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Fire Resistance and Heat Insulation Properties of Perfusion Type Fireproof Glass

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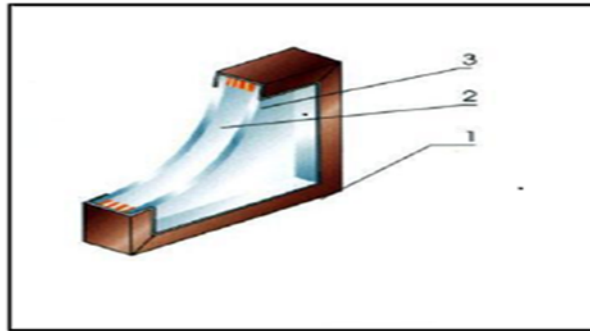
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Abstract. To improve the fire resistance heat insulation performance of fireproof glass, the effect of fire resistance performance of fireproof glass interlayer rubber was explored by adding borax to the potassium polysilicate-based slurry. Characterization and testing were carried out by preparing a silica sol mixture, and the transmittance, S/B-0.45H and interlayer thermodynamics, fire resistance and expansion ratio were further analysed. The results showed that the addition of borax affected the transmittance of perfusion type fireproof glass. As the borax content increased, the light transmittance of the fireproof glass decreased. The effect of borax on the expansion efficiency of potassium polysilicate was obvious. In summary, Borax can improve the fire resistance of polysilicate type perfusion fireproof glass. As the borax content increases, the fire resistance of the fireproof glass increases.

1. Introduction

Fireproof glass is a functional glass that is transparent and can block and control heat radiation, smoke, and flame, as well as control the spread of fire and smoke. To be precise, fireproof glass, as a special glass, is required to maintain its integrity and heat insulation under the specified fire test conditions. Countries such as Britain and France have successively issued a series of specifications and laws on fire resistance materials, such as "fire resistance specification for building design", "fire resistance performance test method and standard for building parts", and "fire resistance specification for high-rise civil building design". It has greatly promoted the rapid development of fireproof glass. For the time being, fireproof glass is mainly used in industrial and civil buildings (especially high-rise buildings), scientific research and military, defense facilities (flammable and explosive and biological, aerospace industrial facilities), modern vehicles (such as marine fireproof glass). Among them, the market for building fireproof glass is the most extensive [1]. Fireproof glass is not only growing rapidly in the construction industry, but also in the shipbuilding industry and rail train manufacturing. These two industries have developed into pillar industries in China. The demand for fireproof glass is also rising, and it has become a top priority in fire resistance materials. Perfusion type fireproof glass has received increasing attention due to its excellent refractory heat insulation properties. It is made by embedding a special fire resistance slurry between two or more pieces of fireproof glass. The fire resistance glue is sealed around the flame-retardant strip, and the fire resistance glue is poured in the middle. After the glue is solidified, it is a transparent gel, which is bonded with the glass to form a fireproof glass member. Its structure is shown in Figure 1:





Note: 1: edge banding tape; 2: fire resistance glue; 3: glass piece.

Figure 1. Grouting fireproof glass

2. State of the art

The UK is the earliest country to develop fireproof glass, especially in the UK, Pilkington has the longest history of developing fireproof glass. It mainly includes three series of fire resistance products: pouring method fireproof glass, composite fireproof glass, laminated safety fireproof glass. Japan has been ahead of European countries in the development of fireproof glass. The products of Japan Plate Glass Co., Asahi Glass Co., Ltd. and Japan Sangtian Glass are world-renowned. The composite fireproof glass developed by Japan Plate Glass Co., Ltd. has excellent quality and is available in many varieties and specifications. Germany's fireproof glass is also relatively developed. The borosilicate transparent tempered fireproof glass is the best. Foreign fireproof glass manufacturing companies focus on the development of lightweight and high UV resistance monolithic special fireproof glass. At the same time, for the composite fireproof glass products with heavy appearance but excellent heat insulation performance, they have also invested heavily in recent years. Pilkington even focused on the production of composite fireproof glass. These all illustrate the importance of heat insulation composite fireproof glass [2].

