Fabrication and characterization of a novel environment-friendly inorganic fireproof adhesive used for fire resistant doorsets

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Abstract. A novel environment-friendly inorganic fireproof adhesive was prepared with sodium silicate, fumed silica, light calcium carbonate, aluminum hydroxide and magnesium hydroxide by high-speed mixing and ball milling. The bond strength, formaldehyde and VOC emissions, thermal properties and fire performance of such adhesive were investigated. The bond strength of the adhesive was increased with the adding of the fumed silica, which reached 1.8 MPa when the amount of fumed silica was 1.5 wt.%. Formaldehyde and VOC emissions of this adhesive were far lower than those of the requirements in Chinese standards. The combustion grade of this adhesive could achieve A1 and its smoke toxicity grade could achieve AQ1, which was the safest grade of flammability for building materials.

1. Introduction
Fire resistant doorsets are the most common way of fire separation in buildings, which can provide sufficient time for evacuation and escape when a fire happens. Adhesive is one of the necessary raw materials in the production process of fire resistant doorsets. In order to ensure that the fire resistant doorsets meet certain integrity and heat insulation under certain heating conditions, China's fire door standard requires that the adhesive used in fire resistant door sets should be harmless to human body. At the same time, it requires that the combustion grade and smoke toxicity of the adhesive must realize non-combustibility (A1) and ZA3. In order to ensure the bond strength between the panel and the core material of the fire resistant doorsets, polyurethane and other organic compounds are often used as the adhesive of fire resistant doorsets, however, these kind of organic adhesive can hardly meet the standard requirements because of their smoke toxicity.[1,6]

In this paper, based on sodium silicate aqueous solution, a novel environmental protection inorganic fire resistant adhesive was prepared by using fumed silica and other inorganic fillers. The adhesive not only has no formaldehyde and VOC emission, but also meets the requirements of fire door standard for adhesive combustion performance.
2. Materials and methods

2.1. Materials

Materials: Sodium silicate, Fumed silica, Calcium carbonate, Magnesium hydroxide, Aluminum hydroxide, Titanium dioxide and Perlite powder.

2.2. Sample preparation

Five adhesive samples were prepared in this work. Sample No.1 was pure sodium silicate aqueous solution. Samples 2# to 5# were prepared as follows, a certain amount of sodium silicate aqueous solution was added into a reactor, then fumed silica was added under strong stirring, after silica was completely dispersed, stirring lasted for 30 minutes, then TiO$_2$, light calcium carbonate, aluminum hydroxide and magnesium hydroxide were added, separately, and stirring lasted for another 30min, the prefabricated adhesives were obtained; the prefabricated adhesives milled for 45min by ball milling, then the fireproof adhesive were fabricated. The contents of 5 samples were listed in Table 1.

| Samples | Na$_2$SiO$_3$ wt.% | SiO$_2$ wt.% | TiO$_2$ wt.% | CaCO$_3$ wt.% | Mg(OH)$_2$ wt.% | Al(OH)$_3$ wt.% | Perlite powder wt.% |
|---------|--------------------|--------------|--------------|---------------|-----------------|-----------------|---------------------|
| 1#      | 100.0              | -            | -            | -             | -               | -               | -                   |
| 2#      | 95.5               | 1.0          | 0.5          | 1.0           | 1.0             | 1.0             | -                   |
| 3#      | 94.5               | 1.5          | 0.5          | 1.0           | 1.0             | 1.0             | 0.5                 |
| 4#      | 91.5               | 1.0          | 1.0          | 2.0           | 2.0             | 2.0             | 0.5                 |
| 5#      | 91.0               | 1.5          | 1.0          | 2.0           | 2.0             | 2.0             | 0.5                 |

2.3. Viscosity and bond strength tests

Viscosity and bond strength of the 5 adhesives samples were tested. Viscosity was measured by rotor viscometer. Bond strength was tested by universal testing machine.

2.4. Formaldehyde and VOC emission tests

The formaldehyde and VOC emission tests were carried out according to Chinese national standard GB 18580-2017[3].

2.5. Thermal analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of the adhesives were carried out under air atmosphere. The temperature range was from room temperature to 700 degrees centigrade. The heating rate was 10°C/min.

