polyurethane rigid foam with good fluidity, viscosity and high strength, the ratio of 4110B, 635B and YD-630 is 0.3:0.3:0.4.

![Figure 2](image)

**Figure 2.** Effect of different polyether polyol ratios on the properties of rigid foam

4.2 Analysis of the influence of the amount of catalyst on the performance of rigid foam

The influence of catalyst PC-8 and PC-46 on the reaction time of rigid polyurethane foam was also analyzed and observed by using the control variable method. The details are shown in Table 6 and Table 7 below.

| Catalyzer | Mass (g) | T₁(s) | T₂(s) | T₃(s) |
|-----------|----------|-------|-------|-------|
| PC-8      | 0.6      | 15    | 70    | 110   |
| PC-8      | 0.7      | 14    | 62    | 105   |
| PC-8      | 0.8      | 13    | 53    | 94    |
| PC-8      | 0.9      | 12    | 52    | 90    |
| PC-8      | 1.0      | 12    | 51    | 92    |

| Catalyzer | Mass (g) | T₁(s) | T₂(s) | T₃(s) |
|-----------|----------|-------|-------|-------|
| PC-46     | 0.1      | 15    | 55    | 128   |
| PC-46     | 0.2      | 14    | 54    | 115   |
| PC-46     | 0.3      | 13    | 53    | 90    |
| PC-46     | 0.4      | 12    | 52    | 88    |
| PC-46     | 0.5      | 12    | 52    | 87    |
As a medium active amine catalyst with low viscosity, PC-8 can promote the reaction between isocyanate and water, improve the generation rate of carbon dioxide, shorten the gel time and improve the reaction rate. Without PC-8, although it can also foam, the slow release rate of carbon dioxide will lead to larger bubbles and brittle foam without strength. With the addition of catalyst PC-8, the reaction rate accelerated and the gel time shortened. However, when PC-8 exceeded a certain amount, the gel time was basically unaffected, and even stopped at the height of foaming, so it was not conducive to actual engineering production. As shown in Figure 3(a), in this formulation system, when the dosage of PC-8 is less than 0.8 g, the gel time decreases with the increase of its dosage and decreases from 70 s to 53 s. However, when the dosage of PC-8 exceeds 0.8 g, the gel time is basically not affected by its dosage, so the amount of PC-8 is best at 0.8 g.

At the same time, as the most commonly used trimerization catalyst, PC-46 can promote the hydroxyl end reaction between isocyanate group and polyol, promote the growth of molecular chain, greatly shorten the nonstick time. Therefore, it plays an important role in the actual foaming production. But without PC-46, the gel reaction rate is much lower than that of the foaming reaction, and the foam will not be foamed, so it will not form a complete body structure. When the dosage of PC-46 is too much, the reaction time is basically not affected and the fluidity of foam forming is poor. The bubble becomes larger and the foam becomes brittle and soft[9]. As shown in Figure 3(b), when the amount of PC-46 is less than 0.3 g, with the increase of the amount of PC-46, the cell becomes smaller and the non-stick time decreases continuously (from 128 s to 90 s); when the amount of PC-46 exceeds 0.3 g, the nonstick time is stable at about 90 s. So, in this foaming system the amount of PC-46 is about 0.3 g.

4.3 Influence of foam stabilizer dosage on properties of rigid foam

The mechanical properties of rigid polyurethane foam are determined by the pore structure and dense form[10]. The addition of foam stabilizer silicone oil not only plays a role in stabilizing foam, but also improves the compatibility of components, such as the solubility of composite materials, the solubility of black and white materials and the thickness of foams. There are many kinds of silicone oil in the market. The selected silicone oil in this system is H-3635 and H-3612, among which H-3635 has better nucleation and H-3612 has better emulsification. In the experiment of formula design, in order to give full play to the best performance of silicone oil, they are often mixed in equal proportion. The specific amount of silicone oil in this system and the pore structure of polyurethane rigid foam are shown in Table 8 below:
### Table 8. Influence of foam stabilizer dosage on properties of rigid foam

| Foam stabilizer | Mass (g) | Foam stabilizer | Mass (g) | Density (g/cm³) | Bubble structure shape                          |
|-----------------|---------|-----------------|---------|----------------|-----------------------------------------------|
| H-3635          | 0.8     | H-3612          | 0.8     | 32.8           | Irregular blister with large pore size         |
| H-3635          | 0.9     | H-3612          | 0.9     | 33.7           | Regular blister, slightly larger pore size     |
| H-3635          | 1.0     | H-3612          | 1.0     | 34.9           | The bubbles are regular and uniform without shrinkage |
| H-3635          | 1.1     | H-3612          | 1.1     | 35.5           | The bubbles are regular, with small aperture and opening |
| H-3635          | 1.2     | H-3612          | 1.2     | 36.1           | The bubbles are irregular, uneven and retracted |

When two kinds of silicone oil are added into the foam, the bubbles are crispy. With the increase of the amount of silicone oil, there will be the phenomenon that the bubble hole will change from large to small and the bubbles are dense and uniform. However, when the silicone oil is added too much, the whole foam becomes brittle and there is shrinkage phenomenon. In order to observe more directly the effect of foam stabilizer type and dosage on the cell structure, the polyurethane rigid foam prepared under different conditions was characterized by SEM. The structure is shown in Figure 4. The characterization results showed that different dosage of foam stabilizer had different effects on the morphology of foams. The amount of foam stabilizer in (a), (b), (c), (d), and (e) 5 diagrams gradually increased, and the cell morphology showed a relative change from irregular to irregular and irregular. As shown in Figure 4(c), the cell morphology is relatively regular. At this time, the dosage of silicone oil H-3635 and H-3612 is about 1.0 g respectively, and the total dosage is about 2.0 g.