The development of domestic fireproof glass is very good, and the current scale has reached more than 150. Only forty companies produce grout-type composite fireproof glass. The single-piece potassium-fireproof glass produced by Guangdong Jingang Company has been widely used in the market by its good fire resistance steel frame structure system, but its poor heat insulation has been controversial. The main domestic grouting type fireproof glass has a fire resistance of fireproof glass due to a large amount of polyacrylamide, and the ultraviolet resistance is not good. With the acceleration of urbanization, the demand for fireproof glass is increasing [3]. Composite fireproof glass with good fire resistance, good economic efficiency, light weight, environmental protection and safety should be studied. The fireproof glass is functionalized as much as possible. The production and promotion of safety glass has been expanded to meet the fire resistance requirements.

3. Methodology

Due to the difference in structure and fire resistance performance requirements, the technical requirements of fireproof glass are also different. The technical specifications for single-piece fireproof glass and composite fireproof glass are significantly different. The perfusion type fireproof glass studied in this subject belongs to the composite fireproof glass. The composite fireproof glass is based on BS EN 13501-2 and GB 15763.1 "Safety glass for construction". GB 15763.1 has detailed provisions for product classification, technical requirements, experimental methods and inspection rules. The main aspects are as follows:

The appearance quality is tested according to the standard GB 15763.1-2009. The test standards are: First, there are no bubbles, cracks, blasts, scratches, degumming, glue and wrinkles; second, the dimensional tolerances and stack differences are within the standard allowable range.

According to the standard GB 15763.1-2009, the transmittance of fireproof glass was tested by visible light transmittance tester. The light transmittance is determined by the thickness of the fireproof glass, as shown in Table 1.

Table 1. Total transmittance of composite fire-resistant glass of different thickness

Total thickness of glass D/mm	Transmittance/%	Total thickness of glass D/mm	Transmittance/%
$5 \leq D < 11$	≥ 75	$17 \leq D \leq 24$	≥ 65
$11 \leq D < 17$	≥ 70	> 24	≥ 60

According to the standard GB 15763.1-2009, the anti-irradiation box is used for the fireproof glass UV resistance test. The glass sample was placed in an irradiation chamber and continuously irradiated with a 750 W ultraviolet lamp for 100 hours. If the light transmittance is reduced by no more than 10%, and the sample does not show significant discoloration, bubbles and turbidity, it is considered to meet the requirements of ultraviolet radiation resistance.

Different countries and regions have different test standards for fire resistance. The fire resistance performance test standard is GB/T 9978.1-2008. A standard heating curve in the test furnace is provided, as shown in Figure 2. This temperature curve has a significant correlation with the actual fire field temperature of some building fires. The standard heating curve essentially provides a standard experimental environmental condition similar to a fire. In this experimental environment, the fire resistance of different components in the building structure was compared. The standard temperature rise curve can be expressed by an exponential formula, as shown in equation (1):

$$T = 345 \log_{10}(480t + 1) \quad (1)$$

T—the value of the temperature rise, and the unit is Celsius (°C);

t—the continuous heating time corresponding to the temperature rise to T, and the unit is hour (h).

