Research and Preparation of Kaolin/Polyurethane Nanocomposites

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Abstract

In this experiment, Kaolin was intercalated and modified with silane coupling agent and dimethyl sulfoxide to increase the compatibility with polyurethane materials; Kaolin/polyurethane composite materials were prepared by one-step foaming method, using universal testing machine, Oxygen index instrument and horizontal and vertical combustion meter were used to measure the mechanical and flame retardant properties of the composites. The results showed that the flame retardant properties of the composites were the best when the amount of organic kaolin was 3%. The burning speed of the composites was the shortest and the flame retardant level was the highest. The tensile strength, Young's modulus, and elongation at break of the composites have been greatly improved.

Keywords

Kaolin, polyurethane, modification,composite.

1. Introduction

As a kind of macromolecule polymer, polyurethane has received a lot of research attention. It has good strength, good shock absorption and shock absorption. This kind of polymer composite between plastic and rubber can not only replace nylon and plastic. And so on, and it is widely used in various parts of life\.The study of rigid polyurethane foams in polyurethane classification is mainly used in various life, transportation, insulation and construction. Facing the rapid development of all walks of life and the continuous improvement of life, a single material can no longer meet people's satisfaction requirements. Due to the limitation of raw materials and the need to solve various aspects of polymer materials, only the use of different modification methods to research and produce new products that can be applied to various fields of life, nanocomposites came into being. This new type of composite material combines the desirable characteristics of high-molecular materials and inorganic materials and is dispersed in the nano-state into polyurethanes. Therefore, this emerging nano-composite material has some unique and excellent properties that have been continuously applied. Various fields.

Through continuous exploration and research, it has been found that the polymer is organically treated by the nano-modification method, thereby improving the overall performance of the polyurethane material. However, due to the structural and technical limitations of the material itself in the development process, the synthesis of polyurethane and it needs to be further explored, thus restricting the further development of this composite material. In order to solve the above problems, it is proposed to modify kaolin, and then use a one-step method to prepare composites of modified kaolin and polyurethane.

2. Experimental Design

2.1 The Main Reagent

Kaolin, KH-550 silane, dimethyl sulfoxide, 95% ethanol, black material (isocyanate) and white material (catalyst A-33 (33% triethylenediamine in dipropylene glycol solution), dibutyltin dilaurate, foam stabilizing Silicone AK8803, crosslinker DMP-30 (2,4,6-tris(dimethylaminomethyl)phenol), polyether polyol 4110, kaolin, distilled water, butter, etc.

2.2 The Main Experimental Equipment

Infrared spectrum analyzer, drying oven, X-ray diffractometer, electron microscope scanner, magnetic stirrer, drying oven, electronic balance, universal testing machine, oxygen index meter, horizontal-vertical combustion analyzer.

2.3 Kaolin Modification

By comparing the literature and previous experiments, it was found that organic polar molecules of dimethyl sulfoxide and silane coupling agents can be inserted directly into the kaolin layer and selected as the modification reagent is more appropriate and the effect is better.

2.3.1 Method for Modifying Kaolin by Dimethyl Sulfoxide

Measure the amount of kaolin and dimethyl sulfoxide in comparison with 1:1, 1:1.5, and 1:2, respectively, and mix thoroughly in water. Place the mixture in a 40°C, 60°C, and 80°C environment using a magnetic stirrer. Stir 6h, 9h, 12h, then filter dry.

Table 1. Ingredients for Kaolin/Polyurethane Composites

Organic Kaolin (wt%)		Polyether 4110 (g)	Catalyst A-33 (g)	foam stabilizer (g)	Crosslinking agent DMP-30(g)	Dibutyltin dilaurate (g)	water (g)	Isocyanate (g)
	0	100	1.5	1	1	0.04	3	130
Dimethyl sulfoxide modified kaolin	1	100	1.5	1	1	0.04	3	130
	2	100	1.5	1	1	0.04	3	130
	3	100	1.5	1	1	0.04	3	130
	4	100	1.5	1	1	0.04	3	130
	6	100	1.5	1	1	0.04	3	130
Silane coupling agent modified kaolin	1	100	1.5	1	1	0.04	3	130
	2	100	1.5	1	1	0.04	3	130
	3	100	1.5	1	1	0.04	3	130
	4	100	1.5	1	1	0.04	3	130
	6	100	1.5	1	1	0.04	3	130
Unmodified kaolin	1	100	1.5	1	1	0.04	3	130
	2	100	1.5	1	1	0.04	3	130
	3	100	1.5	1	1	0.04	3	130
	4	100	1.5	1	1	0.04	3	130
	6	100	1.5	1	1	0.04	3	130

2.3.2 Method for Modifying Kaolin By Silage Coupling Agent

At room temperature, the amount of the silane coupling agent was quantified as 1 g, 2 g, and 3 g, and each was dissolved in a 95% ethanol solution to be fully dissolved to form a silane coupling agent. This hydrolyzed solution was separately fused with 10 g of kaolin. The magnetic stirring was started at 85° C, 90° C, 95° C, stirred for 20 min, 30 min, 40 min, then filtered and dried.

