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Study on Preparation of Insulation and Flame Retardant Building Materials with Inorganic Compound Phenolic Foam

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Inrecent years, phenol-formaldehyde foam has been widely used as an ideal heat-insulating structural material in the construction field. However, the traditional phenolic foam itself has the disadvantages of easy powdering and high production cost. For this reason, this paper studied the preparation of flame retardant building materials with inorganic compound phenolic foam.In this paper, 15% phosphoric acid was used to acidify the fly ash and bentonite to prepare the inorganic composite phenolic foam. The effect of acidification treatment and its addition amount on the performance of the composite phenolic foam was studied. The results show:1) The strength of the composite foams after acidification treatment is higher than that of the non-acidified composite foams, especially the acidified fly ash composite foams have better properties. This shows that the acidified fly ash is more suitable as a filler of composite phenolic foam. 2) The limit oxygen index of the inorganic composite foam is lower than that of phenolic foam. This shows that inorganic material added to the resin matrix is bad for flame retardant effect.

1. Introduction

At present, China's building energy-saving level is still very low, and the use of building insulation materials are mainly non-flame-retardant polystyrene (PS) foam, polyethylene (CPE) foam and polyurethane foam (CPU) rigid foam plastic. Compared with PS, PE, PU foam, phenolic foam has excellent fire - retardant insulation properties.With the deep reform of national policy of building energy conservation and the increasing requirements of building fire protection, building insulation industry appeared a hitherto unknown development opportunity and challenge. This paper introduces the research and application of phenolic foam plate, modified phenolic foam plate with thermal insulation, fire prevention, environmental protection and other excellent properties, puts forward in the field of building energy conservation should be vigorously promoted the application of phenolic foam. In recent years, fire frequently happened in buildings which always leads to collapse and gas explosion causing high temperature and dynamic impact loading on structure at the same time. It not only threatens people's lives and property security, but also produce a large number of harmful fumes, polluting the environment. One of the main ignition sources of urban building fire is the organic insulation material widely used in modern building exterior wall. Flame-retardant problem of building materials has become a hot spot at home and abroad. Phenolic foam as a self-flame-retardant foam in the combustion process does not occur melting, dripping, and it will not produce large amounts of toxic smoke, as well as it has flame retardant, low smoke, low toxicity characteristics and heat resistance and other advantages, it will be in the field of construction as an ideal heat insulation material to be more widely used. In the production process of traditional high solid phenolic resin, phenol and Formaldehyde Solution with the content of 37% were used as reactive monomers, the preparation of phenolic resin (solid content of about 50%) to go through the dehydration can be achieved by the phenolic resin to the solid content (70 ~ 85%) requirements, inevitably produce large amounts of industrial wastewater. At the same time, phenolic foam still has the disadvantages of high production cost and high price, which has hindered the popularization and application of phenolic foam. The flame retardant performance of phenolic foam board and polystyrene foam board was studied by means of the horizontal and vertical combustion analyzer and oxygen index instrument. The results showed that phenolic foam board could not be ignited in the horizontal and vertical combustion analyzer and it only generated carbon black under the action of the flame. The polystyrene foam board would be ignited in 3.6s by

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horizontal combustion test and it was burned completely in 9.6s. When the vertical combustion of polystyrene foam board was tested, it would be ignited in 3.3s and was burned completely in 6.4s. The oxygen index of phenolic foam board was 41, the oxygen index of polystyrene foam board was 24. Finally, the experiment showed that flame retardant performance of phenolic foam board was more excellent than that of polystyrene foam board. Therefore, research and development of low-cost inorganic composite phenolic foam has important economic and social significance.

