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Study on the Properties of Flame Retardant Rigid Polyurethane Foam Materials

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Abstract: ***Flame-retardant rigid polyurethane foam was prepared using a one-step method of all-water foaming in this paper. Following an experimental investigation, the optimum water consumption was determined to be 1.4 g, the optimum addition of tin laurate catalyst was found to be 1 g, and the optimum value of isocyanate index was identified to be 1.1. The rigid polyurethane foam, which had been compounded with MEG, exhibited an oxygen index of 31% at a concentration of 25 wt% and a carbon residue of 34.9% at 570°C. In contrast, the rigid polyurethane foam compounded with MEG' exhibited a residual carbon of 39.3% at 570°C. Both methods demonstrated a notable enhancement in flame retardancy, although this was accompanied by a certain degree of reduction in compression properties. In comparison to the aforementioned methods, the rigid polyurethane foam compounded with MEG' has a less pronounced reduction in compression performance and a superior flame retardant effect.***

Keywords: Rigid polyurethane foam, Expandable graphite, Flame-retardant properties.

1. Introduction

Based on the production and value of the global polyurethane market from 2017-2020, it is clear that the global demand for polyurethane (PU) is growing every year. In 2012, China has become the number one consumer market of polyurethane in the world [1]. Among them, polyurethane foam (PUF) accounts for about 53% of the total product content of the polyurethane market. Rigid polyurethane foam is widely used in construction, automotive and industrial equipment industries because of its high specific strength, good chemical resistance, light weight, and good adhesion to steel, aluminium, stainless steel, and most plastic materials. For these reasons, rigid polyurethane foam accounts for another 26% of the polyurethane foam market, and among the current end-use industries, the construction and automotive industries have the highest demand for rigid polyurethane foam, accounting for about 45% of the global demand. This shows that the construction and automotive industries are expected to be the long-term growth drivers of the polyurethane market [2].

Flame retardant properties have long been an important technical indicator of whether rigid polyurethane foam can be applied, and many countries have enacted a series of laws and regulations on flame retardant properties in their building legislatures [3]. The utilisation of flame retardants can effectively enhance the flame retardant properties of rigid polyurethane foam. However, the flame retardant mechanism of different types of flame retardants varies. Regardless of the specific type of flame retardant, it is essential to ensure that it fulfils one or more of the following functions: In the context of polyurethane foam, the ignition temperature is the point at which the foam begins to burn. At this temperature, the foam undergoes a process of heat absorption, whereby it transforms into substances that are no longer combustible. Alternatively, the foam may react with combustion products to generate substances that are also non-combustible. In some cases, the foam may also undergo a chemical reaction with substances that can terminate the oxidation reaction of the foam. Ultimately, the objective of using flame retardants in polyurethane foam is to achieve the aforementioned processes, which result in the foam becoming flame retardant. For example, Bo Xianming et al. [5] developed a halogen-free composite solid flame retardant TU-1, which is based on red phosphorus as the core and has a coordinated role of other flame retardants. This enables the oxygen index to reach 26.4%, thus achieving UL94 V-0 flame retardant grade. Liu Xingyun and colleagues employed a polyol component comprising 70 parts of sucrose polyether and 30 parts of N, N-dihydroxyethyl aminomethyl diethylphosphonate, without the addition of a flame retardant. This resulted in the production of a rigid polyurethane foam with a self-extinguishing property upon exposure to fire, exhibiting a density of 28 kg/m^3. Bian Chengxiang and colleagues investigated the potential of expandable graphite (EG) to enhance the flame retardant properties of rigid polyurethane foam (RPUF). They prepared EG/RPUF composites with a density of 0.46 g/cm^3 and observed that EG could effectively improve the flame retardant properties of high-density RPUF. At an EG content of 20 wt%, the oxygen index of the composites reached 39.5 vol%, while the mechanical properties of the materials were found to be reduced.