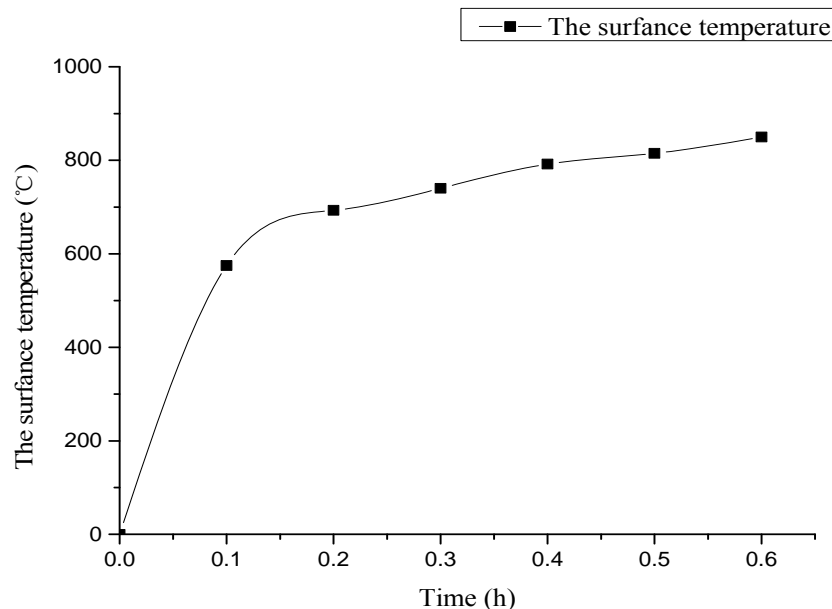


Figure 2. The heating curve of electric furnace for insulation test

The fireproof glass specimen was placed at the door of the modified muffle furnace. The fire endurance was divided into five grades by recording and observing the glass backfire surface temperature and fire resistance time: 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h. During the test, when the

composite fireproof glass cracked, the flame penetrated the glass, and its integrity was broken, thereby achieving the fire endurance. For the heat insulation property, it is judged based on the temperature of the fireproof surface of the fireproof glass. When the average temperature of the composite fireproof glass back surface exceeds the initial temperature of 140°C, it can be determined that the fireproof glass loses the heat insulation effect and reaches the fire endurance limit.

It is a very common and efficient method to add fire-resistant heat insulation additive to the gelation liquid of perfusion type fireproof glass to enhance the fire resistance of fireproof glass [4]. The operation process is simple. A certain amount of fire resistance heat protective agent is added and uniformly mixed before the gel is solidified, and perfusion type fireproof glass is obtained after curing. This method is simple and effective, and a small amount of fire resistance heat insulation agent can achieve a good fire resistance effect. For an organic gelling agent such as a polyacrylamide-based gel, in the production process of a polyacrylamide-based perfusion type fireproof glass, an organic filler such as sucrose, urea or sorbitol is added to the gelling solution. The acid source is introduced therein to react with the organic filler to improve the fire resistance of the interlayer adhesive. The inorganic salt electrolyte is added as a refractory heat insulation aid to further improve the fire resistance, and inorganic additives such as MgCl_2 , $\text{Alk}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, CaCl_2 are widely used, and the effect thereof is particularly remarkable. For the inorganic gelling liquid, it can mainly enhance the fire resistance by adding an inorganic additive when the gel liquid is continuously removed, such as ceramic fiber, glass fiber, glass frit glass beads, inorganic salt and the like.

For polysilicate type perfusion type fireproof glass, some heavy metal salts cannot serve as heat insulation aids because the main raw material is alkaline silica sol. As a heat insulation additive, it must first satisfy good water solubility and alkali resistance, and secondly, it has excellent heat insulation effect, such as some water-soluble salts or organic matter. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is an inorganic salt which has good heat resistance and is easily soluble in water, and has excellent heat insulation properties. These have been reported in many documents. Boron trioxide can also reduce the expansion coefficient of glass in glass, improve its thermal stability, chemical stability and mechanical strength, and improve the gloss of glass. More importantly, the thermal conductivity of boron trioxide is very low. The synergistic flame-retardant effect of borax and chlorinated paraffin on epoxy resin was studied. In addition, in the glass industry, borax also enhances the transmission of ultraviolet light, and also significantly improves the transparency and heat resistance of the glass [5]. In this experiment, the effect of borax on the fire resistance performance of fireproof glass interlayer adhesive was investigated by adding borax to the polysilicate potassium-based slurry.

3.1. Experimental materials and instruments

The raw materials and reagents used in the experiment are shown in Table 2.

Table 2. Experimental materials and reagents

Name	Chemical formula	Specification	Manufacturer
Silica sol	$\text{SiO}_2 \cdot n\text{H}_2\text{O}$	-	Guangdong Suize Environmental Protection Technology Co., Ltd.
Deionized water	H_2O	-	Laboratory homemade
Water soluble silicone oil	-	Analytical purity	Guangzhou Batai Chemical Co., Ltd.
Glycerin	$\text{C}_3\text{H}_5(\text{OH})_3$	Analytical purity	Jining Baiyi Chemical Co., Ltd.
Potassium hydroxide	KOH	Analytical purity	Dingshengxin Chemical Co., Ltd.
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$	Analytical purity	Yixin Chemical Co., Ltd.

The instruments and equipment used in the experiment are shown in Table 3.

