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The flame resistance properties of expandable polystyrene foams coated with a cheap and effective barrier layer

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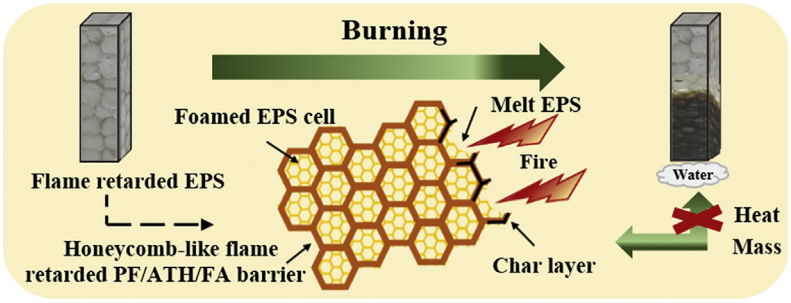
HIGHLIGHTS

- A cheap and effective flame retarded EPS system was developed.
- A synergistic effect of flame resistance between fly ash and aluminum hydroxide was found.
- Fly ash enhanced the compactness of char layer with improved flame resistance and smoke suppression properties.
- The main flame resistance mechanism was the effective barrier effect of the char layer.

GRAPHICAL ABSTRACT



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ABSTRACT

A cheap and effective flame retarded EPS system was developed by using a high silica content based fly ash (FA) synergistic with aluminum hydroxide (ATH) in the thermosetting phenolic resin (PF) coating layer. In this study, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analyses confirmed the formation of a barrier layer which uniformly encapsulated each EPS microsphere. The flammability of EPS-PF/ATH/FA foam with different compositions were characterized by the limited oxygen index (LOI) and UL-94 vertical burning tests, an evident flame retardant effect has been observed with up to 29.6% LOI value and UL-94 V-0 rating. The cone calorimetric analysis (CONE) indicated that the heat release rate (HRR), total heat release (THR) and smoke production rate (SPR) of the resulting EPS-PF/ATH/FA foam decreased obviously, and the foam maintained structural integrity after combustion. The thermal stability of EPS-PF/ATH/FA foams has been evaluated by the thermogravimetric analysis (TGA). It is obvious that the presence of PF-ATH/FA flame retarded binder has delayed the pyrolysis process of EPS matrix by about 10 °C. From analysis conducted on the combusted residues, it can be inferred that the dominant flame retardant action of EPS-PF/ATH/FA foam occurred in the compact char layer, which acted as an effective fire-proofing and heat shielding barrier in the condensed phase.

1. Introduction

EPS foam has been extensively used in construction, packing materials, marine and automobile due to its appealing features such as excellent thermal insulation properties, moisture resistance, effective buffering, good chemical resistance, the convenience of processing, light weight, low cost, etc [1–3]. However, EPS foam is extremely flammable and difficult to be flame retarded

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because of their chemical compositions and large specific surface areas [4]. It can be easily ignited with a LOI value of only 18.0%, with no UL-94 rating. The pyrolysis of EPS complies with a radical chain mechanism, and volatile products which can act as the fuels are produced with the toxic black smoke during the combustion [5]. Lots of serious fire disasters caused by the poor flame retardation of EPS foam have posed great threats to people's properties and lives in recent years [6,7]. Therefore, it is imperative to improve the flame resistance properties of EPS foams. Previous efforts have almost exclusively focused on incorporating halogenated flame retardants into polystyrene matrix before expansion by copolymerizing or blending method [8], while the halogenated flame retardants are environmentally hazardous and toxic to the human body [9]. Thus, the use of halogen-free flame retardants to reduce the flammability of EPS foam and fume products has become a crucial part of the application for EPS materials [10,11]. Recently, the coating method with halogen-free flame retardants has become a promising way to protect materials against fire due to the diversity of flame retardants and the simplicity of processing [12,13]. The flame retarded EPS foam is usually carried out by treatment of EPS microspheres adopting halogen-free flame retardants coating technology followed by foaming and molding. Many thermosetting resins have been used as binders, such as amino resin [4], epoxy resin [12], melamine resin [14] and phenolic resin [15] because of their inherent flame resistance as well as their good compatibility with EPS microspheres and inorganic fillers [16]. The phenolic resin is widely used in flame retardants due to its effective heat resistance, self-extinguishing, low smoke, resistant flame penetration properties. Moreover, phenolic resin materials have good mechanical properties, especially with outstanding instantaneous high temperature burning performance [17].