With the advent of the world's energy crisis, the technologies of energy saving and environmental protection from exterior wall have gradually become hot topics in building industry. Phenolic foam has excellent flame retardant and heat-insulating properties, which can be used as exterior wall material. However, its brittleness and low strength limit the application. In this paper, natural plant fibers are added in phenolic foam before curing process, and the effects of modified method for the fibers and fiber content on the performance of the foam composite are investigated. A process for producing a closed cell phenolic-resin foam material comprising a phenolic-resin polymer and surfactant which is branched, non-ionic, with a hydroxyl value less than 50 achieved by capping excess hydroxyl groups; the material, and a structural laminate employing the material. The material has a thermal conductivity which is low initially and remains low for a long period of time.We summarize the results of previous studies on the invention of short fiber reinforced phenolic foam composition and its preparation and use. The disclosed fiber-reinforced phenolic foams have a seven-fold increase in peel resistance over the unreinforced counterpart foam. The phenolic foam has enhanced fracture toughness without sacrificing the critical fire retardant properties. This paper uses 15% phosphate acid treatment of fly ash and bentonite, preparation of inorganic composite phenolic foam, and studied the influence of the acidification and addition on properties of phenolic foam composite, discusses the phenolic foam preparation process, analyzes the influence of acid curing agent on properties of phenolic foam, create the apparent density and mechanical properties of phenolic foam model. This change would not only make building materials more energy efficient, as well as improve health and environmental impacts.

2. Experiment

2.1 Materials and equipment

Phenol, sodium hydroxide, phosphoric acid, hydrochloric acid (36 wt%), methanol, p-toluenesulfonic acid, these all are analytical grade, Nanjing Chemical Reagent Co., Ltd;Formaldehyde solution (37 wt%), paraformaldehyde, both are analytical grade, Shanghai Ling Feng Chemical Reagent Co., ltd.;Calcium oxide, petroleum ether, polysorbate cool -80, these all are are of analytical grade, Sinopharm Group Chemical Reagent Co., ltd.;Fly ash, Shanghai Yu Ai Technology Co., Ltd.; Bentonite, Anji County, Zhejiang Province eternal refined bentonite factory.

2.2 Experimental method

1) Synthetic resin

The synthesis of high-solids phenol-formaldehyde resin is as follows: In a 500mL four-necked flask equipped with a stirrer, a reflux condenser and a thermometer, a certain amount of phenol and formaldehyde solution were added, paraformaldehyde was added in two batches in succession from the second stage, and the catalyst was added sequentially in three batches from the second stage. In the first stage, the temperature is raised to 85 ℃ and the reaction time is 30 ~ 40 min. In the second stage, the temperature is maintained at 85 ℃ and the reaction time is 50-70 min. In the third stage, the temperature is maintained at 85 ℃ and the reaction time is 50 ~ 70min. In the fourth stage, the reaction temperature is maintained at 75 ℃ and reaction time is 30 ~ 40min, and the reaction product is cooled to below 40 ℃.

2) Preparation of phenolic foam

Phenolic foam preparation method is as follows: The high solid containing phenolic resin is sequentially added with surface active agent, curing agent and fully stirred, then adding foaming agent, and quickly mixed evenly, and finally pour the resin mixture into the mold (50 × 160 × 210mm), foaming and curing at 70℃.

3) Method for treating inorganic material

Bentonite and fly ash were respectively treated with 15% phosphoric acid solution at 80 ± 5 ℃ and 350r / min for 4h, dried and grinded at 60 ℃ for 100 mesh. The solid-liquid ratio of the above treatment methods was 1:5.

4) Preparation of Composite Phenolic Foam

Preparation of composite phenolic foam was prepared using the method described in 2.2.2 for the preparation of phenolic foam.

2.3 Performance testing and characterization methods

1) Compressive strength testing of foam

The compressive strength is determined according to the provisions of GB 8813-2008.

a) Test principle of compressive strength

The vertical stress applied to the specimen can be calculated by the stress of the specimen.If the relative stress of the corresponding maximum deformation is less than 10%, it called the “compression strength.” If the relative maximum stress corresponds to or exceeds 10% of the relative strain, the compressive stress at 10% relative deformation is the result of the test and is called the compressive stress at 10% relative deformation.