Table 3. Experimental instruments

Equipment name	Specification model	Manufacturer
Electronic precision balance	JA2003	Shanghai Hengping Scientific Instrument Co., Ltd.
Electric blast drying oven	HG101-1A	Nanjing Experimental Machine Factory
Three-necked flask	250ml	Shanghai Shangtian Precision Instrument Source Factory
Magnetic heating stirrer	78-1	Dongmai Technology Co., Ltd.
Circulating water vacuum pump	SHZ-D(III)	Zihua Instrument Co., Ltd.
Refrigerator	Haier	Qingdao Haier Group Corporation
Visible light transmittance tester	BTR-1S	Qinhuangdao Xianhe Instrument Equipment Co., Ltd.
Irradiation resistant box	SGR-3	Wuxi Huanwei Technology Co., Ltd.
Muffle furnace	XL1200	Kejing Material Technology Co., Ltd.

3.2. Preparation of heat insulation aid/silica sol mixture

A certain amount of silica sol was poured into a three-necked flask, and a magnetic stirrer was used. The stirring speed was 10 r/s and the stirring temperature was 40 °C. Immediately thereafter, water-soluble silicone oil and polyol are added thereto. In this state, the mixed liquid was stirred for 10 minutes. The heat insulation aid was added and then stirred under vacuum for 10 min. The prepared potassium hydroxide solution was added. The stirring speed was adjusted to 20 r/s. The liquid was stirred for 50 min, cooled to room temperature, evacuated for 10 min, filtered, and then the filtrate was poured into a laminated glass. Then, the glass was solidified for 12 hours in an 80 °C blast dryer, and the composite fireproof glass was prepared. The formulation used for the interlayer adhesive is shown in Table 4.

Table 4. The main formula of inter-layer gel

Sample no	Silica sol	KOH	Na ₂ B ₄ O ₇	SO	Glycerol
S	60	14	0	3	12
S/B-0.25	60	14	0.25	3	12
S/B-0.35	60	14	0.35	3	12
S/B-0.45	60	14	0.45	3	12
S/B-0.55	60	14	0.55	3	12

The transmittance of fireproof glass was tested using a BTR-1S visible light transmittance tester. The experimental procedures and test criteria are consistent with the above. The total thickness of the fireproof glass used in this experiment is 15mm, and the wavelength of visible light is 380-780nm.

The absorption and release heat analysis of the sandwich rubber samples of S/B-0.45 and S fireproof glass was carried out using a U.S. TA differential scanning calorimeter Q2000. First, a certain amount of interlayer adhesive is taken out from the fireproof glass and ground into a powder. A small amount of the sample was placed in a crucible at a temperature range of 0 to 500°C under an argon (Ar) atmosphere, and the rate of temperature increase was set to 10°C / min.

The thermodynamic analysis of the interlayer adhesive in multi-S/B-0.45 fireproof glass and fireproof glass was carried out using a German TZ-209 thermogravimetric analyser. First, a certain amount of interlayer adhesive is taken out from the fireproof glass and ground into a powder. A small amount of the sample was placed in a crucible, and the sample was subjected to thermogravimetric

analysis in a temperature range of 100 to 800°C under an argon atmosphere, and the heating rate was set to 10°C / min.

Since this experiment has just been in the laboratory test stage, the small piece of fireproof glass produced cannot meet the requirements of the size of the test piece required for the conventional component measuring furnace. Therefore, in this experiment, the fire resistance of the composite fireproof glass was tested by a self-made glass frame and a modified muffle furnace. The furnace temperature is automatically controlled by the controller. The furnace temperature rise curve is shown in Figure 3. The temperature rise curve equation is $T = 10.5t + 25$ (T is the temperature corresponding to time t , and t is the experimental time). At the same time, the center temperature of the backfire surface of the sample was measured by a thermocouple and a pocket type numerical display, and the temperature value was measured every 5 minutes.

