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Benign design and the evaluation of pyrolysis kinetics of polyester resin based intumescent system comprising of alkali-activated silica fume

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ABSTRACT

Novel polyester resin based intumesced flame retardant (IFR) coating was fabricated via a facile sol-gel method, which was modified by the Na_2SiO_3 alkali-activated silica fume. The emphasis was placed on its flame retardancy and pyrolysis kinetics, it focused on benign design and in-depth research on the flame retarding mechanisms of the inorganic-organic hybrid coating. The results demonstrated that the specimen doped alkali-activated silica fume (2 wt%) exhibited the highest flame retardant efficiency through cone calorimeter (CC) test, evidenced by the peak heat release rate (p-HRR) value of 128 kW m^{-2} (decreased by 42.1% compared with the sample without silica fume). Pyrolysis kinetics calculated using modified Coats-Redfern integral method determined that the D_3 diffusion model governed the pyrolysis process, due to the formation of silicon phosphate and sodium silicate, as well as the continuous protecting layer, leading to an increase in the value of E_a during 112–251 °C. It established that the incorporation of appropriate Na_2SiO_3 activated silica fume in polyester resin based IFR was conducive to benign design of inorganic-organic hybrid coating.

1. Introduction

The research and development of flame retardants has contributed a lot to the human security, which mainly are divided into the following categories: halogenated and organic phosphorus flame retardant, intumescent flame retardant (IFR), and the inorganic-organic hybrid. Halogenated and organic phosphorus flame retardants have dominated the market owing to their high inhibiting effects on free radical reaction during combustion, but environmental hazards are generated due to their toxicity and hardly degradation or recycling. As persistent organic pollutants for contaminating environment, they pose huge threat to the human health and biodiversity [1], there is therefore a significant effort made by technologist and scientist to develop an alternative to them with increasing environmental consciousness. IFR, as a new type of flame retardants with low smoke and toxicity, consists of an acid source, a carbonizing agent, and a blowing agent, which are dispersed in polyester or acrylic resin, forming a swelling carbonaceous char during the process of combustion, but weak heat stability and water-repellency properties limit its extensive applications [2,3], and the benign design of IFR composite is still at nascent stage and required for further improvements. Consequently, the inorganic-organic hybrids have attracted considerable attentions through doping novel nano-fillers [4,5], as silicates, clays, inorganic hydroxides, carbonaceous materials, metal oxides, polysilsequioxanes, and their combinations are employed to prepare flame retardant for enhancing fire resistance efficiency. The formation of compact and intact char layer during combustion imparts thermal insulation and barrier effect for inhibiting the formation and escape of volatiles [6]. Mechanisms involved in flame retardants are manifested as the physical effects including (i) cooling effect, (ii) fuel dilution, or (iii) formation of a protective layer (coating), and the chemical effects containing (i) gaseous and (ii) condensed phase [7].

Furthermore, hotspots of flame retardants have gradually transformed into designing novel hybrid materials, which meet the requirements of recycling and sustainability, besides an effective flame resistance. And the new flame retardant chemistry would be using ceramic/glass precursors, which melt under fire conditions to form a protective ceramic/glass shield on the surface of the burning polymer [8]. Therefore, the modified metakaolin based geopolymer was employed to prepare fire resistant coating due to its amorphous and noncombustible features [9,10]. Tang et al. [11] suggested that polyaromatic rings connected with P, N, and Si were formed by introduction

Abbreviations: IFR, intumescent fire retardant; TG, thermogravimetry; DTG, derivative thermogravimetry; SEM, scanning electron microscopy; XRD, x-ray diffraction; APP, ammonium polyphosphate; PER, pentaerythritol; CC, cone calorimeter; TTI, Time to ignite; HRR, heat release rate; FPI, fire performance index; FGI, fire growth index; p-HRR, peak heat release rate; WL, weight loss; THR, total heat release; av-EHC, average effective heat of combustion; IPN, inter-penetrating polymer network

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Table 1
Ingredients of IFR coatings comprising of alkali-activated silica fume (wt%).

Samples	Polyester resin/%	PER/%	APP/%	Urea/%	$Na_2SiO_3{\cdot}9H_2O$/%	H_2O/%	Silica fume/%
S0	14.81	7.41	12.96	7.41	1.85	55.56	0
S1	14.81	7.41	12.96	7.41	1.85	55.56	1
S2	14.81	7.41	12.96	7.41	1.85	55.56	2
S3	14.81	7.41	12.96	7.41	1.85	55.56	3
S4	14.81	7.41	12.96	7.41	1.85	55.56	4

of modified kaolinite, which migrated to the surface during combustion and reacted with IFR, forming a ceramic-like silicon-phosphate structure for restraining heat and mass transfer. Kumar et al. [12] suggested that adding 8 wt% fly ash in intumescent formulation improved its flame retardancy, and organo-modified nanoclay was also employed to prepare coatings [13]. Xiao et al. [14] pointed out that the additional of 1 or 2 wt% organoclay caused reduced heat release rate (HRR), smoke production rate, and total smoke production. Mustafa et al. [15] investigated the synergistic effects of mineral fillers (clay and wollastonite) based IFR coating, suggested that additional Si-O containing functional groups were determined for its high-temperature stability. Zhou et al. [16] suggested that hollow glass microsphere promoted the formation of dense and compact charred layers, which prevented the charred layers from cracking. Because silicone-based fire-retardant additives are less toxic than additives based on phosphorus and halogen [17], and also the siliceous nanoparticles possess other remarkable properties such as high photo and thermal stability, chemical inertness, bright, and wavelength tunable emission with long fluorescence lifetime [18], there is thereby an urgent need but it is still a significant challenge to rationally design and delicately tailor for advanced fire resisting and highly efficient IFR.