![Figure 4. Influence of foam stabilizer dosage on hard bubble morphology](image)

**4.4 Analysis of the influence of isocyanate index and the amount of water on the properties of rigid foam**

**Table 9. Analysis of the influence of isocyanate index and water consumption on the properties of rigid foam**

| Polyether polyol (g) | Water (g) | Isocyanate index | PM-200 (g) | Density (g/cm³) |
|----------------------|-----------|------------------|------------|-----------------|
| 100                  | 4.1       | 1.4              | 140        | 36.8            |
| 100                  | 4.1       | 1.5              | 150        | 37.3            |
| 100                  | 4.1       | 1.6              | 160        | 38.7            |
| 100                  | 4.2       | 1.4              | 140        | 35.7            |
| 100                  | 4.2       | 1.5              | 150        | 36.1            |
Under the condition of a certain amount of polyether, the addition of PM-200 and water will cause the change of isocyanate index and the polyisocyanate PM-200 contains more rigid structures, which are helpful to the stability of foam size and the improvement of compressive strength. In the actual production of polyurethane foam, it is necessary to control the amount of water used to prepare foam with different density. As shown in Figure 5 below, with the increase of water volume, the density of hard foam gradually decreases, so it is necessary to strictly control the water volume. When the density is constant, the increase of water will increase the reaction process of isocyanate, which will increase the foam strength. At the same time, the reaction is exothermic and the intensification of reaction process will lead to the increase of the temperature of the system. Therefore, the protective measures should be taken in the test.

Water is the only foaming agent in this reaction system. It replaces the former 245fa, 141b, NP and other physical foaming agents. It has the advantages of low price, easy access, non-toxic and harmless to the environment. In the foaming process, if the amount of water is less, the carbon dioxide produced after the reaction will be less, so the foaming ratio is lower. As the amount of water increases, the carbon dioxide produced by the reaction increases correspondingly and the pore size of the cell becomes smaller and smaller. The density of the foam decreases and its hardness becomes smaller and smaller with the increase of water volume, and the foam is hard and brittle. Therefore, on the premise of meeting the requirements of hardness and density, it is very important to choose the amount of water to prepare the rigid polyurethane foam with small pore size and uniform density.

The isocyanate index of the all water foaming system is higher than that of the general PIR foaming system. It is generally controlled about 1.5. Too much or too little will affect the density, stability and strength of the foam. In the whole water foaming system, increasing the crosslinking density can improve the isocyanate index. It can be seen from the test (Figure 5, Table 9) that in this system to gain the polyurethane foam with a density of about 35.1 g/cm³, the amount of water should be controlled at about 4.3 g, and the amount of PM-200 should be controlled at about 150 g.

![Graph showing the effect of different amount of water and isocyanate index on the density of rigid foam](image)

Figure 5. Effect of different amount of water and isocyanate index on the density of rigid foam.
Based on the above results, the optimized formula design of the high-performance polyurethane is shown in Table 10. It has the advantages of reasonable diffusion speed, high strength, low viscosity and good fluidity.

| Material name                        | Mass of polyols per 100 parts (g) |
|--------------------------------------|-----------------------------------|
| 4110B polyether polyol               | 30                                |
| 635B polyether polyol                | 30                                |
| YD-630 all water polyether           | 40                                |
| PC-8                                 | 0.8                               |
| PC-46                                | 0.3                               |
| H-3635                               | 1.0                               |
| H-3612                               | 1.0                               |
| Water                                | 4.3                               |
| Cross linking agent sucrose          | 4                                 |
| PM-200                               | 150                               |

5. Conclusion
In conclusion, the preparation of polyurethane rigid plastic foam requires the formulation design and optimization improvement based on the performance requirements. In this paper, the following conclusions are obtained through systematic formula design and analysis:

1. The use of a single polyether to prepare water blown polyurethane rigid plastic foam regulating foam has poor effect on brittleness and fluidity. It requires high hydroxyl value and high official energy polyether with low hydroxyl value and low viscosity polyether.

2. The combination of PC-8 and PC-46 two types of catalysts can effectively shorten the gel and non-stick time, and significantly improve the foaming rate. The combination of B-3635 and B-3612 two foam stabilizers make the foams more uniform and stable.

3. In this paper, a design formula of polyurethane rigid plastics with a density of 35.1g/cm³ was determined. Within the allowable range of error, this formula has the advantages of reasonable diffusion speed, high strength, small viscosity, good fluidity, low cost.

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