2.4 Preparation of Composite Materials

(1) The modified kaolin is placed in a drying box to remove the kaolin moisture.

(2) Place the treated kaolin and polyether polyol in a beaker and mix well with a motorized mixer at a speed of 2500 r/min.

(3) Add the catalyst, dibutyl tin dilaurate, foam stabilizer, cross-linking agent and water to the beaker and mix it with electric mixer at room temperature.

(4) Add isocyanate and stir constantly.

(5) When the temperature rises and the mixture gradually whitens, it is injected into the mold immediately.

(6) The resulting foam is later matured in a drying oven.

The specific ingredients are shown in Table 1, in which the experimental parameters are controlled:

(7) The temperature during foaming is controlled at 18~25°C; (2) Mold temperature: 20±5°C.

3. Results and Analysis

3.1 Composite Material Oxygen Index Analysis

The Limiting Oxygen Index (LOI) is used to characterize the flame retardancy of the sample under test and refers to the minimum oxygen content required for the sample to be stably burned in oxygen-nitrogen mixed gas under the specified conditions. It can detect the flame-retardant properties of the material. The level of oxygen index determines the degree of difficulty in the combustion of the material. The lower the oxygen index, the more easily the material is combustible. The higher the oxygen index, the stronger the flame retardancy of the material. The test indexes are LOI ≤ 22% for flammable materials, 22% <LOI <27% for flammable materials, and L0I ≥ 27% for nonflammable materials.

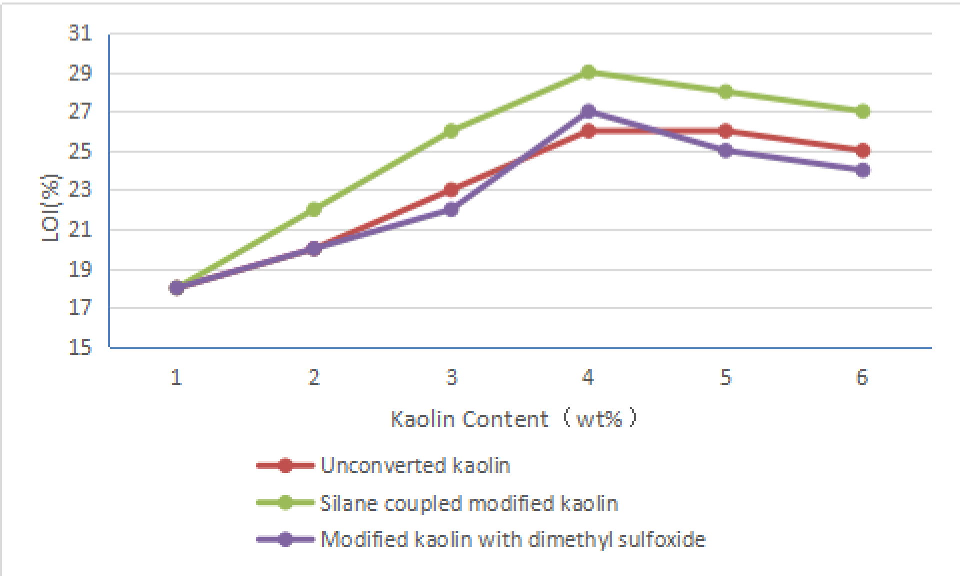

Fig. 1. Oxygen index map of composite materials with different kaolin loadings

Figure 1 shows the variation curves of the limiting oxygen index of composite materials with different kaolin loadings. From the figure, the oxygen index of pure polyurethane is only 18%, and the addition of kaolin can increase the oxygen index of the material. With the increasing amount of kaolin added, the oxygen index of the composites also increased, and the oxygen index of the composites modified with silane coupling agents reached a maximum of 29%, and the composite oxygen index of dimethyl sulfoxide can be achieved. 27%, have reached the level of flame retardant, indicating that the addition of modified kaolin can further improve the material's combustion performance. And when the organic kaolin content increased to 3%, it was a nonflammable material at this time.