Our previous study found that alkali-activated silica fume modified by polydimethylsiloxane and polyacrylamide exhibited high flame retardant efficiency and thermal stability [19], ascribed to the enriched amorphous silica sol, which was formed through alkali-activation of silica fume (an industrial solid waste during production of ferrosilicon). And it is beneficial to form a compact siliceous protective layer after chemical activation in theory [8], but the explorations to investigate the effect of alkali-activated silica fume on the fireproof performance of IFR are lacking, and the pyrolysis kinetics of IFR comprising of silicate is rarely reported. Consequently, the preparation of novel IFR coating with Na_2SiO_3 activated silica fume was investigated with plywood as the carrier, the target of this study focuses on providing an in-depth evaluation of flame retarding mechanisms, boosting the development of cost-efficient and eco-friendly IFR coating using industrial solid waste. The optimum content of silica fume was established by the flame retardancy, which was tested under a cone calorimeter (CC). The pyrolysis kinetics calculated using modified Coats-Redfern integral method aimed to elucidate the retardant mechanisms of alkali-activated silica fume doped IFR, and the structure characterization was conducted by the techniques as scanning electron micrograph (SEM) and x-ray diffraction (XRD).

2. Experience and methods

2.1. Raw materials

Silica fume was collected from the Linyuan company of Xi'an, and the experimental silica fume was obtained sequentially through water flotation, filtration, drying the filtrate, mechanical ball-milling, and sieving. After abovementioned preprocessing techniques, the starting material of silica fume held a density of 1.62 g cm^{-3} and Blaine specific surface area of 25 $m^2 g^{-1}$, the chemical composition tested by X-ray fluorescence was 87.18 wt% SiO_2, 6.89 wt% Al_2O_3, 1.18 wt% Fe_2O_3, 0.66 wt% K_2O, 0.60 wt% CaO, 0.45 wt% MgO, 0.28 wt% Na_2O, 0.32 wt % SO_3, and 2.11 wt% loss on ignition. The analytically pure $Na_2SiO_3{\cdot}9H_2O$, as the alkali-activator to convert the silica fume into siliceous sols, was purchased from Tianjin Fuchen chemical reagent company. The starting materials of IFR coating contained analytically pure polyester resin, ammonium polyphosphate (APP), urea, and pentaerythritol (PER), were all purchased from Shanghai chemical reagent company. The plywood was purchased from timber processing plant of Xi'an with second-class flame retardancy.

2.2. Preparation of samples

The siliceous sol was prepared by slowly dispersing silica fume into the alkali-activated solution within 5 min, which consisted of 1 g $Na_2SiO_3{\cdot}9H_2O$ and 30 g distilled water as shown in Table 1, and the beaker was placed in a magnetic stirrer of 60 r min^{-1} under 60 °C. The content of silica fume was 0.54, 1.08, 1.62, and 2.16 g, respectively, which were numbered as S1, S2, S3, and S4. The IFR coating without silica fume was numbered S0 with the unmodified raw plywood denoted Sr as the control. And then the 4 g PER, 7 g APP, 4 g urea, and 8 g polyester resin were added sequentially under 60 °C within 3 min, maintained a continuous stirring of 200 r min^{-1} approximately 30 min to form a homogeneous paste, with a bottom concave glass covered on the beaker for restraining evaporation. Finally, the paste binder was manually brushed on the surface of plywood with a thickness of less than 0.5 mm tested by the film thickness gauge (PosiTector 200, America), the angle between the brusher and plywood surface was 55–65°, the surface drying time and drying time were 32 min and 2.2 h, respectively. The amount of coating was approximately 500 g m^{-2}.

2.3. Characterizations

CC (ZY6243, Zhongnuo instrument Co., China) test was carried out on the samples of 100 × 100 × 3 mm^3 according to BS ISO 5660-1:2015. The specimens were conditioned to equilibrium at 70% and 28 °C prior to testing. Each specimen wrapped in a single layer of aluminium foil was exposed horizontally to an external radiation intensity of 40 kW m^{-2}. During the test, the following parameters were determined including HRR, time to ignite (TTI, s), peak heat release rate (p-HRR, kW m^{-2}), total heat release (THR, MJ), average effective heat of combustion (av-EHC, MJ kg^{-1}), and weight loss (WL), the av-EHC was calculated by formula av-EHC = THR/WL.

Non-isothermal pyrolysis kinetics was investigated by thermogravimetric (TG) analysis in the Mettler analyzer (Germany) under nitrogen atmosphere during the heating process of 50 ~ 950 °C with a heating rate of 20 °C min^{-1}, the sample was obtained by vertical cutting the sample about 10 mg and smashed into powder.

The SEM of the char layer after CC test was observed by a Quanta 200 SEM under 20 kV previously covered by a conductive golden layer, and the coating sample after burning was selected a flake char layer with an area approximately 0.8 mm^2. The XRD patterns of samples before and after CC test were recorded by a D/MAX-2400 X-ray diffractometer equipped with a rotation anode using Cu Kα radiation.