Using water as blowing agent and EG as flame retardant, the one-step preparation method of all-water foaming is a highly efficient, halogen-free, green and low-cost method of preparing flame-retardant rigid polyurethane foam. However, while all-water foaming and EG as a flame retardant do significantly improve the flame retardant properties of rigid polyurethane, there are still many problems in the foam preparation process, such as poor dimensional stability and reduced mechanical properties. In order to further understand the causes of each problem, it is the significance of this research to reduce the negative effects on other aspects such as mechanical properties while retaining the good flame retardant properties of flame retardant rigid polyurethane foams by modifying and compounding EG.

2. Experimental section

2.1 Material

Table 1: Raw materials and their main performance parameters

Raw material name	*Company*
Polyether polyols	Guangzhou Qihua Chemical Co.
Diphenylmethane Diisocyanate (MDI)	Guangzhou Qihua Chemical Co.
Dibutyltin dilaurate	Shanghai McLean Biochemical Technology Co.
Triethanolamine	Tianjin Zhonglian Chemical Reagent Co.
Deionised water	Laboratory self-made
Silicone oil	Tianjin Yongda Chemical Reagent Co.
Expandable Graphite (EG)	Shijiazhuang Kepeng Flame Retardant Material Factory
Silicon boron modified graphite (MEG)	Manufactured in the laboratory
Ammonium polyphosphate (APP)	Shanghai Ron Reagent
Aluminium hydroxide (ATH)	Fuchen Chemical Reagent Company
Ammonium Polyphosphate (APP) and Aluminium Hydroxide (ATH) Compound EG (MEG')	Laboratory self-made

2.2 Experimental Step

2.2.1 Preparation of MEG

Configure the ethanol solution with a mass concentration of 90%, add the appropriate amount of EG and silane coupling agent, stir with an electric mixer at 270 r/min for 2 h, then add the appropriate amount of boric acid, and stir the reaction with the same rotational speed at room temperature for 1.0 h. When the stirring is completed, filter and put into the drying oven at 85 ℃ for 7 h, and then the MEG was produced.

2.2.2 Preparation of flame retardant rigid polyurethane foam

Add 2g of dibutyl tin dilaurate, 1g of silicone oil, 1.4g of deionised water, 0.6g of triethanolamine to 54.39g of polyether polyol, then stir with an electric stirrer at 1000r/min for 3min, and then add an appropriate amount of MEG' (APP & ATH compounded EG) according to the needs of different control groups and continue stirring for 3min. The combined polyether was made. Then 60g of MDI was added to the combined polyether and stirred with an electric stirrer at 1000r/min for 20s, then quickly cast into the mould with a mould cover, and then put it into an oven at a constant temperature of 100°C for 4 hours of curing. Finally, the samples were taken out by opening the mould, removing the skin of the samples, cutting them according to the standard and keeping them sealed.

In this experiment, in order to observe the effect of different MEG content on the performance of flame retardant rigid polyurethane, the addition of MEG will be prepared in multiple experiments with a variety of samples at 0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt% and 25 wt%. Then MEG is replaced by MEG' (APP & ATH compounded EG), and control experiments are conducted with the same addition amount and procedure.

2.3 Sample Tests

The sample is cut into 30mm*30mm*20mm square, and then compressed by CMT6104 microcomputer-controlled electronic universal testing machine at a rate of 10% deformation of the radial thickness of the specimen per minute until the thickness of the specimen becomes 85% of the original thickness, and then the compression performance of the sample is characterised. According to GB/T2406 standard using JF-3 type oxygen index meter to test the limiting oxygen index (LOI), the sample size of 80mm * 10mm * 10mm. using TGA-50 type thermal gravimetric analyser for thermal performance testing, powder samples 2-5mg, the heating rate of 20°C / min, the starting temperature for the room temperature, the termination temperature of 570 ℃, with reference to the GB/T27761-2011 standard. T27761-2011 standard.