It is further illustrated that the lamellar structure of organic kaolin dispersed in polyurethane produces a barrier effect. When combustion occurs, the organic kaolin sheet can play a role in isolating the flammable volatiles and oxygen released from the combustion of the material, thereby increasing the barrier effect. The flame-retardant properties of composite materials, and the effect of kaolin, the more lamellar layers in the polyurethane, the stronger its combustion performance, and when the content of organic kaolin is too high, the oxygen index changes little and there is a decline. The trend is mainly due to the decrease in the surface effect and the decrease in the degree of order of the organic kaolin sheets arranged on the polyurethane surface. Therefore, organic kaolin acts on polyurethane in the optimum range, and the combustion performance is best at this time.

3.2 Horizontal-Vertical Combustion Test Analysis of Composite Materials

In this experiment, the combustibility of composite materials was investigated by two methods: horizontal combustion test and vertical combustion test. Horizontal burning test is to place the sample horizontally, record the burning time and distance after ignition, and then measure the burning speed of the material. The vertical burning test is to record the time period during which the test sample is in flaming combustion and flameless combustion, respectively, and observes the combustion state of the sample.

Table 2. Horizontal Vertical Burning Test Results

Organic kaolin content (wt%)		Horizontal burning time (s)	Horizontal burning rate (cm/s)	Vertical burning time (s)	Vertical burning speed (cm/s)	Flame retardant level	Note
	0	5.85	12.82	10.40	7.21		Unburned to the first marking, obvious droplets
Unmodified kaolin composites	1	6.24	12.01	10.81	6.94	FH-3	Droplet, burning more powerful
	2	6.28	11.95	10.24	7.32	FH-3	Droplet
	3	6.80	11.03	10.92	6.87	FH-3	
	4	6.50	11.54	10.74	6.98	FH-3	
	6	6.54	11.47	10.49	7.15	FH-3	
Dimethyl sulfoxide modified kaolin composites	1	6.35	11.82	12.60	5.95	FH-3	Droplet
	2	6.86	10.94	10.80	6.94	FH-3	
	3	7.33	10.23	12.67	5.92	FH-2	
	4	7.04	10.65	11.30	6.64	FH-3	
	6	7.08	10.60	9.57	7.84	FH-3	
Silane coupling agent modified kaolin composites	1	6.86	10.93	17.10	4.39	FH-3	Droplet
	2	7.27	10.31	19.60	3.83	FH-3	
	3	7.49	10.01	23.80	3.15	FH-1	Do not drop
	4	7.39	10.15	21.50	3.49	FH-1	Do not drop
	6	7.09	10.58	16.30	4.60	FH-2	

Table 2 shows the horizontal and vertical combustion results of composites modified with different modifiers and modified kaolin. It can be seen from the table that as the content of organic kaolin gradually increases, the burning speed has a downward trend, and the modifiers are different. There is also a difference in the burning rate, in which the kaolin composite modified by the silane coupling agent has no dripping phenomenon during combustion, and the flame retardant level can reach FH-1, while the addition of unmodified kaolin shortens the burning rate. However, the flame-retardant effect is not obvious, indicating that the addition of organic kaolin increases the flame retardancy of polyurethane and can minimize the loss caused by the quality of the material in the same period of time, effectively inhibits the cracking in the combustion reaction, and has a barrier effect. When the content of organic kaolin reaches 3%, the composite material has the fastest burning speed, the highest flame retardant level, and the best combustion performance. The flammability rating of composites modified with silane coupling agents was significantly increased. When the content of organic kaolin was higher than 2%, the measured materials were smoke-free when burning, and the flame-retardant level was increased. When the amount of added kaolin was reached 3%. When there is no dripping phenomenon, the flame retardant grade is FV-1 grade, which belongs to high flame-retardant material. It shows that organic kaolin can improve the droplet condition of polyurethane and can effectively improve the flame retardancy of polyurethane.

3.3 Analysis of Mechanical Properties of Composite Materials

This time, the tensile strength and hardness of polyurethanes and composites were tested to analyze the effect of the amount of organically modified kaolin added on the mechanical properties of the material.