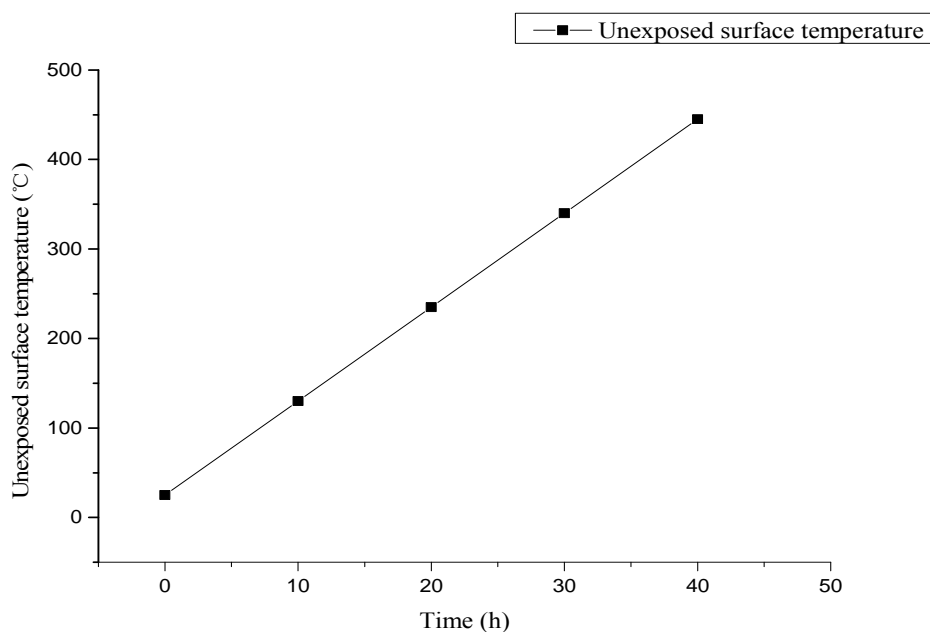


Figure 3. The heating curve of electric furnace for insulation test

During the test, when the composite fireproof glass cracked and caused the flame to penetrate the glass, its integrity was considered to be broken, thereby achieving the fire endurance. For the heat insulation property, it is judged based on the temperature of the fireproof surface of the fireproof glass.

The S interlayer adhesive and S/B series interlayer rubber samples were tableted and then placed in a 500°C muffle furnace for 5 min. The shape and thickness of the interlayer adhesive were then measured using the scale. The volume $V_1(\text{dm}^3)$ of each original sample was calculated. Then, the expanded samples were placed in water, and the volume $V_2(\text{dm}^3)$ of the discharged water was measured. DI (Degree of Intumescence) is calculated according to formula (2):

$$DI = \frac{V_2 - V_1}{V_1} \quad (2)$$

4. Results and discussion

4.1. Light transmittance test

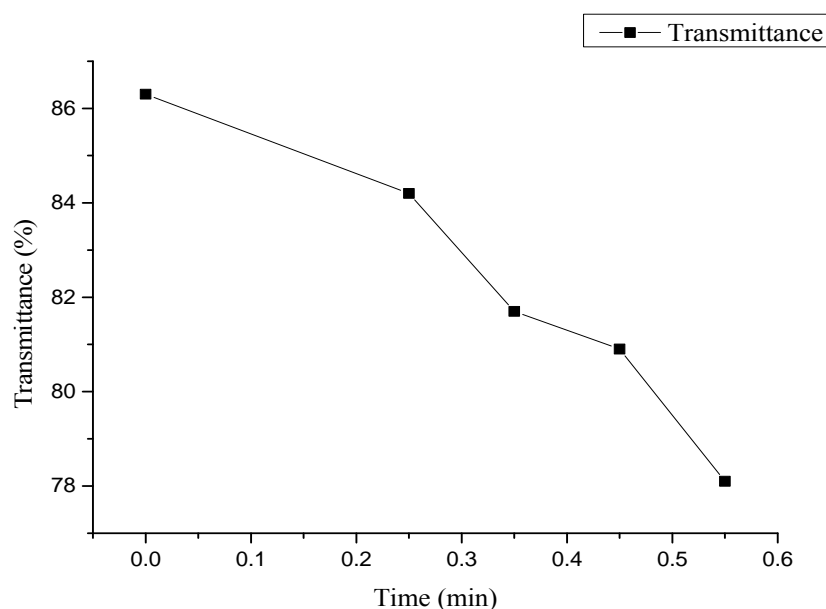


Figure 4. The transmittance change of fireproof glass with the addition of $\text{Na}_2\text{B}_4\text{O}_6 \cdot 10\text{H}_2\text{O}$

