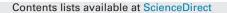
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Water-based flame retardant coating using nano-boehmite for expanded polystyrene (EPS) foam



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ABSTRACT

Expanded polystyrene (EPS) foam has been successfully flame retarded by a water-based coating containing nanoparticles of boehmite and poly(vinyl alcohol) (PVOH) as char former. Boehmite enhances the charring of PVOH. The influence of suspension viscosity, coatings number, impregnation time and drying method was studied to monitor the amount of coating deposited and the coating thickness. The coating suspension is able to penetrate into the core of the foam. EPS without hexabromocyclododecane (HBCD) is upgraded from F to E rating according to the NF EN ISO 11925-2 standard when the penetration of coating suspension into the core is high enough, due to the formation of a char layer reinforced by nano-boehmites even if EPS does not shrink away from the flame.

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1. Introduction

Since the beginning of the twentieth century, synthetic polymers have become increasingly important materials in industry. As plastic processing technologies, the addition of a blowing agent became a natural extension of polymer processing. Presently, foam extrusion, injection molding, molded bead, x-linked foam, reactive foaming, and gelation are well-known methods of making polymeric foams, and polymeric foams have become a well-developed branch in the polymer industry. The most successful polymeric foam is probably expanded polystyrene (EPS) due to its numerous useful advantages, such as good cushioning properties, acoustical and thermal insulation, ease of processing, low cost and light weight [1]. Nevertheless EPS presents serious fire hazards and needs to be flame-retarded [2].

Expanded polystyrene is typically made by suspension polymerization of a mixture of styrene monomer(s) and flame retardant in water to form beads of styrenic polymer. The small beads (e.g., averaging about 1 mm in diameter) are pre-expanded with steam and

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http://dx.doi.org/10.1016/j.porgcoat.2016.04.036 0300-9440/© 2016 Elsevier B.V. All rights reserved. molded again with steam to produce large blocks (e.g., up to several meters high and 2–3 m wide) that are cut in the desired dimensions. Flame retardants for expanded polystyrene foams have many requirements including thermal stability, substantial solubility in styrene, and high flame retardancy. Hexabromocyclododecane (HBCD) is widely used in thermoplastic polymer compositions to impart flame retardant properties to the compositions. EPS foams fire retarded with typically low levels of HBCD (0.5–1 wt%) [3], provide adequate time for occupants to escape in the event of fire and contribute to protect human lives and property from fire.

Currently, HBCD is the most popular flame retardant in EPS. Nevertheless, some halogenated flame retardant chemicals are now recognized as global contaminants and are associated with adverse health effects in animals and humans, including endocrine and thyroid disruption, immune-toxicity, reproductive toxicity, cancer, and adverse effects on fetal and child development and neurologic function [4–6]. Therefore, the application of halogenated flame retardant has been strictly regulated, or even banned in some countries. In February 2011, the European Union announced that HBCD, the brominated flame retardant used in polystyrene building insulation, will be banned. The REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) identified HBCD as being persistent in the environment, bioaccumulative in biological systems, and toxic. HBCD has been moved from the "candidate list" of chemicals under review. The ban of HBCD took effect effective on August 21, 2015 and is implemented through the European Union's REACH program [7].

Due to this problematic, the research on a new alternative for environmentally friendly flame retardant to replace HBCD becomes an urgent and a great interest for academics and industries.

Besides HBCD, other halogenated [8,9] or halogen-free [10-13] flame retardant systems have been used. Nevertheless, halogen-free flame retardants generally need to be used in larger amounts to be effective. The incorporation of such large amounts of additives in foam can prevent the foam processing. Therefore, flame retardant coating appears as an ideal method to reduce the flammability of EPS foam. Several teams have developed such coatings [14-17].