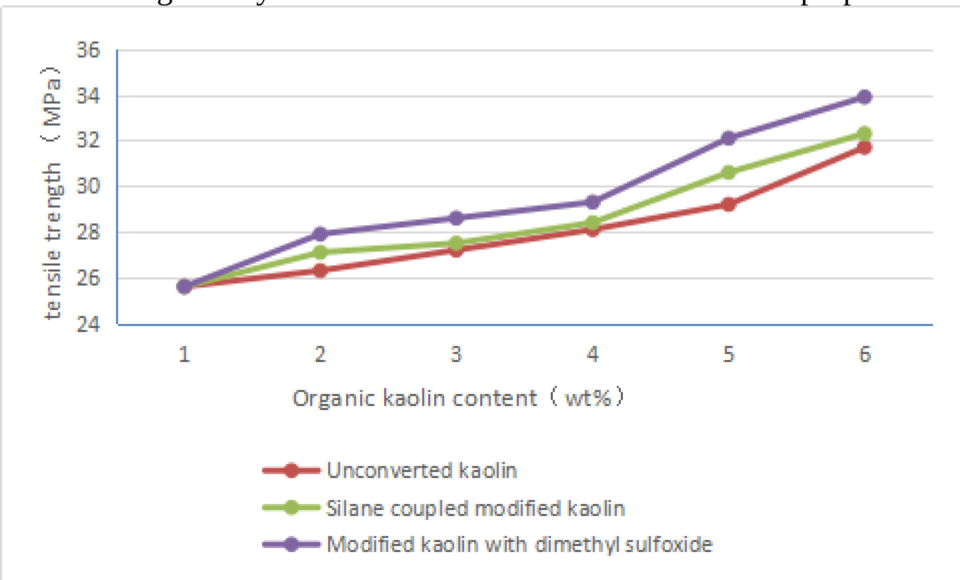

Fig. 2. The tensile strength of composites when the amount of kaolin is added

It can be seen from Figure 2 that the tensile strength of several composites increases with the increase of kaolin content, and there are also differences in the variation trends of the modifiers. However, in general, the addition of kaolin significantly increases the tensile strength of the polyurethane. The tensile strength of the modified kaolin composite is also much higher than that of a pure kaolin composite, and the composition of kaolin and polyurethane treated with the silane coupling agent is also improved. The composite has the highest tensile strength.

Table 4 shows the composites modified by silane coupling agent. It can be seen that with the addition of organic kaolin, the tensile strength and hardness of the composites change, and the mechanical properties of the composites are affected. This is because the modified organic kaolin works better in polyurethane bonding and increases the mechanical properties of nanocomposites. With the continuous addition of organic kaolin, the connection density of raw materials is strengthened, and the interaction of composite materials is increased, which in turn increases the strength and toughness of the materials, but the hardness decreases. When organic kaolin is added to a certain value, there will be agglomeration of lamellae in the polyurethane, which will increase the brittleness of the material, and the elongation at break will decrease accordingly, and the hardness will rise instead.

Table 3. Test results of mechanical properties of composite materials

Silane coupling agent modified kaolin content (wt%)	Tensile Strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)	hardness (level)
0	25.6	435	5.62	60
1	27.9	453	5.82	59
2	28.6	467	5.97	58
3	29.3	492	6.23	57
4	32.1	439	6.78	61
6	33.9	410	7.11	64

From the table, it can be seen that with the addition of organic kaolin, the tensile strength and Young's modulus exhibited by the material increase accordingly, but the elongation at break increases first and then decreases. The hardness also decreases first and then increases with the increase of kaolin. When the content of organic kaolin reaches 3%, the tensile strength, Young's modulus, and elongation at break of the composite material are greatly improved. Through comprehensive analysis, it can be concluded that this content of organic kaolin increases the strength of polyurethane and Hardness, mechanical properties are significantly enhanced.

3.4 Density Analysis of Composite Materials

The effect of the modified kaolin on the properties of the polyurethane was analyzed by the density detection of the polyurethane and the composite material. In this experiment, the prepared sample was tested according to the density test specification of GB/T6343-1986. The sample was tested five times and averaged. According to the density calculation formula: p = l0 \ x (m / V), P is the apparent density, g / cm \, m is the measured sample mass, g; v is the sample volume, cm \ .