After adding $\text{Na}_2\text{B}_4\text{O}_6 \cdot 10\text{H}_2\text{O}$, the light transmittance of the fireproof glass changes as shown in Figure 4. The wavelength of visible light is 380-780 nm. As the additive content increases, the light transmittance of the fireproof glass generally decreases slightly. Borax can be used as a cross-linking agent. A small amount of borax can promote the cross-linking of Si-OH between silica sol colloids to form a Si-O-Si network structure, thereby reducing the number of -OH and enhancing the mechanical strength of the interlayer adhesive. In addition, borax as a crystal also affects the transmittance of glass [6]. When the amount of borax is too large, the molecular chain rotation between the polysilicate potassium molecules is hindered, the rigidity is increased, the fluidity is poor, and even the fluidity is completely lost. The actual light transmittance is at least greater than 80%. Therefore, the amount of borax added is optimal at 0.45%.

4.2. Thermodynamic analysis of S/B-0.45 and S interlayer adhesives

In order to investigate the thermal stability of the potassium silicate-based sample after adding borax, the sample was placed in an Ar atmosphere for scanning calorimetry and thermogravimetric characterization. The test results are shown in Figures 5 and 6. Polysilicates contain free water and bound water. After heating, the water vapor is released to form a swelling property, and the intumescent layer forms a thermodynamic barrier [7]. As shown in Figure 5, for the polysilicate-based sample, there are two absorption peaks at 50 °C and 210 °C, respectively. The absorption peak at 50 °C is due to the release of free water and the decomposition of hydrogen bonds in the silyl alcohol. Another peak at 210 °C is ionic bound water in the polysilicate. In particular, there is an exothermic peak at 350 °C. The -Si-O-Si- group is formed by polymerization of a Si-OH group in the polysilicate. Finally, the endothermic peak at 435 °C is due to a melt change in the solid phase transition of the silicate.