To the best of our knowledge, all these coatings contain halogenated compounds. Then there is still a need to propose a more environmentally friendly flame retardant coating. Poly(vinyl alcohol) (PVOH) considered as environmentally friendly is a good choice for polymer coating due to its good adhesion property with substrate, no need solvent in coating process, and its charring behavior during burning. As other metal hydroxides, boehmite and pseudo-boehmite have already used to impart flame retardancy in a couple of polymers: ethylene-vinyl acetate copolymer [18,19], polycarbonate/acrylonitrile butadiene-styrene blend [20], poly(methyl methacrylate) [21], polyethylene [22], polyamide 6 [22], polyamide 11 [23], polyester [24,25], polyethersulfone [26] or PVOH [27]. As both boehmite and PVOH are hydrophilic, boehmite can be incorporated into PVOH without pretreatment, only by simply dispersing the two components in water. The dispersibility of boehmite in water is an advantage to obtain the water-based flame retardant coating in a water soluble polymer. It has already been proved that pseudo-boehmite nanoparticles disperse very well in PVOH and improve significantly its flame retardancy: limiting oxygen index increases from 19.5 for pure PVOH to 30 for PVOH filled with 37.5 wt% of pseudo-boehmite nanoparticles. Moreover these nanoparticles enhance charring of PVOH [27]. This article describes the results of a collaborative work concerning the development of a flame retardant coating for EPS foams and leading to three patents [28–30]. The efficiency of the coating to improve the flame retardancy of EPS foams is assessed according to the NF EN ISO 11925-2 standard which is generally required for many applications of EPS foams. Two EPS foams (with and without HBCD) are used to identify the possible synergism or antagonism between the developed coating and HBCD whose modes-of-action are different.

2. Materials and methods

2.1. Materials

Precipitated boehmite mineral filler under commercial name of CAM was supplied by Saint Gobain Ceramic Materials. It has ellipsoid particle shape, a specific surface area (BET) of $149 \text{ m}^2/\text{g}$, pores

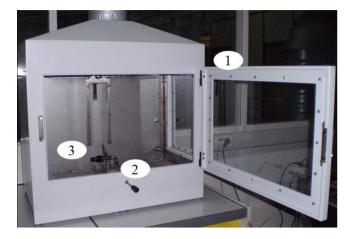


Fig. 1. Standardized single flame source fire test apparatus NF EN ISO 11925-2 and their main components.

volume and mean pore size of 0.43 cm³/g and 11.5 nm respectively (data from manufacturer).

The partially hydrolyzed polyvinyl alcohol (PVOH) was purchased from SEKISUI and used without any purification. Its degree of hydrolysis is 87–89 mol%, with viscosity of 24.5–27.5 cPs, and pH of about 5–7.

Two types of EPS were used as substrate of coating, EPS without HBCD with apparent density of $14.16 \pm 0.33 \text{ kg/m}^3$, and EPS-HBCD with apparent density of $16.17 \pm 0.51 \text{ kg/m}^3$. For dip coating in aqueous coating dispersion, EPS blocks were sized according to the required dimensions for fire tests: $250 \times 90 \times 60 \text{ mm}^3$.

2.2. Processing methods

2.2.1. Preparation of aqueous coating dispersion

Dried filler was pulverized in a pulverizator during 10 s at 6000 rpm. The pulverized filler was then dispersed in de-ionized water under mechanical mixing during 4 h. The 16 wt% of aqueous PVOH solution was prepared by dissolving the polymer in de-ionized water at around 80 °C for 4 h under mechanical mixing, until a homogeneous solution was formed. After cooling to room temperature, 1000 g of the coating suspension was prepared by mixing 625 g of 18 wt% of filler aqueous dispersion with 375 g of 16 wt% of PVOH solution. The whole solution was stirred vigorously until a homogenous dispersion was obtained. Consequently, the filler/polymer weight ratio in dried film is fixed to 65/35. To obtain the dried film (studied in Section 3.1), 5 g of aqueous coating dispersion was dried in a petri dish.

2.2.2. Static dip coating method of EPS block

The dip coating process was applied on the EPS-HBCD samples as required for preliminary assessment of their fire behavior. The first step consists in a 5 min manual dipping system in coating solu-

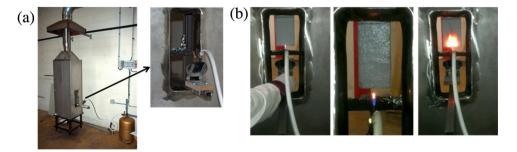


Fig. 2. Simulated single flame source fire test NF EN ISO 11925-2 apparatus (a) and (b) burning process.

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