3. Analysis of Results and Discussion

3.1 Effect of Water Consumption on the Properties of Rigid Polyurethane Foam

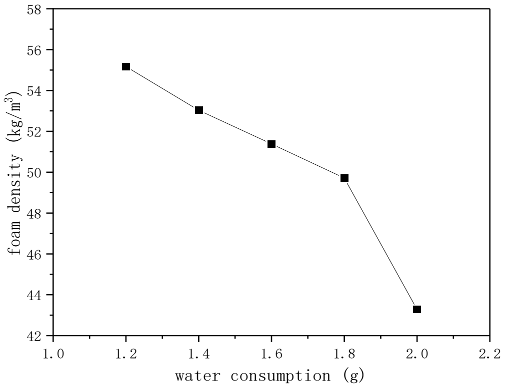


Figure 1: Effect of water consumption on the density of polyurethane foam

As can be seen from Figure 1, with the increase of water consumption, the density curve of polyurethane foam shows a decreasing trend, i.e., the density of foam decreases with the increase of water consumption, especially after the water consumption reaches 1.8g, the decrease is more significant. This is due to the participation of water as a blowing agent in the synthesis of polyurethane foam, water and MDI reaction to generate urethane, urethane is easy to decompose CO_2 gas, and the increase in water consumption leads to an increase in the generation of CO_2 gas, the foam volume expansion, the density of the foam decreased.

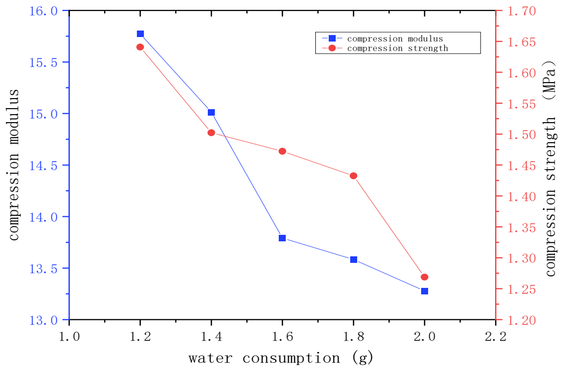


Figure 2: Effect of water consumption on compression strength and compression modulus of polyurethane foam

As can be seen from Figure 2, the overall trend of the polyurethane foam compression strength and compression modulus curves is decreasing. Then the strength and modulus of polyurethane foam decrease with the increase of water consumption. The reason is that the increase of water consumption leads to the increase of CO_2 gas produced by the reaction between water and MDI, the foam volume expands, the density decreases, the density of the bubble holes becomes smaller, and the walls of the bubble holes become thinner, which ultimately leads to the decrease of the compression strength and compression modulus of rigid polyurethane foam.

3.2 Effect of Isocyanate Index on the Properties of Rigid Polyurethane Foam

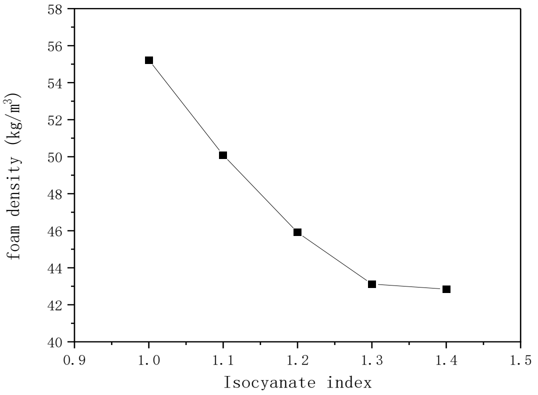


Figure 3: Effect of isocyanate index on the density of polyurethane foam

According to Figure 3, the density curve of polyurethane foam shows a decreasing trend until the isocyanate index reaches 1.2, and the decreasing amplitude basically remains unchanged. That is, the density of rigid polyurethane foam decreases with the rise of isocyanate index. most of the isocyanate groups of MDI react with the hydroxyl group in the polyether polyol, and a small number of reaction with water, due to the isocyanate index is too small, the amount of isocyanate groups reacting with water is less, the foaming expansion rate is small, and the foam has a higher density. When the isocyanate index is too large, the amount of isocyanate groups reacting with water is more, the foam expansion rate is larger, and the density of the foam decreases, but after the isocyanate index reaches 1.2, the density of MDI remains unchanged because MDI itself contains a rigid aromatic ring structure.

