Journal of Alloys and Compounds 743 (2018) 108–114

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Comparative study on flame retardancy of silica fume-based geopolymer activated by different activators

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ARTICLE INFO

Article history:
Received 14 October 2017
Received in revised form
15 January 2018
Accepted 22 January 2018
Available online 31 January 2018

Keywords:
Flame retardancy
Geopolymer
Silica fume
Micro-structure
Composite

ABSTRACT

With the thirst for exploring an eco-friendly and cost-effective flame retardant, the silica fume-based geopolymeric coating was prepared with 20 different activators by sol-gel method using expanded polystyrene (EPS) board as carrier. Its flame retardancy was measured by limit oxygen index (LOI), vertical burning (UL-94), and cone calorimetric test (CCT). The micro-structure was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR), fourier transform infrared spectroscopy (FT-IR), and thermogravimetry/differential scanning calorimetry (TG/DSC), respectively. Results showed that the sample activated by KOH/Na_2SiO_3 exerted the highest flame retardancy with a dense and smooth morphology, which highly facilitated the reaction of "depolymerization-rearrangement" process, favored the formation of Q^4_2 structures and cross-linkages, leading to an increase in the content of bound water wrapped within matrix. When the novel siliceous thermal barrier layer was covered on the surface of EPS, and its flame retardancy was improved significantly, such as the enhancements of time to ignition (TTI) and LOI, companied with decrease in peak heat release rate (p-HRR). Finally the effect of alkali-activators on the flame retardancy of silica fume-based geopolymeric coating was elucidated, the K^+ owning to its low pH-dependent and weak affinity to water, together with Na_2SiO_3 was beneficial for the formation and growth of siliceous gels.

1. Introduction

With the development and research of building techniques, EPS insulation systems have been widely used for building's envelopes as roofs, floors, and walls, which hold low density, excellent impact resistance, low energy consumption, and recyclable feature, but the key issue is the inflammability that limits its extensive applications [1]. Consequently flame retardant has been energetically advocated in recent decades, the chlorinated and brominated flame retardant held very large market share due to the formation of gas phase products of incomplete combustion and increased char yield, which enhanced the flame retardancy through release of nonflammable gases, endothermic reactions, and charred layer. However, the simultaneous release of toxic gases and smoke has raised concerns over environmental pollution, when the flame-retarded EPS burns during heating or high temperature, contributed to the predominating cause of injuries or property damage involved in city conflagration. The halogen flame retardant modified EPS has been a huge reservoir of toxic, bioaccumulative, and persistent organic pollutants [2], sufficient attentions have been devoted to reducing or eliminating the toxicity via replacing the halogen element with nontoxic or less-poisonous compound as Si, P, and N.

Morgan [3] suggested that silicate was used as a combination filler/preceramic system for providing thermal protection to the underlying polymer through formation of a protective ceramic barrier on top of the polymer. Metakaolin-based geopolymeric coatings on both stainless and mild steel substrates were prepared to improve their thermal barriers [4], and fly ash was exploited in intumescent formulation to reduce the flammability of wood [5]. Organo-modified nanoclays have attracted considerable attentions for improving the thermal stability of expansive flame retardant material [6,7]. Shen [8] pointed out that rice husk pyrolysis char and porous silica could convert into the homogeneous carbon–silica nano-composites, Wang [9] proposed the synergistic effect between MCM-41 and intumescent flame-retardant in natural

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https://doi.org/10.1016/j.jallcom.2018.01.302
0925-8388/

rubber composites. Khobragade [10] found that organo-modified clay surfaces might decompose at high temperatures, rendering organo-modification problems in melt-compounding and decreasing the flame retardancy of nano-composites. Therefore, organic-inorganic hybrid coating has been the developing trend for the flame retardant, which could improve the thermal stability of organic coating, and also created added-value of inorganic materials.

On the other hand, inorganic oxide fillers could be used as building blocks in nanocomposites, which included spherical silica particles, layered silicates (e.g. montmorillonite), alumina, and nanotubes. Among inorganic oxide fillers, the silica particles have received increasing attentions due to their well-defined ordered structure, high surface area, cost-effective production, and the ease surface modification [11]. Laoutid [12] evaluated the flame retardant effect of hydrated lime, partially and completely hydrated dolomitic limes in polyethylene and ethylene vinyl acetate copolymers, and pointed out that calcium hydroxide fraction played an important role in the generation of an intumescent mineral residue during combustion. Zia [13] suggested that synergistic effect of clay and wollastonite towards heat shielding, char expansion, morphology, composition, gaseous products, and residual weight, enhanced the fire protection of reinforced intumescent fire retardant coating. Zhu [14] confirmed that appropriate addition of nano-silica into traditional IFR system could improve the fire protection properties. The nano-silica has attracted extensive attentions for improving the ageing resistance of organic structural materials [15,16], due to its strong hydrophilicity, resulted in the hardly dispersal to form a homogeneous distribution.

