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Synergistic effects of organically modified montmorillonite on the flame-retardant and smoke suppression properties of transparent intumescent fire-retardant coatings

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ABSTRACT

A series of novel montmorillonite polyphosphate (OPEA) flame retardants were successfully synthesized by chemical grafting of cyclic phosphate ester acid (PEA) with different contents of organically modified montmorillonite (OMMT). Their chemical structures were confirmed by Fourier transform infrared spectroscopy (FTIR) and ^{1}H nuclear magnetic resonance spectroscopy (^{1}H NMR). Five types of transparent fire-retardant coatings applied to plywood boards were prepared by mixing melamine formaldehyde resin with PEA or OPEAs. The transparency analysis reveals that chemical grafting of PEA on the surface of OMMT imparts a high degree of transparency to the resulting fire-retardant coatings due to the uniform dispersion and completely exfoliated states of the MMT platelets in the coatings, as determined from X-ray diffraction patterns and transmission electron microscopy images. The fire protection tests show that the introduction of OMMT decreases the mass loss, char index, and flame spread rating of the coatings, concomitant with an increase in the intumescent factor. The cone calorimeter and smoke density tests reveal that incorporation of OMMT remarkably decreases the heat release and smoke production of the coatings, which is ascribed to a more thermally stable, compact and intumescent char layer formed during combustion, judging from digital photographs and scanning electron microscopy images. Further, the synergistic flame-retardant and smoke suppression effects of OMMT in the coatings depend on the content of OMMT, and excessive OMMT will decrease the synergistic effects. The thermogravimetric analysis shows that the thermal stability and residual weight of the coatings increase efficiently with increasing OMMT content. The FTIR and elemental analysis demonstrate that the incorporation of OMMT generates more phosphorus-rich cross-linked char and aromatic char in the condensed phase, thus effectively reducing the heat release, smoke production, and mass loss of the coatings.

1. Introduction

Intumescent fire-retardant coatings are considered as one of the most efficient and cost-effective fire protection methods to protect substrate materials against fire. Usually, intumescent fire-retardant coatings are composed of three basic ingredients, namely, a carbon source, a blowing agent, and an acid source in which are mixed flame-retardant fillers and proper binders [1]. Upon exposure to flame or high temperature, intumescent fire-retardant coatings can swell and form a thick porous char layer that serves as a protective barrier for the underlying materials against fire and heat. However, most intumescent fire-retardant coatings are opaque due to their mode of preparation, in which the additive-type intumescent flame retardants are mixed together with a proper binder directly. The opaque coatings will greatly damage the natural appearance of wood surfaces, which restricts its application in some special fields such as high-quality furniture, historic buildings, cultural relics and heritage conservations [2]. Therefore, the development of transparent fire-retardant coatings has attracted considerable attention in the materials science community, to meet the increasing demands of fire protection and decoration in wood products.

A highly efficient approach to the preparation of transparent fire-retardant coatings is the reaction of reactive-type flame retardants containing both a carbon source and an acid source (e.g., phosphorus-containing compounds) with a matrix-resin-containing gas source (e.g., amino resin) [3,4]. The phosphorus-containing compounds, being a typical type of reactive-type flame retardant, can be directly bonded to

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the flame-retardant segments on the polymer backbone of the matrix resin, producing better flame-retardant efficiencies, thermal behaviors, and transparencies than those of conventional additive-type flame retardants [5,6]. The flame-retardant effect of phosphorus-containing compounds mainly relates to the amount and position of phosphorus atoms in the compound structure, and phosphorus-containing compounds with a cyclic structure exhibit an enhanced flame-retardant effect and thermo-oxidative stability [7]. Moreover, the barrier efficiency and fire protection of intumescent fire-retardant coatings are also strongly affected by the anti-oxidation property and the mechanical strength of the intumescent char layer [8]. To further enhance the anti-oxidation property and the mechanical strength of the char layer, many researchers have focused on introducing various types of organic oligomers and flame-retardant segments into the structure of phosphorus-containing compounds, such as polyethylene glycol [2], epoxy resin [3], organic siloxane [9] and silicon-containing compounds [10]. However, some functional groups such as those in epoxy resin release a large amount of smoke particles, increasing fire hazards [11]. Therefore, it is necessary to develop the transparent fire-retardant coatings with good flame retardant and smoke suppression properties.

Recently, the incorporation of a small amount of nano-fillers into intumescent systems shows great potential for enhancing the thermal, mechanical, smoke suppression, and barrier properties of the materials either by physical and/or chemical synergistic effects [12]. In our previous study, nano-silica was used as a highly efficient synergist for enhancing the flame retardancy and smoke suppression properties of transparent intumescent fire-retardant coating, and the cyclic phosphate ester grafted with nano-silica imparted a high degree of transparency to the resulting coatings [13]. It was found that the high transparency of the coatings is due to the homogeneous dispersion of nano-silica with particle sizes less than the wavelength of visible light. Although the synergistic effect of nano-silica has been gratifying, it is essential to further improve the smoke suppression and flame-retardant efficiencies of transparent fire-retardant coatings. Among the large variety of nano-fillers, layered montmorillonite (MMT) has been identified as a promising synergistic agent for improving the flame-retardant efficiency and thermal stability of intumescent materials, and the synergistic effect is widely ascribed to the strengthening of the intumescent char layer by MMT platelets [14,15]. Isitman et al. found that layered MMT nanoparticles had a better synergistic flame-retardant effect in intumescent retarded polylactide composites compared to spherical nano-silica [16]. Apart from the positive synergistic effect, the micron-sized lateral dimensions of the MMT platelets greatly scatter the incident light because the sizes of the MMT platelets are larger than the wavelength of visible light, thus decreasing the optical transparency of the transparent coatings [17]. Some studies have found that the high exfoliation degree of the MMT platelets in the matrix can eliminate the light scattering of MMT platelets due to the molecular level dispersion of MMT with sizes less than the wavelength of visible light [18,19]. Therefore, the high exfoliation degree of MMT in the matrix is believed to be the key factor in imparting a high degree of transparency to the fire-retardant coatings.