2.6. Fire performance tests

The combustible classification and smoke toxicity of the samples were carried out in accordance with Chinese national standard GB 8624-2012[4] and GB/T20285-2006[5].
3. Results and discussion

3.1. Viscosity and Bond strength tests

Fig. 1 Viscosity of inorganic fireproof adhesives

Fig. 1 showed the viscosity test data of sample 1# to 5#. It can be seen from the diagram, the addition of fumed silica could significantly increase the viscosity of the glue, when the fumed silica content is 1.5% for optimal, continually increase the content of silica, the viscosity of the glue system will increase dramatically and the preparation of adhesive fast curing at room temperature. Therefore, the content of fumed silica should be controlled between 1.0% and 1.5%.

Fig.2 Bond strength of inorganic fireproof adhesives

Fig. 2 showed the test results of the bond strength of the samples 1# to 5#. It can be seen from the figure that the addition of fumed silica can not only significantly improve the viscosity of the glue, but also greatly improve its bond strength, among which the content of fumed silica is 1.5%. The cause may be the formation of cross-linked structures in sodium silicate solution.
3.2. Formaldehyde and VOC emission tests

In recent years, with the continuous development of the decoration market, a variety of problems have arisen, especially indoor formaldehyde and VOC released in the living environment do great harm to the human body. The formaldehyde and VOC emission test results of the four inorganic fireproof adhesives prepared in this work are not detected (n.d.). The highest requirement of formaldehyde emission of domestic building materials in national standard GB 18580 is grade E1, and the limit value of harmful substances in architectural coatings in GB18582 is water-based coatings, which is less than 80g/L, which is far higher than the national standard requirements. It indicated that the inorganic fireproof adhesive prepared in this work is an environmental-friendly adhesive.

3.3. Thermal analysis

Figure 3 showed the TG results of inorganic fireproof adhesives and PU adhesive. It can be seen from the figure that the initial decomposition temperature of the inorganic adhesive is about 80°C, and the maximum decomposition temperature reaches 150 °C. In addition, the final mass loss is within 20% when the decomposition temperature reaches 700 °C. The addition of fumed silica can decrease the mass loss rate of the inorganic adhesive. When the content of fumed silica is 1.5% (5#), the mass loss of the adhesive at 700 °C is only 10%. The reason is that the inorganic adhesive can form a ceramic-like insulation layer during heating, and the insulation layer will not be further decomposed with the increasing of temperature. When the adhesive is used for the bonding of the fire door panel, the integrity of the fire door can be guaranteed, and the purpose of fire prevention and heat insulation can be achieved.

The polyurethane adhesive begins to decompose at 100°C and decomposes from room temperature to 700°C. At 700°C, the mass loss reaches about 80%. Although the organic adhesive can form a carbonized layer when heated, with the increase of temperature, the carbonized layer will be further decomposed and ashed, thus losing the ability to insulate the heat.

3.4. Fire performance

The combustion characteristics and smoke toxicity of materials or components in fire are the key factors affecting rescue and escape when a fire happens. As a fire separation product, fire door should not only have a certain degree of thermal insulation and integrity in case of fire, but also ensure that it has no contribution to the combustion spread and smoke toxicity in case of fire. Therefore, the various materials of fire door products must ensure their own fire safety. Table 2 showed the combustible classification and smoke toxicity results of the inorganic fireproof adhesives. It can be seen that the combustion grade of the four inorganic fireproof adhesives prepared in this paper can reach A1, and the smoke toxicity can reach AQ1, which are the highest grade of materials.
Table 2 Fire performance of inorganic fireproof adhesives

| Samples | Temperature rising | Mass Loss | Time to ignite | Combustible Classification | Toxicity |
|---------|-------------------|-----------|----------------|---------------------------|----------|
| 2#      | 3                 | 23        | 0              | A1                        | AQ1      |
| 3#      | 3                 | 22        | 0              | A1                        | AQ1      |
| 4#      | 2                 | 22        | 0              | A1                        | AQ1      |
| 5#      | 1                 | 19.1      | 0              | A1                        | AQ1      |

4. Conclusion
A novel inorganic fireproof adhesive prepared in this work was not only environmentally friendly, that was, the emissions of formaldehyde and VOC were not detected, but also its combustion grade can reach A1 level, and the smoke toxicity is AQ1 level, both of which are the highest safety levels.

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