Hydrated mineral fillers, such as aluminum hydroxide and magnesium hydroxide are widely used flame retardants. In terms of aluminum hydroxide, the dominant flame retardant mechanism is the endothermic dehydration reaction which leads to the dilution of combustible gases and the cooling of flame zone [18,19]. However, to effectively reduce the fire hazards, very high loadings is necessary, which leads to a significant deterioration of the mechanical performance [20]. Efficient barrier effect is another crucial flame retardant mechanism [21]. When EPS foams degrade during combustion, a barrier layer is subsequently formed due to the aggregation of hydrated mineral at the surface, and this layer cuts off the supply of flame with flammable gases and protects the underlying polymer from burning [22–24]. Nonetheless, the EPS foams cannot satisfactorily meet the flame retardant requirement with a single addition of hydrated mineral flame retardant [11].

To enhance the flame retardant properties of hydrated mineral filled thermosetting flame retarded binder, different additional halogen-free flame retardants can be used as synergistic agents, such as SiO_2, Fe_2O_3, clay, etc [9]. These fillers used in combination with flame retardants can facilitate the formation of compact residues and subsequently enhance the fire-proofing and barrier effects [23]. Although these fillers are effective to improve the flame retardant system, they are expensive to be used in the application. It is desirable to explore some cheap and effective agents to improve ATH derived flame retardant system. Fly ash generated in thermal power plants during the combustion of coal as a waste or by-product is mainly composed of SiO_2 and Al_2O_3 [25,26]. Most fly ash disposal methods eventually lead to the dumping of ash on open land, and the environmental hazards of fly ash have been fully recognized [26].The comprehensive utilization of fly ash has already been done in agriculture as soil amelioration agent, geopolymers, high value fly ash concrete, mesoporous materials, etc [27], while it has not been received much attention as a potential fire retardant.

The present work aims to investigate the synergistic flame resistance effect of a kind of fly ash on flame retarded EPS-PF/ATH foam. ATH and FA provided their own action towards flame resistance property improvement of EPS foam. A cheap and effective hybrid flame retardant system has been developed in this work. The combustion performance for EPS foam samples was evaluated, the morphology of combusted residues and the flame retardant mechanism were also characterized and analyzed.

2. Experimental details

2.1. Materials

EPS beads, with a granule size of 1.0–1.2 mm, were an industrial product of Qingdao Chemical Co., Ltd, China. The phenolic resin was supplied by Shandong Shengquan Chemical Co., Ltd, China. Aluminum hydroxide was generously supplied by Qingdao Hainuozhongtian Chemical Co., Ltd, China. Class F fly ash obtained from the thermal power plant at Qingdao in China was used as silica source in this investigation, consisting a total silica (40.5%) and aluminum oxide (16.7%) composition of 57.2%.

2.2. Preparation of the flame retarded EPS foam

The process to produce flame retarded EPS foam is illustrated in Fig. 1. A stable and compatible inorganic–organic hybrid binder was firstly prepared by mixing thermosetting PF and synergistic fillers (ATH/FA) together. The formulation is summarized in Table 1. At the second stage, the calculated amount of EPS microspheres were mixed with flame retarded binder until a homogeneous physical blocking layer was formed during the process of blending. At the last stage, the EPS beads with a thin physical barrier layer were filled into a molding device to expand under 100 °C steam, and then the resulting EPS foam sample with sufficient rigidity for demolding was taken out and post cured at 50–60 °C for at least 4 h. Finally, the well-squeezed flame retarded EPS foam with honeycomb-like barrier structure was obtained.

2.3. Characterization methods

2.3.1. The limited oxygen index test

LOI test was conducted on a CF-3 oxygen index apparatus (Jiangning Analysis Instrument Co., China). The specimens used for the test were $100 \times 10 \times 10$ mm^3 according to ISO4589.

2.3.2. The UL-94 vertical burning test

The UL-94 vertical burning test was carried out on a CZF-3 horizontal and vertical flame tester (Jiangning Analysis Instrument Co., China) with specimen dimension of $127 \times 12.7 \times 10$ mm^3 according to UL-94 ASTM D3801. Five specimens for each sample were tested in the burning measurements.

2.3.3. Butane spray combustion test

Jet 800 °C flame with a butane spray gun for 3 min at a constant distance of 5 cm, meanwhile, a digital camera was used to record the phenomena generated during the combustion. The specimens used for the test were $50 \times 50 \times 50$ mm^3.

2.3.4. Cone calorimeter test

An FTT standard cone calorimeter (Fire Testing Technology Limited, UK) was used to evaluate the flammability of samples according to ISO5660. The specimen with a dimension of $100 \times 100 \times 10$ mm^3 was irradiated with an external heat flux of 50 kW/m^2 which represented a moderate fire [11]. The measured flammability parameters included HRR, THR, SPR and mass retention (MR).