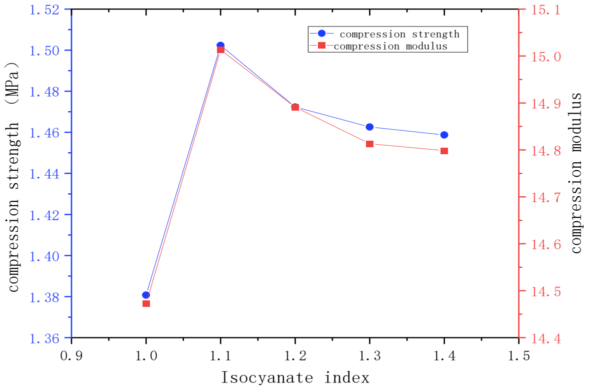


Figure 4: Effect of isocyanate index on compression strength and compression modulus

As can be seen from Figure 4, the compression strength and modulus curves of polyurethane foam firstly increase greatly, and after reaching the extreme value point, the curves show a slow decreasing trend until levelling off. With the increase of isocyanate index, the compression strength and compression modulus of rigid polyurethane foam will be enhanced, but it is not a linear enhancement without upper limit, and it has an extreme value. When the isocyanate index reaches 1.1, the rigid polyurethane foam has the best compression performance. Continuing to raise the isocyanate index, the compression strength and compression modulus of rigid polyurethane foam decreases, and eventually tends to level off. MDI contains rigid structure of the aromatic ring structure, as well as the reaction of the generation of urethane, urea and other high strength, usually containing such groups of the chain is called the ‘hard chain segment’. The higher the isocyanate index during foaming, the higher the crosslink density of this rigid structure of hard chain segments, and the stronger the cohesion of the foam molecules, so that the foam obtained often shows good compression strength and dimensional stability [8].

3.3 Effect of Catalyst Dosage on Moulding Time of Rigid Polyurethane Foam

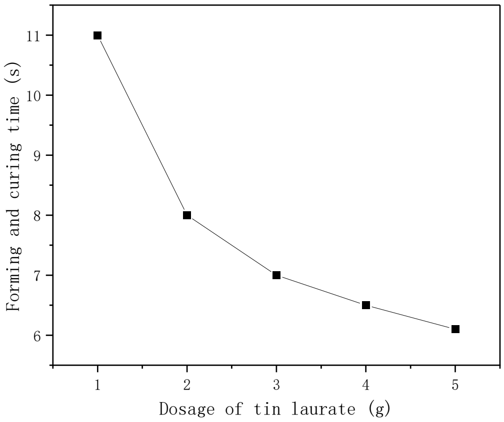


Figure 5: Effect of tin laurate dosage on foam moulding time of rigid polyurethane foam

As can be seen from Figure 5, the polyurethane foam foaming time curve shows a decreasing trend until the levelling off point (3g), the curve decline is basically unchanged. Increased amount of tin laurate, rigid polyurethane foam foaming time is shortened, but when the amount of tin laurate up to 3g, its effect is not obvious, and the foam volume with the addition of 1g of tin laurate rigid polyurethane foam compared to the obvious reduction. Stannum laurate can make the gel reaction rate is greater than the foaming rate, promote the growth of molecular chain, accelerate the reaction between isocyanate group and hydroxyl group, so that the foam to form a complete structure of the time is shortened. However, excessive amount of stannous laurate will make the gel reaction rate much higher than the foaming rate, affecting the diffusion of the bubble holes, resulting in the foam expansion times become smaller.