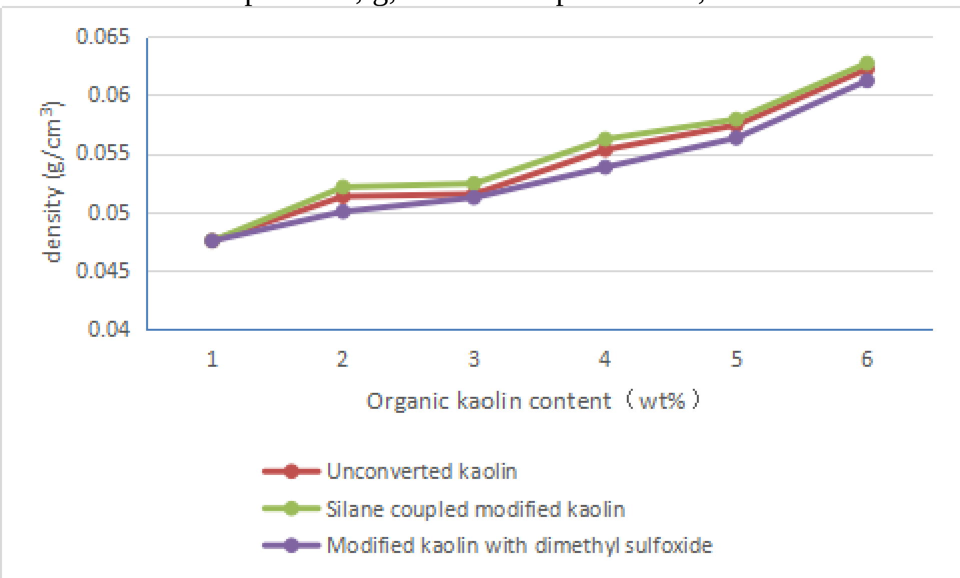

Fig 3. Density change curves of composites with different kaolin additions

Figure 3 shows that the addition of organic kaolin affects the density of the composites, which in turn influences the performance characterization of the materials. It is not difficult to find from the table that with the same volume, with the increasing content of organic kaolin, various composite materials Density is also increasing. The density of unmodified kaolin composites has been improved compared to pure polyurethane, but the modified kaolin has a higher density of composites and the density of kaolin composites treated with silane coupling agents has generally increased. It shows that the increase of kaolin spacing makes the polyurethane intercalation kaolin more thoroughly and evenly, and most of them are intercalated and exfoliated.

The ratio of the material density to the compressive strength can be defined as the specific compressive strength, which can characterize the mechanical properties of the material. It can be shown that the appropriate density value can improve the mechanical properties of the material, and the tensile strength and the elongation at break can be affected by the change of the density. When the density is low, the compressive strength of the material can be enhanced, and the high-density composite material reduces the compressive strength. When the density reaches a certain value, the number of chemical bonds that the formed polymer network can receive external force increases, and the composite material is stretched. The strength also increases, so there is an optimum range for the amount of organic kaolin added, which can significantly improve the mechanical properties of the composite.

4. Conclusion

Through the oxygen index test, horizontal-vertical combustion measurement, universal testing machine testing and density analysis of kaolin/polyurethane nanocomposites, the mechanical properties and combustion performance of the composites after organic kaolin were analyzed. The following conclusions can be drawn:

(1) After kaolin was added, the combustion performance of the composites was significantly improved. After the kaolin was modified, the oxygen index of the composites was significantly higher than that of pure polyurethane. And the kaolin modified by the silane coupling agent can make the composite material reach the flame retardant level. The level burning test reaches FH-1 level, and the vertical combustion experiment reaches the FV-1 level. It is further concluded that organic kaolin acts on polyurethane in an optimum range, and when the content is 3%, the composite has the best combustion performance.

(2) By testing the mechanical properties of composite materials, it can be seen that the addition of organic kaolin increases the tensile strength and hardness of polyurethane, and with the addition of different amounts, the mechanical properties are also different, and can be seen comprehensively through several sets of controlled tests. When the addition amount reaches 3%, the mechanical properties of the material are optimal.

(3) Through the above analysis and density test, it can be found that the modified and unmodified kaolin have different effects on the density of the composites. The addition of kaolin increases the density of the composites and enhances the mechanical properties of the polyurethane to some extent. Furthermore, the organic kaolin content also has an effect on the density. When the content reaches a certain value, the density is relatively low, and the polyurethane has a good compatibility with the polyurethane. At this time, the addition of the organic kaolin makes the mechanical properties of the composite material reach the strongest.

(4) It can be seen from the comparison of the three composite materials and pure polyurethane that the addition of kaolinite significantly enhances the mechanical properties and the combustion performance of the composite materials. The kaolin was treated with dimethyl sulfoxide and a silane coupling agent rather than unmodified. The performance of kaolin is more obvious, and the effect is also different with the increase of the amount of addition. It is observed that the modification effect of the silane coupling agent is more obvious, and the polyurethane is better intercalated into the kaolin, so that the composite material has various performances. Both are optimal, and the optimum amount is 3%.

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