b) Sample preparation and number of samples

The thickness of the specimen is50±1mm, when using the product with molded skin, the sample should take the original product of the original thickness, but the minimum thickness of 10mm, the maximum shall not exceed the sample width or diameter. The compression surface of the specimen is square or round, and the area is between 25$cm^2$and 230cm^2. It is preferable to use a square prism specimen with a pressure surface of (100 ± 1) × (100 ± 1) mm. The parallelism error between the two planes should be less than 1%. Rigid foam plastic products or thick plate in the preparation of samples, sampling methods and quantity should refer to the provisions of the standard foam products, at least five samples.

c) Calculation method

σm=102×FmA0 (1)

In the formula, σmis the compressive strength, kPa; $F_m$represents the maximum amount of compression, N; A_0represents the initial cross-sectional area of the specimen, mm^2.

The compressive elastic modulus is calculated as follows:

E=σm×Fexe (2)

In the formula, Eis the compressive elastic modulus, kPa; $F_e$represents the compressive force within the proportional limit, N; x_e represents the displacement at F_e, mm.

2) Bending strength testing of foam

The flexural strength was determined according to the method specified in GB 8812-2007.

a) Test principle

The load head applies the load to the specimen supported on the two bearings at a certain speed. The load should be applied perpendicularly to the center of the two fulcrums, record the load and deformation, and calculate the flexural strength and the apparent flexural modulus.

b) Sample preparation and number of samples

Sample preparation should not deform the cell structure of the sample. The specimen may be covered with one or more surface skin, such as a band skin, which should be recorded with at least five samples per group. The specimen was placed symmetrically on the support and the load head was moved at a constant velocity, and the pressure was applied perpendicular to the longitudinal axis of the specimen. The test speed is (20±1) mm/min.

c) Calculation method

The flexural strength is calculated as follows:

R=1.5FR×Lbd2 (3)

In the formula, R is bending strength, kPa; $F_R$is the maximum applied load, kN; L represents the span between the twoseats, mm; bis the width of the sample, mm; d is the thickness of the sample, mm.

The apparent bending elastic modulus is calculated as follows:

E=L34bd3×Ftxt×L105 (4)

In the formula, E represents the apparent flexural modulus of elasticity, kPa; F_t represents the load corresponding to the deformationxt, kN; xtis the corresponding deformation, mm.

3) Limit oxygen index test of foams

Limit oxygen index with reference to GB / T 2406-93 “plastic combustion performance test method” provisions of the determination.

The sample is vertically fixed in the combustion tube, so that oxygen and nitrogen mixed gas flow from the bottom up ignite the top of the sample, while timing and observation of the sample combustion length, compared with the provisions of the criteria. A set of samples was tested in different oxygen concentrations to determine the minimum oxygen concentration at which the plastic just kept stationary, expressed as a percentage of the oxygen content of the mixture.

4) Thermal conductivity test of foam

The thermal conductivity of foam sample was tested by T322 thermal conductivity analyzer of C-THERM Company of Canada.

3. Results

3.1 Compressive and flexural properties of inorganic composite phenolic foam

The relationship between the addition of inorganic materials and the compressive strength of the composite phenolic foam is shown in Figure 1. The relationship between the flexural strength of the composite phenolic foam is shown in Figure 2.

