Highly efficient flame-retardant glass-fiber-reinforced polyamide 6T system based on a novel DOPO-based derivative: Flame retardancy, thermal decomposition, and pyrolysis behavior

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ABSTRACT

A novel bridged 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivative (PN-DOPO) was used to fabricate a flame-retardant glass fiber-reinforced polyamide 6T (GFPA6T). The effects of PN-DOPO on the flame retardancy, thermal decomposition, and pyrolysis behavior of GFPA6T was systematically investigated, compared to neat GFPA6T and its composite flames retarded by aluminium diethylphosphinate (OP1230). The flame retardancy, thermal stabilities, and burning behaviors of the composites were evaluated by vertical burning test (UL-94), limiting oxygen index (LOI), thermogravimetric analysis (TGA), and cone calorimeter test. Moreover, the flame-retardant mechanism was analyzed by pyrolysis-gas chromatograph/mass spectrometer (Py-GC/MS), Fourier transform infrared coupled with the thermogravimetric analyzer (TG-FTIR), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. Results reveal that the modified GFPA6T, with the addition of 15 wt% PN-DOPO, achieves a V-0 rating and LOI value of 28.9%, whereas introducing OP1230 at levels up to 17.5 wt% can achieve a V-0 rating and LOI value of 40.1%. The superior flame retardancy for GFPA6T/PN-DOPO system can be attributed to two factors as follows: the release of pyrolytic gases containing phosphorus-based aromatic structures and nonflammable gases at the early stage, thereby playing an important role in the gas phase, and the formation of char layer consisting of phosphorus-containing char layer and polyaromatic structures in the condensed phase. In comparison, diethyl-phosphorus oxides and their derivatives are detected in the gas phase for GFPA6T/OP1230 samples, and the residues consist of aluminum phosphorus oxides, polyphosphates, and a slight amount of charred polymer.

1. Introduction

Semi-aromatic polyamide is a kind of engineering plastics with lower moisture uptake and higher temperature corrosion resistance compared to aliphatic polyamide [1–3]. Polyamide 6T (PA6T), as a semi-aromatic nylon, comprises terephthalic acid and hexanediamine. Glass fiber-reinforced PA6T (GFPA6T) is used widely in electronic components, and automobile parts because of high electrical insulation properties coupled with excellent physical and tensile properties [3–5]. The application of GFPA6T involves heating in an infrared device or is used in a high-temperature environment for extended periods. However, GFPA6T is inflammable [4], and the combustion is constantly accompanied by the production of toxic gas and smoke, thereby restricting the wide application of GFPA6T, particularly in electronic or electrical equipment and transportation [3]. Thus, enhancing the flame retardancy of GFPA6T is a crucial issue.

A commonly used method for reducing the flammability of thermoplastics is by introducing a flame retardant (FR) additive into polymer via melt processing. An ideal FR additive must have a favorable compatibility with the matrix [6–8]. The environmental and health profiles [9,10] and FR additive costs are also crucial factors for a successful commercial application [11–14]. Furthermore, an additive must have a sufficient thermal stability to survive the melt processing condition of the polymer matrix [15–17]. The processing temperature of PA6T ranges from 310 °C to 320 °C [18], and minimal FR can survive during the processing. In recent years, the widely used and available nonhalogenated FR systems for high-temperature polyamide are mainly focused on aluminium alkyl-phosphinates (AlPi). Horrocks et al. [19] reported the combined effects of aluminium diethylphosphinate (OP1230) coupled with zinc stannate (ZS) on a glass fiber-reinforced

high-temperature polyamide (HTPA-GF). The results demonstrate that AlPi can be used as an effective FR for HTPA-GF, providing a limiting oxygen index (LOI) > 40% and a V-0 rating at 15 wt% loading. The introduction of ZS at levels up to 3.75 wt% can maintain the V-0 rating and the LOI at approximately 40%. Seefeldt et al. [4] investigated the FR impact of AlPi on HTPA-GF (PA6T/DT). The change in Underwriters Laboratories 94 vertical burning test (UL-94) classification from no rating (NR) for GFPA6T to V-0 rating for GFPA6T-AlPi (15 wt%) and the significant increase in LOI values from 24.0% to 47.7% suggest that AlPi is an effective FR for PA6T/DT. The results reveal that AlPi acted in the gas and condensed phases during thermal decomposition.

The reported FRs for PA6T are confined to aluminum hypophosphite and alkyl-phosphinates, and the application of other FRs on HTPA-GF is rarely reported. A recent work in our laboratory reports a novel phosphaphenanthrene oxide based on a bridged 9,10-dihydro-9-oxa- 10-phosphaphenanthrene-10-oxide (DOPO) derivative (PN-DOPO) [20,21]. The starting decomposition temperature ($T_{5\%}$) of 348.8 °C is higher than the processing temperature of PA6T, and the maximum decomposition temperature (T_{max}) is 429.3 °C. Furthermore, the melting temperature is 187 °C, suggesting that the FR will melt with the polymer matrix in the process and result in a favorable dispersion. PN-DOPO can be a potential FR alternative solution for PA6T given the specific thermal behavior.

In this manuscript, the effect of PN-DOPO on the flame retardancy, thermal decomposition, and pyrolysis behavior of GFPA6T containing 35 wt% glass fiber was systematically investigated relative to a formulation comprising the commercially available OP1230. The flame retardancy and combustion behavior of the flame-retardant GFPA6T composites (GFPA6T/FR) were evaluated by UL-94 and cone calorimetric analysis. The thermal stability of GFPA6T/FR was investigated by thermogravimetric analysis (TGA), and the residues and released gases after TGA at different temperatures were also characterized by Fourier transform infrared (FTIR) spectra. The pyrolysis behaviors of GFPA6T/FR systems were studied by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS). The char morphology and element distribution of the composites after cone calorimetric tests were investigated by scanning electronic microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and Raman spectroscopy. The flame-retardant mechanism of GFPA6T/FR systems was also discussed.