Usually, the organically modified clays produced by the ion-exchange reaction can enlarge the inter-platelet spacing between the clay layers and obtain the desired exfoliation degree of clay in the matrix concomitant with the optimum polymer properties [20]. Kaya et al. revealed that the epoxy nanocomposites containing OMMT particles exhibited better transparency and flame retardancy than those with MMT due to the better exfoliation of the clay layers in the matrix [21]. Suin et al. prepared exfoliated polycarbonate/clay nanocomposites using phosphonium-modified OMMT via conventional melt and solution blending techniques, which greatly maintained the optical transparency of PC in the nanocomposites [22]. Landry et al. found that the dispersion quality of clay in the acrylate coatings strongly affected both the mechanical and optical properties, and the better dispersion quality of clay in the coatings corresponded to a higher optical transparency [19]. However, MMT modified by a common modifier including alkyl ammonium salt is not easy to combine with the intumescent flame retardants [23]. To obtain favorable MMT dispersion in intumescent systems, MMT modified by intumescent flame retardants via chemical grafting or ion exchange is highly desirable [24]. Makhlouf et al. synthesized a novel intumescent flame retardant (IFR), a melamine salt of montmorillonite phosphate, and revealed that chemical grafting of IFR on the surface of MMT could produce both good MMT dispersion and high flame-retardant efficiency in linear low-density polyethylene [25]. Huang et al. found that phosphorus-nitrogen flame-retardant treatment for MMT by an ion-exchange reaction can improve both the dispersion of MMT in the polyurethane (PU) matrix and the flame retardancy and thermal stability of the nanocomposites [26]. As a result, it is anticipated that grafting phosphorus-containing compounds on the surface of OMMT could produce a high exfoliation degree of the MMT layers in the transparent fire-retardant coatings. Further, the high exfoliation degree of the MMT layers shows great potential for imparting excellent flame retardancy and smoke suppression properties concomitant with a high degree of transparency to the fire-retardant coatings. However, there are few reports on the application and study of OMMT nanoparticles for preparing transparent fire-retardant coatings via the chemical grafting method.

In this study, a phosphate ester acid (PEA) with a cyclic structure was synthesized. The OMMT was prepared by modified MMT with an alkyl ammonium salt, and then grafted into the structure of PEA by the reaction of edge and interlayer hydroxyl groups in OMMT with the P—OH groups in PEA. Four types of montmorillonite polyphosphate (OPEA) flame retardants with different OMMT contents were synthesized. The chemical structures of PEA and the OPEAs were characterized by FTIR and ^{1}H NMR. A series of transparent fire-retardant coatings were produced by thoroughly mixing PEA or OPEAs with amino resin. The influence of OMMT on the optical transparency, thermal stability, fire protection performance, flame retardancy, and smoke suppression properties of the transparent fire-retardant coatings were intensively investigated. In addition, SEM-EDS (SEM-energy dispersive spectroscopy) and FTIR analysis were used to investigate the morphologies and chemical structures of the char layers after the cone calorimeter test, and the potential synergistic flame-retardant and smoke suppression mechanisms of OMMT in the coatings were also proposed.

2. Experimental

2.1. Materials

Phosphoric acid (PA) with a mass concentration of 85% was supplied by Hunan Huihong Chemical Reagent Co., Ltd. (Changsha, China). N-butyl alcohol (*n*-BA) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Pentaerythritol (PER) was provided by Shanghai Qiangshun Chemical Reagent Co., Ltd. (Shanghai, China). Melamine formaldehyde resin (MF, model 303-80, 58%–62% in *n*-BA) was supplied by Jiyang Sanqiang Chemical Reagent Co., Ltd. (Shandong, China). Clay (Na^+-MMT) with a cation-exchange capacity of 65 mmol/100 g was produced by Zhejiang Fenghong Clay Chemical Co. Ltd. (Zhejiang, China). The OMMT was prepared by modifying the clay with an alkyl ammonium salt according to the literature method [27]. First, 20 g clay was dispersed in 400 mL of deionized water in a 500 mL three-necked distilling flask with magnetic stirring for 1 h at the ambient temperature, and then an aqueous solution of 10 g cetyltrimethylammonium bromide (CTAB) was added into the dispersion and stirred for 2 h at 80 °C. After that, the clay dispersion was cooled down and washed with distilled water until no Br^- irons could be reacted by $AgNO_3$. The obtained precipitate was filtered and dried at 80 °C for 48 h, and acquired organically modified montmorillonite (OMMT). All the reagents mentioned above were used as received.