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Influence of nano-silica on the flame retardancy and smoke suppression properties of transparent intumescent fire-retardant coatings

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ABSTRACT

A cyclic phosphate ester acid (PEA) was synthesized by the reaction of phosphoric acid (PA), pentaerythritol (PER) and *n*-butyl alcohol (BA). Then nano-silica was successfully introduced into the structure of PEA to obtain SPEAs with different nano-silica contents. The chemical structures of PEA and SPEAs were confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR). A series of fire-retardant coatings coated on the plywood boards were prepared by mixing of melamine formaldehyde resin with PEA and SPEAs. The transparency analysis indicates that the incorporation of nano-silica into the coatings through chemical grafting method acquires high degree of transparency due to the homogeneous dispersion of each element in the coatings, judging by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The influence of nano-silica on the thermal stability, flame retardancy and smoke suppression properties of coatings were investigated in details by cabinet method test, tunnel method test, cone calorimeter test, smoke density test, thermo-gravimetric analysis (TG), FTIR, SEM and EDS. The results show that the values of weight loss, char index, flame spread rating, heat release rate, total heat release, smoke production rate, total smoke release and specific optical density of the coatings are remarkably decreased with the introduction of nano-silica, which is due to the formation of a compact and intumescent char layer during combustion. The TG results demonstrate that the incorporation of nano-silica increases the thermal stability and residual weight of the coatings. The char residue analysis reveals that the nano-silica enhances the char-forming ability, intumescence and antioxidation property of the coatings due to the synergistic effect existed between phosphorus and silicon, leading to a stronger shielding effect in condensed phase. Based on these facts, the introduction of nano-silica could promote the formation of a more compact and intumescent char layer and then effectively reduces the heat and smoke release, thereby enhancing the flame retardancy and smoke suppression properties of coatings.

1. Introduction

The use of intumescent fire-retardant coatings is one of the most effective ways to protect substrates against fire. When heated, intumescent fire-retardant coatings can swell and form a thick porous layer, which acts as a physical barrier to prevent the underlying material against the flame or heat [1]. The traditional intumescent fire-retardant coatings are prepared by physically blending the intumescent flame retardants with matrix resin directly, which usually lead to the opacity of coatings [2,3]. However, some special facilities such as ancient buildings, culture relics, heritage conservations and architectural decorations need to use transparent intumescent fire-retardant coatings for maintaining their original morphology [4]. Therefore, it should be given great attention on the research and developing of transparent intumescent fire-retardant coatings.

Generally, transparent intumescent fire-retardant coatings are prepared by combining the reactive-type flame retardants with matrix resin rather than by mixing the additive-type flame retardants with matrix resin directly, which usually consist three active ingredients (acid source, carbon source, blowing agent) in the chemical structure of the coatings [4,5]. Phosphorus-containing compounds as a typical kind of reactive-type flame retardant contain both carbon source and acid source, which can react with matrix resin and then form transparent fire-retardant coatings grafting flame retardant segments [6–8]. Phosphate ester acid (PEA) with cyclic structure is considered as a promising flame retardants for preparing transparent fire-retardant coatings with high fire protection efficiency [9]. Hu et al. synthesized a cyclic polyphosphate by the reaction of polyphosphoric acid, pentaerythritol

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and polyethylene glycol through a two-step reaction, and then reacted with amino resin to obtain novel transparent fire-retardant coatings [4]. Shi et al. synthesized novel PEPA-containing polyether flame retardants by the reaction of 1-oxo-4-hydroxymethyl-2,6,7-trioxa-L-phosphabicyclo [2.2.2] octane (PEPA), phosphorus oxychloride ($POCl_3$) and polyether with different structures (PEG, PPG, and PTMG), and then applied it as a reactive-type flame retardant in amino transparent intumescent fire-retardant coatings [10]. Moreover, to endow transparent fire-retardant coatings with excellent flame retardancy, some studies focused on the introduction of functional groups and flame retardant elements such as epoxy resin[11], silicon-containing epoxy compounds [9], polyethylene glycol [12,13] and organic siloxane [6] into the structure of phosphorus-containing compounds. But some functional groups such as epoxy compounds will release a large amount of smoke particles during burning, resulting in the increase of fire hazards [14]. In case of fire, the damage from smoke sometimes exceeds the fire itself [15]. Therefore, it is necessary to develop high efficiency transparent fire-retardant coatings with excellent flame retardancy and smoke suppression properties.

The incorporation of nano-sized fillers as synergist into intumescent systems shows great potential to enhance the flame retardancy and smoke suppression properties of intumescent coatings by enhancing the charring and reducing the formation of gaseous combustibles and soot particles [16,17]. As is known, silica nanoparticles as 0D particulate materials have attracted much attention due to their high thermal stability and heat insulation property [18]. It has been indicated that the nano-silica is a promising alternative to improve the flame retardancy and smoke suppression properties of intumescent systems due to the synergistic effect between silicon and phosphorus [19,20]. But the directly incorporation of nano-silica into transparent coatings by physical mean will sacrifice the optical transparency of the coatings due to the difference in a refractive index between the nano-silica and matrix resin [21,22]. Some studies indicated that the nano-silica with special treatment can use to prepare transparent silicone rubber compounds [22], transparent waterborne ultraviolet-curable polyurethane [23], transparent UV-cured coatings [24,25] and transparent fluorocarbon coatings [26]. Alongi et al. showed that the silica coatings assembled by Layer by Layer (LbL) not only maintain the original morphology of cotton fibres and polyester fabrics but also enhance the flame retardant and smoke suppression properties of the underlying substrates [27–29]. However, there are relatively few studies on the application and study of nano-silica in transparent intumescent fire-retardant coatings as flame retardant.