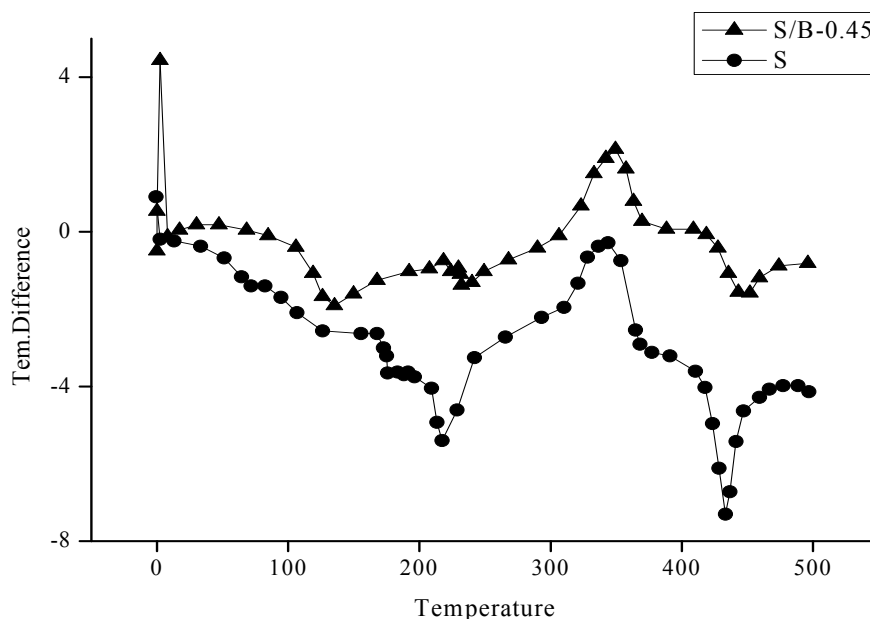


Figure 5. DSC curves of S and S/B-0.45 sample

From the TGA-DTG curve in Figure 6, it can be concluded that all silicate samples contain four stages of mass loss processes $<120^{\circ}\text{C}$, $120\text{--}330^{\circ}\text{C}$, $330\text{--}420^{\circ}\text{C}$ and $>420^{\circ}\text{C}$. The four stages correspond to four DTG peaks. The first stage is the release of free water and silanol hydrogen bonds. Its corresponding DTG peak is at 110°C . The weight loss in the second stage is due to the release of ion-bound water. The corresponding DTG peaks of the samples were 205°C and 221°C , respectively, which affected the swelling behaviour of the dried silicate. The weight loss in the third stage is due to the dehydration reaction occurring when the Si-OH group in the polysilicate is polymerized to form a Si-O-Si group, and the corresponding DTG peak is at 358°C . Finally, the final stage of mass loss is at 430°C . The corresponding DTG peak is at 433°C due to the decomposition of the silicate. Therefore, the decomposition process of all silicate samples is basically the same, and only in the range of $120\text{--}330^{\circ}\text{C}$, the mass loss of S/B-0.45 is the smallest. The DTG peak of the pure silicate is at 205°C , while the DTG peak of S/B-0.45 is at 221°C . For the S/B-0.45 sample, a small amount of borax lost a little weight. Since the boron trioxide decomposed by boron trioxide replaces the position of the ion-bound water in the silica gel, the amount of ion-bound water is reduced. On the one hand, the borax is melted by heat to form a slight sealing effect on the gel layer, thereby forming a cover layer; On the other hand, borax acts as a cross-linking agent to further form Si-O-Si bonds between the polysilicate potassium molecules, so that the structure of the interlayer adhesive is tighter and more stable, and the thermal weight loss at this stage is smaller. Borax inhibits the rapid pyrolysis of the silica gel matrix. The weight loss rate peak shifts to the right, and the amount of ion-bound water decreases, which increases the residue rate. A better barrier to smoke and harmful gases is formed.