3.4 Effect of MEG Dosage on Compression Properties of Flame Retardant Rigid Polyurethane Foamables

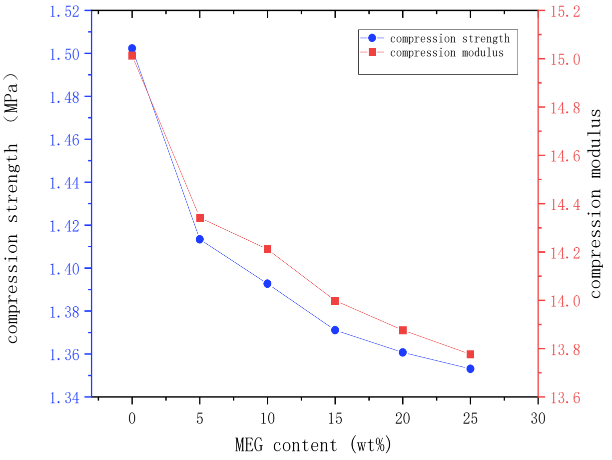


Figure 6: Effect of MEG content on compression strength and compression modulus of flame retardant rigid polyurethane foam

As can be seen from Figure 6, the compressive strength and compressive modulus curves of polyurethane foam show a decreasing trend until the addition amount reaches 15 wt%, and then the decreasing trend gradually slows down. The addition of MEG leads to an obvious decrease in the compression strength and compression modulus of flame retardant rigid polyurethane foam. However, the compression properties tend to be stable after the addition amount reaches 15 wt%. This is due to the large particle scale of MEG, which is less compatible with the polyurethane matrix. When the MEG particles pass through the bubble holes and the strut part, it will lead to the inhomogeneous structure of the bubble holes and defects, so the bubble holes can be easily damaged, which leads to the reduction of the compression strength and compression modulus [9].

3.5 Effect of MEG' Dosage on Compression Properties of Flame Retardant Rigid Polyurethane Foam

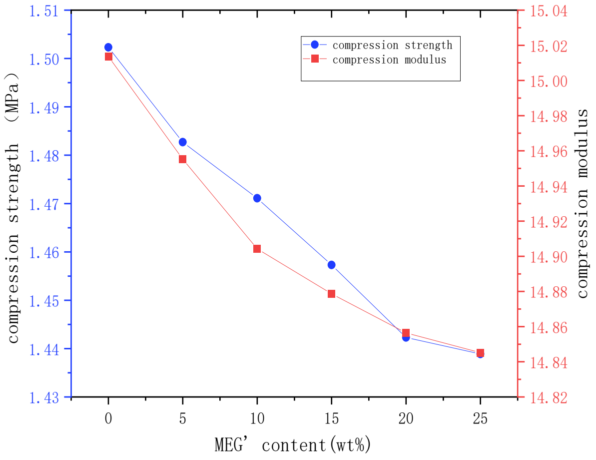


Figure 7: Effect of MEG' content on compression strength and compression modulus of flame retardant rigid polyurethane foam

As can be seen from Figure 7, the compressive strength and compressive modulus curves of polyurethane foam show a decreasing trend. The compression strength and compression modulus of flame retardant rigid polyurethane foam decrease slightly with the increase of MEG' content, and finally tend to be stable. The addition of a large amount of flake EG will greatly improve the flame retardant properties of flame retardant rigid polyurethane foam, but it will cause the compression properties of the foam to be greatly reduced, but the APP & ATH compound system, which reduces the amount of EG, reduces the damage of EG to the polyurethane matrix, and at the same time retains the good flame retardant properties.