In this study, a phosphate ester acid (PEA) with cyclic structure was synthesized by reaction of phosphoric acid (PA), pentaerythritol (PER) and *n*-butyl alcohol (BA). The nano-silica was introduced into the structure of PEA to obtain silica-modified cyclic polyphosphate (SPEAs). Four kinds of SPEAs with different nano-silica contents were synthesized. The chemical structures of PEA and SPEAs were confirmed by ^{1}H NMR and FTIR. The PEA and SPEAs were mixed thoroughly with melamine formaldehyde resin to prepare a series of transparent fire-retardant coatings. The flame retardant and smoke suppression properties of the coatings were intensively investigated by cabinet method test, tunnel method test, cone colorimeter test and smoke density test. The thermal degradation behaviors of the coatings were analyzed by thermo-gravimetric analysis. Finally, the char residues left after cone calorimeter test were examined by SEM, EDS and FTIR and their relationships with flame retardant and smoke suppression mechanisms were discussed.

2. Experimental

2.1. Materials

Phosphoric acid (PA, 85% in water) was supplied by Hunan Huihong Chemical Reagent Co., Ltd. (China). Pentaerythritol (PER) was supplied by Shanghai Qiangshun Chemical Reagent Co., Ltd. (China). N-butyl alcohol (BA) was supplied by Sinopharm Chemical Reagent Co., Ltd. (China). Melamine formaldehyde resin (MF, model 303-80, 58–62% in *n*-butyl alcohol) was purchased from Jiyang Sanqiang Chemical Reagent Co., Ltd. (China). (3-Aminopropyl) triethoxysilane (KH550) was provided by Shanghai Aladdin Industrial Corporation (China). Nano-silica was supplied by Chengdu Gracia Chemical Technology Co. Ltd. (China), with the average primary particle size being 15 nm and the specific surface area being 200 ± 25 m^2/g. All the reagents mentioned above were used as received.

2.2. Preparation of PEA and SPEAs

The mixture of PA (92.24 g, 0.8 mol), PER (29.95 g, 0.22 mol) and BA (5.93 g, 0.08 mol) were added into a 500 ml three-neck flask and magnetically stirred under refluxing for 4 h at 105 °C. A light yellow transparent liquid product was obtained and named as PEA.

KH550 modified silica was prepared according to literature method [30] with some modifications. Firstly, 20 g silica nanoparticles were dispersed in 300 ml alcohol and added into a three-neck flask under magnetic stirring. Then, 1 g KH550 was added into the silica nanoparticles dispersion and the mixture was stirred under refluxing for 4 h at 120 °C. After that the nano-silica dispersion was cooled down and separated by centrifugation. The separated silica was washed by ethanol for five times and then dried at 60 °C overnight. The obtained dry powder was amino-functionalized nano-silica (KH550-SiO_2).

SPEAs were prepared by dropping the KH550-SiO_2 into the above PEA system and stirred under refluxing for 4 h at 120 °C. PEA and KH550-SiO_2 were reacted with mass ratio of 99:1, 98:2, 97:3 and 95:5, respectively. The SPEAs with 1 wt%, 2 wt%, 3 wt% and 5 wt% of KH550-SiO_2 were marked SPEA1, SPEA2, SPEA3 and SPEA4, respectively.

2.3. Preparation of transparent fire-retardant coatings

Fifty grams of PEA or SPEAs ethanol solution (60 wt%) and 60 g MF *n*-butyl alcohol solution (58–62 wt%) were mixed thoroughly to get homogenous transparent coatings. The obtained coatings were coated on the plywood boards (100 mm × 100 mm × 4 mm, 75 mm × 75 mm × 4 mm and 600 mm × 90 mm × 4 mm) with the wet coating density of 500 g/m^2. This process was repeated for several times until the coatings were cured to thick transparent film at room temperature. The thickness of the coatings was 0.4 ± 0.02 mm according to the average of five determinations. The plywood boards with the dimensions of 300 mm × 150 mm × 4 mm was coated with the wet coating density of 250 g/m^2. This process was repeated for several times, and the thickness of dry film was 0.2 ±0.02 mm. The coatings obtained from PEA and SPEA1-SPEA4 were marked as MSPE0 and MSPE1-MSPE4, respectively. In addition, PEA was directly mixed with 3 wt% KH550-SiO_2 at room temperature, then fifty grams of the mixture ethanol solution (60 wt%) was mixed with 60 g MF *n*-butyl alcohol solution (58–62 wt%) to obtain MSPE5 coating.

2.4. Measurements and characterization

FTIR spectra were obtained from a Fourier transformation infrared spectroscopy (Nicolet Nexsus 670) at 1 cm^{-1} resolution, and the sample of char residues after cone calorimeter test was analyzed by using KBr pellet. The FTIR spectra were recorded over the range of 4000–500 cm^{-1}. ^{1}H NMR spectra were obtained at room temperature on a Bruker Ascend 500 MHz NMR spectrometer with D_2O as the solvent.

The transparency of fire-retardant coatings was measured in a LS116-type light transmittance meter (Shenzhen Linshang Technology Co. Ltd, China). All the samples were coated on the transparent glass slide with the thickness of 0.2 ± 0.02 mm. Each glass side was with the