2. Experimental

2.1. Materials

The GFPA6T (Zytel HTN53G50HSLRHF BK083, melting point ~315 °C) used in this work was purchased from Dupont Co., USA. The OP1230 (Exolit) was supplied by Clariant GmbH. PN-DOPO was prepared in our laboratory [20]. The chemical structures of the studied bridged DOPO-based FRs (PN-DOPO) and the commercial additive are presented in Scheme 1.
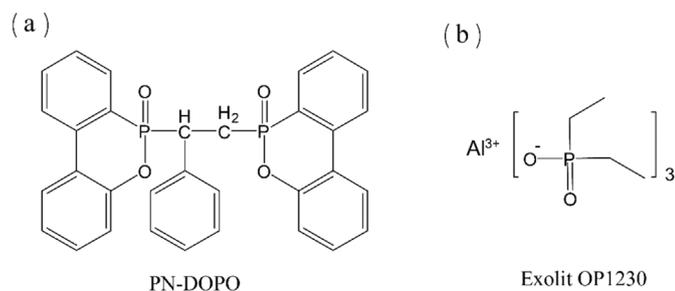
Scheme 1. Chemical structure of (a) PN-DOPO and (b) Exolit OP1230.

2.2. Preparation of GFPA6T/FR

Initially, the GFPA6T resin was dried in a vacuum oven at 100 °C for 5 h, and OP1230 coupled with PN-DOPO was dried in a vacuum oven at 80 °C for 10 h prior to processing. The different contents of FRs were mixed with GFPA6T (containing 35 wt% glass fibers) by tumbling all the ingredients, and the FR additives were added by 10, 12.5, 15, and 17.5 wt%. Then, the mixtures were fed into a twin-screw extruder (L/D = 20), and the temperatures of the seven heating zones were 280 °C, 290 °C, 300 °C, 310 °C, 320 °C, 315 °C, and 310 °C. The rotational speed was fixed at 150 rpm. Next, the extrudates were cut into pellets. Finally, the pellets were compression-molded in 10 MPa at 315 °C and cut into standard testing bars for UL-94, LOI, and cone calorimeter tests.

2.3. Measurement

The flame retardancy of GFPA6T/FR was measured by UL-94 vertical burning and LOI tests. The LOI values were evaluated according to ASTM D2863-97 with the 3D size of 130.0 mm × 6.5 mm × 3.2 mm. The UL-94 vertical burning ratings were assessed according to ASTM D3801 with the 3D size of 130.0 mm × 13.0 mm × 3.2 mm. The combustion behavior of the samples with the 3D size of 100.0 mm × 100.0 mm × 6.0 mm was measured with a cone calorimeter device (Dual Cone Calorimeter, Fire Testing Technology, East Grinstead, UK) exposing a radiant cone at a heat flux of 50 kW/m^2 according to ISO5660-1. The tests were repeated thrice, depending on whether the deviation between the results was < 10%. The cone calorimeter enables the quantitative analysis of materials by providing parameters [22,23], such as time to ignition (TTI), peak heat release rate (pk-HRR), average of heat release rate (av-HRR), average of effective heat combustion (av-EHC), total heat release (THR), total smoke rate (TSR), average CO yield (av-COY), average CO_2 yield (av-CO_2Y), and residue yield (Residue).

TGA was experimented by using a Q50 apparatus (TA Instruments, USA) in nitrogen with a flow rate of 60 mL/min. Samples (approximately 8 mg) placed in the Al_2O_3 pans were heated from 20 °C to 700 °C at the heating rate of 10 °C/min to record the TGA and differential thermogravimetric analysis (DTG) curves. The onset decomposition temperature ($T_{5\%}$) of polymers is evaluated by the temperature of 5 wt% weight loss, and T_{max} refers to the temperature of the maximum mass loss rate, obtained from the DTG curves.

SEM was used to study the surface morphology of the burning residue after the cone calorimeter tests on an environmental SEM (Quanta FEG 250, FEI Instruments, USA) under an acceleration voltage of 10 kV. A thin layer of gold was sprayed on the surface prior to SEM observation.

Energy dispersive spectrometry (EDS) provided a chemical analysis of the char layer after combustion. The EDS analyses were conducted on Quanta FEG 250 SEM equipped with an EDS accessory at an acceleration voltage of 30 kV.

The samples (approximately 8 mg) suspended at different temperatures during TGA were characterized by FTIR. FTIR spectroscopy was performed using Nexus 670 infrared spectrometer (USA) as KBr pellets.

Py-GC/MS tests were performed in a pyrolyzer (PY-2020iD, Frontier Laboratories Ltd., Japan). A chamber was used to heat the samples for thermal pyrolysis. The samples were set to 700 °C at a heating rate of 1000 °C/min and maintained for 30 s. The inert atmosphere was high purity helium. The experimental parameters were as follows: MS indicator was operated in the electron impact mode at an electron energy of 70 eV, and ion source temperature was 200 °C. The pyrolysis mass spectrometry analyses were repeated several times to obtain reproducibility. The components detected from Py-GC/MS were contrasted with NIST mass spectral database.

XPS was recorded with a VG Escalab Mark II spectrometer (VG Scientific Ltd., UK) using Al Kα source at a base pressure of