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Preparation, properties and characterizations of halogen-free nitrogen–phosphorous flame-retarded glass fiber reinforced polyamide 6 composite

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Abstract

Halogen free nitrogen–phosphorous flame retardants (PMOP) were prepared through reaction of melamine and polyphosphoric acid in the presence of flame retardant modifier CM with silicotungistic acid as a catalyst in aqueous solution. FT-IR, XRD, DSC and TGA techniques were used to characterize the reaction product PMOP. The obtained flame retardants were then used to prepare flame retardant (FR) polyamide 6 (PA6) composite reinforced with glass fiber (GF) and the factors affecting the flame retardancy of the material were also investigated. The FR GF reinforced PA6 composite and the obtained charred layers were analyzed by utilizing TGA, SEM, FT-IR and XRD. The properties of the charred layer were connected with the flame retardancy of the corresponding material to reveal the flame retarding mechanism of FR GF reinforced PA6 composite. The experimental results show that PMOP flame retardant consists of melamine polyphosphate, melamine phosphate and possible melamine pyrophosphate. The presence of CM was found to improve the flame retardancy of FR GF reinforced PA6 composite. It was experimentally found that PMOP flame retardant, which is comparatively stable in the range of processing temperatures of PA6, is particularly suitable for flame retarding PA6 reinforced with GF. With increasing the flame retardant content, the flame retardancy of the FR reinforced material is not improved so obviously. However, the increase in the GF content greatly improves the flame retardancy of the composite, because GF greatly increases the char yield of material, decreases the maximal thermal decomposition rate, promotes the formation of charred layer with $(PNO)_x$ structure and greatly increases the strength of the charred layer. The prepared FR GF reinforced PA6 composites have good comprehensive properties with flame retardancy 1.6 mm UL 94 V-0 level, tensile strength 76.8 MPa, Young's modulus 11.7 GPa, Izod notched impact strength 4.5 kJ/m^2, flexural strength 98.0 MPa and flexural modulus 7.2 GPa, showing a better application prospect.
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1. Introduction

Polyamide materials, as engineering thermoplastics, are playing a more and more important role in modern industrial applications. As well known, engineering thermoplastics pure polyamides (especially PA6 and PA66) are endowed with relatively high tensile strength, high ductility, good chemical resistance, good abrasion, low friction coefficient, good electrically insulating property and easy processing properties. However, polyamides also have some disadvantages such as high moisture absorptivity, poor dimensional stability, low heat distortion temperature, poor low-temperature impact strength and easy flammability [1,2]. So, reinforcing modification needs to be conducted on the pure polyamide materials. Most industrial areas require the reinforced polyamide composites. Generally, the used reinforcing fillers involve glass fibers [3,4], wollastonite [5,6], magnesium salt (M-HOS) whisker [7], carbon fiber [8,9], PET fiber [10], carbon nanotubes [11,12] and Kevlar fiber [13]. Industrially, glass fiber is the filler which is mostly utilized in reinforcing polyamide

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materials (PA6 and PA66) due to its low cost, good availability and simple filling process. After the addition of glass fiber to PA6 or PA66, the dimensional stability, heat distortion temperature, impact resistance, resistance to chemical solvent, aging resistance and moisture absorption resistance of the corresponding composites all are improved markedly. In recent years, the application volume of glass fiber reinforced PA6 and PA66 presents a fast increasing trend. The typical applications of glass fiber reinforced PA6 and PA66, which takes up an important station in the entire engineering plastics, can be largely found in the car, mechanical instruments, electric industries, national defense industries, aviation industries, etc.

PA6 and PA66 are flammable materials. The glass fiber reinforced PA6 or PA66 composites are even more combustible than the pure polyamide material due to the "candlewick effect" of glass fiber, which greatly limits their applications in electric industries, including electrical connectors, switch components, wire ties, electrical housings and so on [1,14]. So, how to enhance their flame retardancy becomes a big challenge. Many attempts have been made to impart fire retarding property to glass fiber reinforced PA6 and PA66 materials and obtained a great success [1, 15–21].