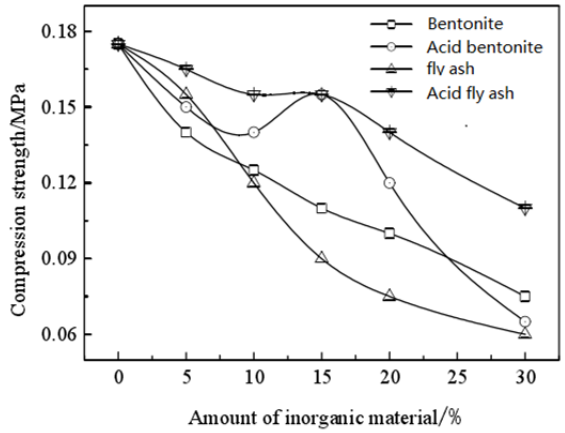

Figure 1: Compressive strength of inorganic composite phenolic foam

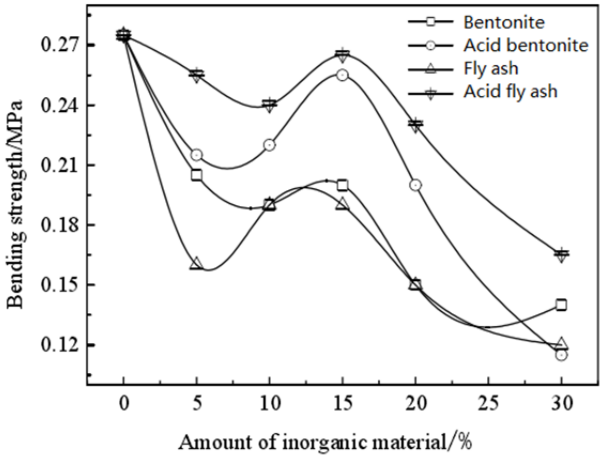

Figure 2: Flexural Strength of Inorganic Composite Phenolic Foam

From figure 1, with the addition of inorganic materials, the compressive strength of phenolic foam except acidification bentonite increased slightly at the addition of 15%, and the compressive strength of other composite foams decreased gradually, while the compressive strength of the composite foams after acid treatment is higher than that of the non-acidified composite foams, especially the acidified fly ash composite foams have the highest compressive strength. From figure 2, with the increase of inorganic materials, the flexural strength of the composite phenolic foam decreases first, then reaches the peak value when the inorganic material is 15%, and then decreases gradually. Comparing with the compressive strength, the flexural strength of the composite foams after acid treatment is higher than that of the non-acidified inorganic phenolic foams. The results showed that the mechanical properties of the inorganic composite phenolic foam were improved to some extent after acidification treatment.

3.2 Flame retardancy of inorganic composite phenolic foam

The flame retardancy of the inorganic phenolic compound foam is shown in Figure 3.

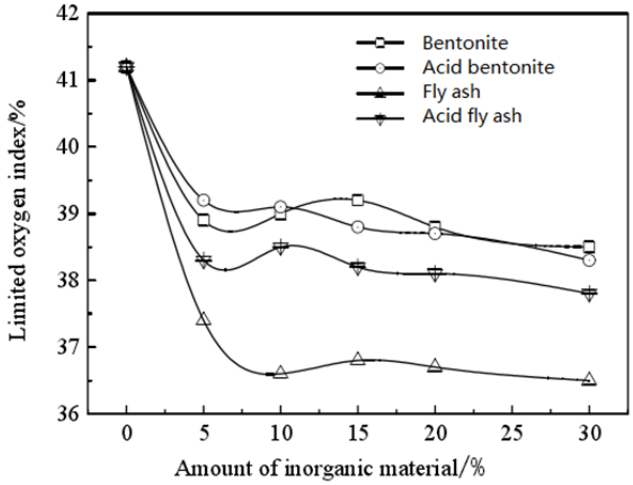

Figure 3: Limit oxygen index of inorganic compound phenolic foam

From figure 3, with the increasing amount of inorganic materials, the limiting oxygen index of composite foams has similar trend, and all of them show a decreasing tendency. The oxygen index of composite foams without acidizing treatment decreases more remarkably, and the bentonite composite The limiting oxygen index of the foam is slightly higher than that of the composite phenolic foam of fly ash. The oxygen index of the composite phenolic foam changed little after acid treatment, and remained at about 39%. The oxygen index of the composite phenolic foam was slightly higher than that of the non - acidified fly ash composite phenolic foam after acidification treatment. The results showed that the addition of inorganic materials had no positive effect on the flame retardancy of the composite foams, but decreased the limit oxygen index of the composite foams, and the addition of inorganic materials and the acidification treatment had little effect on the oxygen index of the composite foams.

3.3 Thermal conductivity of inorganic composite phenolic foam

The thermal conductivity of the composite phenolic foam with 30% inorganic material is shown in Figure 4.