3.6 Effect of MEG and MEG' on the Thermal Stability of Flame Retardant Rigid Polyurethane Foam

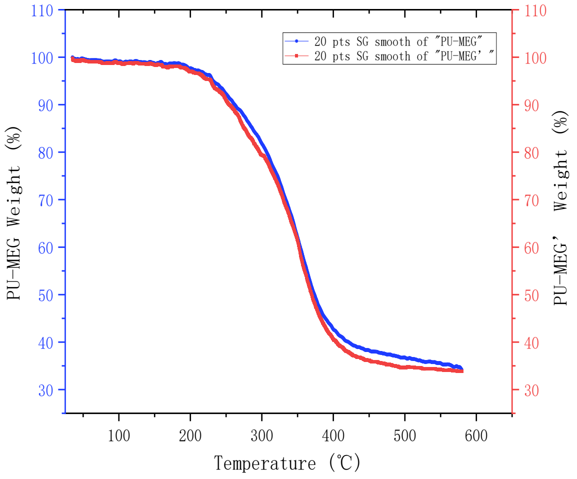


Figure 8: TG curves of flame retardant rigid polyurethane foams with 25 wt% MEG and MEG'

From Figure 8, it can be seen that the TG curve of polyurethane foam maintains flat at the stage of 0-200°C, decreases sharply at the stage of 250-350°C, and then tends to be flat at the stage of 400-600°C. The flame-retardant rigid polyurethane foam with 25% MEG content starts to degrade rapidly with increasing temperature around 231°C. Until around 400°C MEG starts to expand by heat and forms a dense carbon layer, which acts as a heat insulator and makes the foam more thermally stable. At 570°C, the temperature increase was stopped and the thermal degradation ended with a final residue of 34.9%.

Flame retardant rigid polyurethane foam with a MEG' content of 25 wt% at about 204°C because APP started to react with the foam, the thermal stability was gradually reduced and the substance was rapidly degraded, and ammonia, water and polyphosphoric acid were generated simultaneously; Until around 380°C, MEG' was affected by polyphosphoric acid, the rate of thermal expansion became faster, and a dense charcoal layer was formed quickly; On the other hand, affected by the ATH water loss reaction, the temperature of the foam decreases, while the flammable gas concentration is diluted and an aluminium trioxide spacer layer is generated, which serves as a heat barrier and makes the foam more thermally stable. At 570 °C, the temperature increase was stopped and the thermal degradation ended with a final residue of 39.3%.

3.7 Effect of MEG on the Flame Retardancy of Flame Retardant Rigid Polyurethane Foam

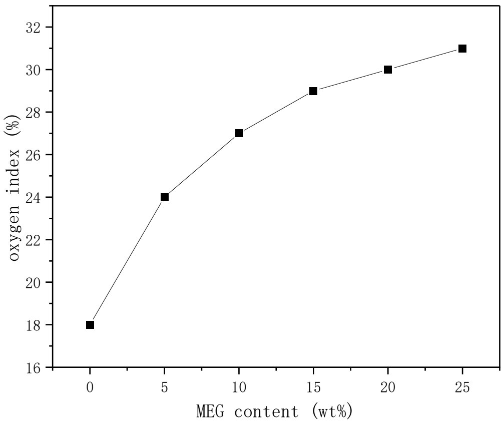
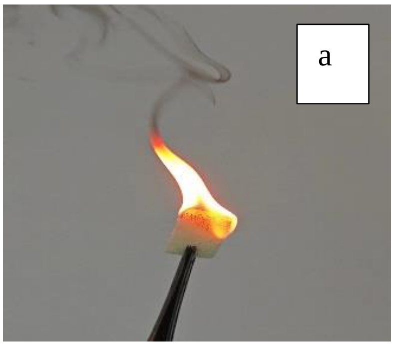
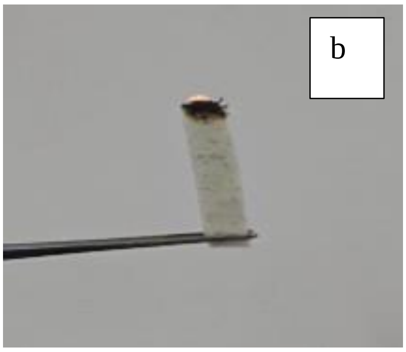