However, the concept of “end-of-waste” requires the possibility to consider a waste product as secondary raw material instead of a refuse, which is a revolutionary assumption introduced in the European Directive on Waste [17]. Silica fume, a by-product of silicon ferroalloys, holds pozzolanic reactivity and filler effect, which could be transformed into sol enriched $Si(OH)_4$ under an alkaline solution, followed by coagulation, colloids formation, gel formation, and restructuring, resulted in the formation of an amorphous aluminosilicate matrix named geopolymer [18]. Giancaspro [19] found that a thin layer of fire-resistant paste composed of geopolymer and hollow glass microspheres was applied to the facing to serve as a protective fire barrier and to improve the fire resistance. The noncombustible aluminosilicate matrix held a strong adhesive force on the surface of EPS due to its volumetric water absorption and the mercerization [20,21], and also a flame-retardant effect in theory, but the investigations on the flame retardancy of silica fume-based materials are lacking. Therefore, novel alkali-activated silica fume-based flame retardants were prepared via sol-gel method, the characterizations were conducted by varied techniques including the LOI test, vertical burning (UL-94) test, CCT, SEM, ^{29}Si MAS NMR, TG/DSC, FT-IR, and XRD.

2. Experiment and methods

2.1. Preparation of silica fume-based coating

2.1.1. Raw materials

Silica fume, a kind of grey powders, was obtained from Linyuan Co. of Xi'an in ShanXi province with a density of 1.62 g cm^{-3} and a Blaine specific surface area of 25 $m^2 g^{-1}$, the content of SiO_2 analyzed by X-ray fluorescence (XRF) was 87.18% as shown in Table 1. Chemical activators, analytically pure $Na_2SiO_3 \cdot 9H_2O$, KOH, and NaOH, were produced in HongYan reagent factory of Tianjin. Polydimethylsiloxane (PDMS), as the modifier to improve the water resistance, were purchased from with a kinematic viscosity of 350 $mm^2 s^{-1}$. Polyacrylamide (PAM), served as the thickener and film-forming agent, was produced by the reagent factory of Shanghai. Expandable graphite (EG), served as the charring agent to improve flame retardancy, was obtained from Qingdao chemical group with an expansivity of 300 and a grain size of 48 μm. Titanium dioxide served as the pigment was purchased from HongYan reagent factory of Tianjin with an average grain size of 25 μm. The EPS was purchased from thermal insulation material factory of Xi'an with a thermal conductivity of 0.041 W $(m K)^{-1}$.

2.1.2. Preparation of silica fume-based coating

The sol riched in $Si(OH)_4$ was prepared by dispersing 50 g silica fume into the chemical activator mixture under magnetic stirring at 60 rpm and 60 °C, which included Na_2SiO_3, NaOH, or KOH as shown in Table 2, the addition process lasted about 0.5 h. And then the PAM, PDMS, EG, and TiO_2 were added into the aforesaid sol in order under stirring, the content of them were 1 wt%, 1.5 wt%, 3 wt%, and 5 wt% respectively, followed by stirring at 60 rpm and room temperature for 1 h and standing the solution for 10 h, finally the silica fume-based coating was obtained from the filtrate through a suction filtration. The samples were numbered S1 to S20 with the unmodified EPS as the reference numbered S0.

2.1.3. Preparation of EPS coved by silica fume-based coating

The EPS was employed as the carrier to evaluate the flame retardancy of silica fume-based coating, which was brushed on the surface of EPS for 3 times, the interval time was about 20 min. The surface drying time and drying time were 18 min and 2 h, respectively. After brushing the silica fume-based coating on the EPS for 3 times, the coating thickness was approximately 0.8 mm tested by the film thickness gauge (PosiTector 200, America). The adhesive force of coating belonged to the three-level grade according to the GB/T9755-2001 standard of synthetic resin emulsion coatings for exterior wall, which satisfied requirement of common engineering applications.

2.2. Characterizations

2.2.1. Flame retardancy

The LOI test was measured on an oxygen index meter (DX8355, Guangdong Daxian Instrument Co., China) according to ASTM D2863-2008 with $65 \times 6.5 \times 3.0$ mm^3 specimens. Vertical burning (UL-94) test was performed on a vertical burn instrument (DX8522, Guangdong Daxian instrument Co., China) according to ASTMD 2863-2008 with $125 \times 13 \times 3.0$ mm^3 specimens. CCT was performed on a cone calorimeter (ZY6243, Zhongnuo instrument Co., China) according to ISO 5660 with $100 \times 100 \times 3$ mm^3 specimens. The external heat flux was 30 kW m^{-2}. The TTI was observed by naked eye, the p-HRR and total heat release (THR) were calculated, the fire performance index (FPI) was defined as the ratio of TTI to peak heat release rate, which was considered as an important parameter to evaluate the propensity to flashover in a full-scale fire, the smaller the value of FPI, the greater the tendency for flashover [22]. The retardant appearance of p-HRR imparted a longer escape time, and the lower value of HRR meant an inferior destructive capacity.

2.2.2. Microstructure analysis

Micro-morphology observation was recorder by Quanta 200 SEM under 20 kV voltage. XRD patterns of samples were detected by D/MAX-2400 X-ray diffractometer equipped with a rotation anode using Cu Kα radiation. TG/DSC curves of samples during the heating process of 50–950 °C were measured by Mettler analyser under nitrogen atmosphere with a heating rate of 20 °C min^{-1}. FTIR spectra were measured using FTIR-650 spectrometer in absorption mode, the range was 3000–500 cm^{-1} with a spectral resolution of