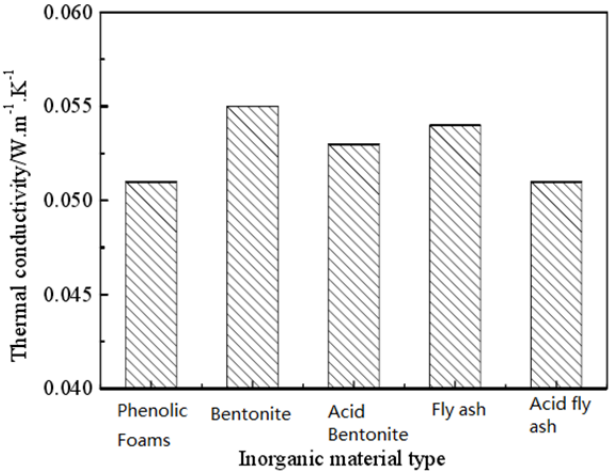

Figure 4: Thermal Conductivity of Inorganic Composite Phenolic Foam

Figure 4 shows that inorganic materials with no addition of phenolic foam compared to the thermal conductivity of inorganic materials composite foam thermal conductivity than pure phenolic foam has increased. The thermal conductivity of the composite phenolic foam after acidification treatment is slightly lower than that of the composite phenolic foam, and the thermal conductivity of the composite phenolic foam after acidification treatment is the most obvious, almost equals to pure phenolic foam. The results show that the inorganic materials have some effect on the acidification treatment, and the inorganic materials have little effect on the performance of the composite foams.

4. Conclusion

With the rapid development of thermal power industry, China's annual emissions of fly ash nearly 20 million tons, a large number of inefficient fly ash accumulation, not only take up a lot of land, and serious pollution of the environment. The preparation of building thermal insulation materials by using phenolic materials such as fly ash and bentonite is the general trend. Based on the analysis of the properties of the inorganic composite phenolic foam, the following conclusions can be drawn: The acidified fly ash is more suitable as filler for composite phenolic foam; after the inorganic material is added to the resin matrix, forming a "wick" effect, it is unfavourable to the retardant effect.

Reference

Coppock V., Zeggelaar R., Wenham R., Hobbs L., 2015, Method of making a phenolic foam board. New Chemical Materials.

Jamison K.L.T., Boardman D.A., 2016, A new fire performance test for cavity wall insulation. In MATEC Web of Conferences, 46, 02004. EDP Sciences.

Jeannerat D., Pupier M., Schweizer S., Mitrev Y.N., Favreau P., Kohler M.., 2015, Discrimination of hexabromocyclododecane from new polymeric brominated flame retardant in polystyrene foam by nuclear magnetic resonance. Chemosphere, 144, 1391-1397.

Jokisch C., Weiser J., 2013, Multi-layer composite materials comprising a foam layer, corresponding method of production and use thereof. US.

Liagkouridis I., Lazarov B., Giovanoulis G., Cousins I., 2016,Chemical mass transfer of an organophosphate flame retardant between product source and dust in direct contact.

Lindsay C.I., Hill S.B., Hearn M., Manton G., Everall N., 2011, Mechanisms of action of phosphorus based flame retardants in acrylic polymers. Polymer International, 1183-1192.

Nutt S.R., Shen H., 2014, Preparation and properties of phenolic foam insulation material. Construction and Building Materials, 122, 27-28.

Uygunoğlu T., Sevcan Ö., Metehan Ç., Effect of plaster thickness on performance of external thermal insulation cladding systems (ETICS) in buildings. Construction and Building Materials, 122, 496-504.

Vytenis B., Lucas D., Eisenberg D., Singla V., Dedeo M., Blum A., 2012, Flame retardants in building insulation: a case for re-evaluating building codes. Batiment International, Building Research and Practice, 40(6), 738-755.

Wicklein B., Kocjan A., Salazar-Alvarez G., Carosio F., Camino G., Antonietti, M., 2015, Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. Nature Nanotechnology, 10(3), 277-83.

Xu H., 2013, Research on the building flame retardants in polymer insulation materials. China Building Materials Science & Technology, 144, 478-480.