Figure 9: Effect of MEG content on oxygen index of flame retardant rigid polyurethane foam

Figure 9 shows that the overall trend of the polyurethane foam oxygen index curve is increasing. The oxygen index of flame retardant rigid polyurethane foam increases with the increase of MEG addition. However, after the MEG content reaches 15 wt%, the increase in oxygen index becomes insignificant until the oxygen index of the flame retardant rigid polyurethane foam reaches a maximum value of 31% at a MEG content of 25 wt%.





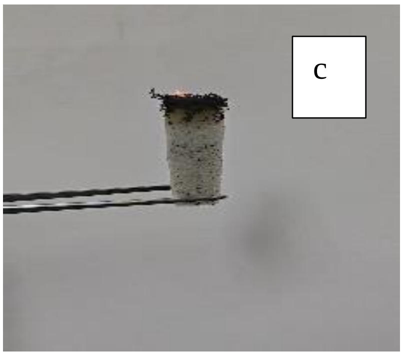


Figure a above shows a rigid polyurethane sample with no flame retardant added; figure b shows a rigid polyurethane sample with 15 wt% MEG as a flame retardant; and figure c shows a rigid polyurethane sample with 15 wt% MEG' as a flame retardant. All three figures are taken from the burning condition of the sample strip in air one second after complete ignition.

From the above three figures, it can be seen that both MEG and MEG' are very effective in enhancing flame retardancy.
The introduction of silica-boron ceramic precursor on the surface of MEG formed B_2O_3, a glassy substance that can promote the char formation of the substrate, and SiO_2, which can enhance the refractory ability of the char layer during the combustion process, which suppressed the 'popcorn effect' of EG, improved the barrier effect of the char layer, and slowed down the combustion [10]. And MEG 'in the combustion process, APP reaction generated polyphosphoric acid, polyphosphoric acid promotes the generation of dense carbon layer, while ATH occurs water loss reaction, reducing the temperature of the combustion region, dilute the concentration of combustible gases, and the production of aluminium trioxide protective layer, improving the barrier effect of the carbon layer, slowing down the combustion of the material [11].

4. Conclusion

In this paper, flame retardant rigid polyurethane foam is prepared by all-water foaming, and the effects of various factors and methods on rigid polyurethane foam are investigated. The conclusions are as follows: (I) the density and compression performance of rigid polyurethane foam both decrease with the increase of water consumption, and the optimal water consumption is 1.4g; (II) the density of rigid polyurethane foam decreases with the increase of isocyanate index, and the compression performance is the opposite, but the compression performance reaches the optimal after the isocyanate index is increased to 1.1, and then basically stays unchanged; (III) the dosage of stannum lauroylacetate catalyst is increased, and the reaction reaction of rigid polyurethane foam forming time decreases, the expansion volume becomes smaller, and the optimal addition amount is 1g; (IV) rigid polyurethane foam compounded with silica-boron modified expandable graphite (MEG), its flame retardancy is greatly improved, and the more MEG is added, the better the flame retardancy is. At 25 wt%, the oxygen index reaches 31%, and at 570°C, the residual carbon reaches 34.9%, but the compression performance of flame retardant rigid polyurethane foam also decreases significantly; (V)Ammonium polyphosphate (APP) and aluminium hydroxide (ATH) compounded with expandable graphite (MEG') can also greatly increase the flame retardant property of rigid polyurethane foam, at 570°C, the residual carbon At 570°C, the residual carbon amount reaches 39.3%, although the compression property of flame retardant rigid polyurethane foam decreases, but the decrease is not obvious, and its flame retardancy also meets the requirements.

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