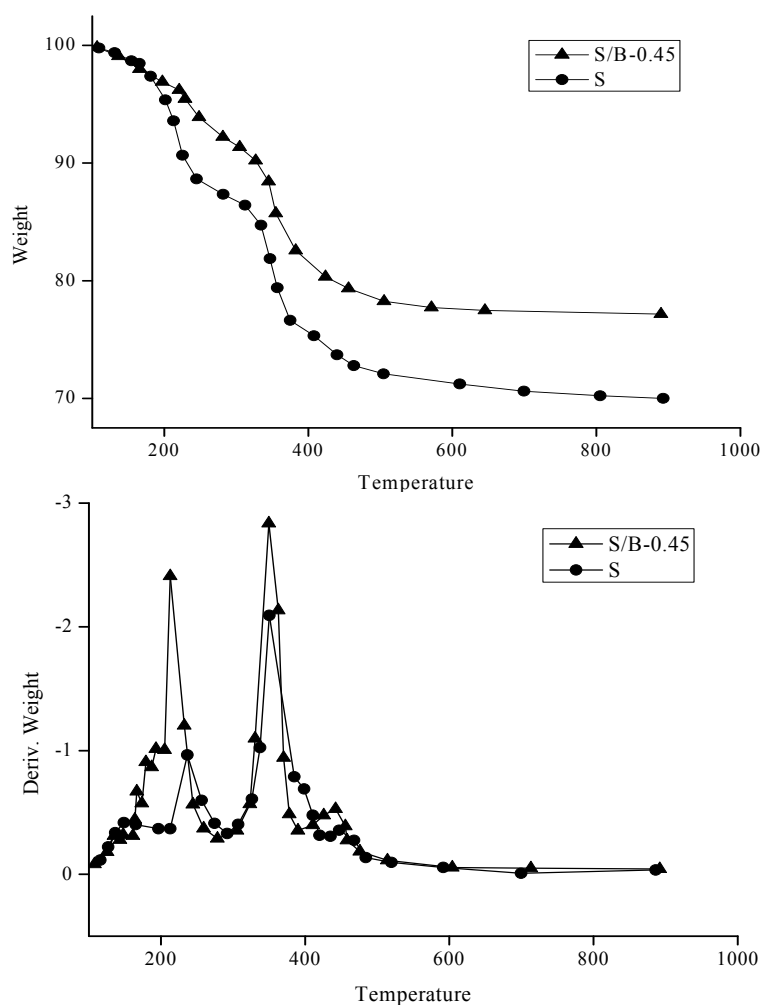


Figure 6. TG and DTG curves of pure S and S/B-0.45 samples

4.3. Fire resistance test

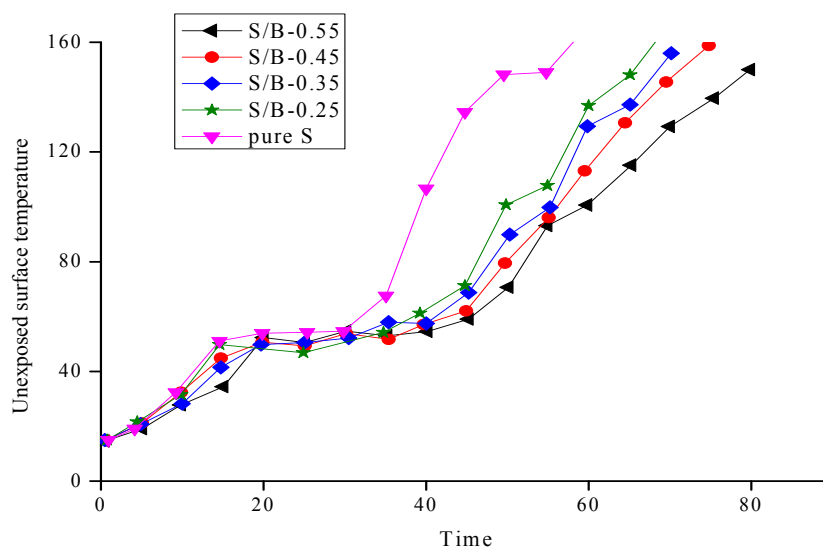


Figure 7. The experimental results of simulated fire resistance of fireproof glass

In order to verify whether the addition of borax will improve the fire resistance of the fireproof glass and explore the effect of the amount of borax added on the fire resistance of the composite fireproof glass, a series of fire resistance tests were performed. Under the experimental conditions, it can be concluded from Figure 7 that for the pure polysilicate potassium interlayer adhesive sample, when the centre temperature of the backfire surface reaches 140°C, the corresponding fire protection time reaches 50 min. However, under the same conditions, the S/B series of samples exceeded 60 min. As the amount of borax increases, the fire resistance of the composite fireproof glass is correspondingly improved. Specifically, when the amount of borax is 0.45% and the center temperature of the back surface reaches 140°C, the corresponding fire resistance time has reached 72 min.

4.4. Expansion rate experiment

The fire resistance of fireproof glass is related to the expansion ratio of the interlayer rubber in case of fire. In the case of the same matrix material, the higher the expansion ratio, the thicker the heat insulation layer, the better the heat insulation effect [8]. After the S series samples have been tested, their volume before and after expansion is shown in Table 5. The addition of borax can increase the expansion ratio of the interlayer adhesive to a certain extent. As the borax content increases, the expansion ratio gradually increases. When the borax content is 0.45%, the expansion ratio of the interlayer rubber reaches 4.83 times.

Table 5. The expansion of the volume data of S and S/B samples

Sample	Volume before expansion $V_1(\text{dm}^3)$	Volume after expansion $V_2(\text{dm}^3)$	Expansion ratio DI
S	0.68	3.22	3.75
S/B-0.25	0.71	3.61	4.08
S/B-0.35	0.68	3.82	4.62
S/B-0.45	0.69	4.12	4.83
S/B-0.55	0.68	4.01	4.89

5. Conclusion

The fire resistance glue was prepared by solidifying a silica sol with a KOH solution. The composite fireproof glass having excellent fire resistance and light transmittance is prepared by adding the inorganic filler borax heat. Then, the fire resistance properties of the two heat insulation auxiliaries were compared. Based on the above analysis and performance tests, the following conclusions are drawn:

First, the addition of borax affects the transmittance of the potassium silicate perfusion type fireproof glass. As the borax content increases, the light transmittance of the fireproof glass decreases;

Second, borax plays a significant role in promoting the expansion efficiency of potassium polysilicates in case of fire;

Third, the addition of borax can improve the fire resistance of the potassium silicate perfusion type fireproof glass. As the borax content increases, the fire resistance of the fireproof glass increases. Under the experimental conditions, when the amount of borax is 0.45%, the corresponding fire resistance time can reach 72 minutes. Therefore, borax can promote cross-linking between poly silicate molecules, thereby improving the fire resistance of fireproof glass.

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