Halogen-containing flame retardant additives are often industrially used in decreasing the combustibility of glass fiber reinforced PA6 and PA66 and prove to be very effective [15–17]. These additives include chlorinated compounds such as hexachlorocyclopentadiene [22], Dechlorane Plus [15], bis(hexachlorocyclopentadieno)-cyclooctane [23], etc. and brominated compounds such as brominated epoxy [19,24], brominated poly(phenylene oxide) [16,19], brominated polystyrene [25], decabromodiphenylether [17], etc. But halogenated flame retardants encounter many problems, e.g. some halogenated additives can catalyze fuel-forming reaction which is detrimental to the fire retardancy. To obtain satisfactory flame retardancy, a relatively high amount of additives is required together with metal oxide synergists, resulting in decreased mechanical properties and increased specific gravity of the obtained composite. In addition, the halogenated FRs also cause reduction in tracking index [1], cause corrosion to the processing equipment and generate corrosive and toxic combustion products (especially the "dioxin").

As a result, halogen free retardants are the preferred additives used in glass fiber reinforced PA6 and PA66. These halogen free retardants are divided into inorganic products [1,19,21,26,27], phosphorus-based products [1,18,28–31], nitrogen-based products [1,19,32] and phosphorus–nitrogen-based products [1,20,26,33]. The investigation of inorganic additives is concentrated on aluminum hydroxide ($Al(OH)_3$) [26], magnesium hydroxide ($Mg(OH)_2$) [21,26,27] and zinc borate [19,26]. In order to achieve a relatively high flame retarding level, big inorganic FR loading (generally 50–60 wt%) and surface modification are needed, leading to inferior mechanical properties and complicated preparation process. Among phosphorous additives, such as red phosphorus [18,28], phosphine oxide [29], phosphonate [30] and phosphonitride [31], etc., which can effectively flame retard reinforced PA6 and PA66, only red phosphorus can be actually applied on a large scale [1]; however, its red color and generation of highly toxic hydrolysis product phosphine in use are also problems. Melamine and its derivatives such as melamine cyanurate, melamine sulfate, etc. are often used as nitrogen-containing additives in glass-reinforced PA6 and PA66 [1,19,32]. Sometimes, melamine and its derivatives need combination with other compounds to exert their optimum efficiency. The main advantages of melamine-based systems are that they have chemical structures very similar to that of polyamides and then possess good compatibility with matrix polyamides. However, the main disadvantage of melamine-based additives such as melamine cyanurate is their increase in melt flow and promotion of dripping of polyamides during combustion and hence relative ineffectiveness in glass fiber reinforced composites, particularly leading to a severe "candle effect" of glass fiber. Nitrogen–phosphorous (N–P) systems seem to be very useful in flame retarding glass fiber reinforced PA66 [1,20,26,33]. These additives include melamine phosphate [33], melamine polyphosphate [20], ammonium polyphosphate [26]. Due to their halogen free, relatively high efficiency and no release of toxic and corrosive gases during combustion, they are representative of the developing trend of flame retardants applied in glass-reinforced polyamides. There are many studies on flame retardant PA66 with N–P systems but only few reports on PA6 [1]. Wang et al. [34] investigated the flame retarding efficiency of melamine polyphosphate in PA66 and PA6. They found that the fire retarding efficiency of melamine polyphosphate in glass-reinforced PA66 is obviously better than that in glass-reinforced PA6 and the flame retardancy of the latter was not improved at UL 94 test.

In this study, halogen free melamine-based intumescent flame retardants were prepared to apply in glass fiber filled PA6 and a satisfactory flame retarding efficiency was obtained. The structure, mechanical and flame retarding performance, and flame retarding mechanism of the prepared flame retarded glass-reinforced PA6 composite were discussed. The influence of the prepared flame retardant and glass fiber contents on the flame retardant properties (LOI and UL 94 flame retardancy level) and the mechanical performance of the reinforced PA6 composite were also investigated.

2. Experimental

2.1. Materials

The following materials were used as received: polyamide 6 (PA6, with relative viscosity of 3.2 in 98% H_2SO_4 solvent, as granulate product supplied by Baling Petrochemical Co., China), melamine (MEL, chemically pure, supplied by Chengdu Kelong Chemical Plant, China), polyphosphoric acid (PHPO, chemically pure, supplied by Chengdu Kelong Chemical Plant, China), glass fiber (GF, 4.5 mm in length, supplied by Tongxiang Zhenshi stock incorporation limited, China), silicotungistic acid (STA, reactant degree, supplied by Hunan Xiangzhong Fine Chemical Plant, China), flame retardant modifier, i.e. caprolactam (CM, chemically pure, supplied by Shenyang Xinxi Reagent Plant).

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