

# Synergistic effect of a novel triazine charring agent and ammonium polyphosphate on the flame retardant properties of halogen-free flame retardant polypropylene composites



Caimin Feng, Minyi Liang<sup>1</sup>, Jiali Jiang, Jianguang Huang\*, Hongbo Liu\*

School of Applied Chemical Engineering, Shunde Polytechnic, Foshan 528333, China

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## ABSTRACT

A novel triazine charring agent poly(4,6-dichloro-N-butyl-1,3,5-triazin-2-amine-ethylenediamine) (CNCD-DA) was synthesized, which had good thermal stability and char-forming ability. The synergistic effects between ammonium polyphosphate (APP) and CNCD-DA on flame retardant properties and mechanism of polypropylene (PP) were investigated by the limited oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test (CCT), scanning electron microscopy (SEM), laser Raman spectroscopy analysis (LRS), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The results illustrated when the mass ratio of APP to CNCD-DA was 3:1 with 30% loading, the intumescent flame retardant (IFR) showed the best synergistic effect with LOI value reaching 36.5%, and the IFR could greatly suppress the generation of the flame and smoke during combustion. The results from SEM, TGA, LRS and FTIR indicated that during the combustion IFR could form a continuous and intumescent char containing P—O—P and P—O—C crosslinking structures and polyaromatic structures, thus effectively retard the combustion of PP.

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## 1. Introduction

Polypropylene (PP) is a widely used thermoplastic in many fields, such as automobiles, housing, electronic and electric materials, wires and cables, due to its easy processing, low density, good chemical resistance, excellent mechanical performance and low cost. However, its inherent flammability is a main shortcoming, which does restrict its applications in some fields required good flame retardant performance. Therefore, it is important to improve the flame retardant properties of PP [1–18].

In recent years, intumescent flame retardants (IFRs) are well known as a new generation of flame retardants for polyolefin, and have drawn much attention because of their environment-friendly characteristics [1–5]. Traditionally, intumescent flame retardants (IFR) usually contains of three main ingredients: an acid source, a char-forming agent, and a gas source. Acid source is generally a dehydrating agent or a carbonized accelerator, such as phosphoric acid, boric acid, and phosphate, etc. [4–7]; Char-forming agent is

mainly polyhydric compound, such as pentaerythritol or its derivatives [4,5]; gas source produce gases upon heating, for example, urea, melamine, polyamide etc. [4]. The ammonium polyphosphate (APP)/pentaerythritol (PER)/melamine (MEL) system is the first used IFR system, and is the most common researched [4–7].

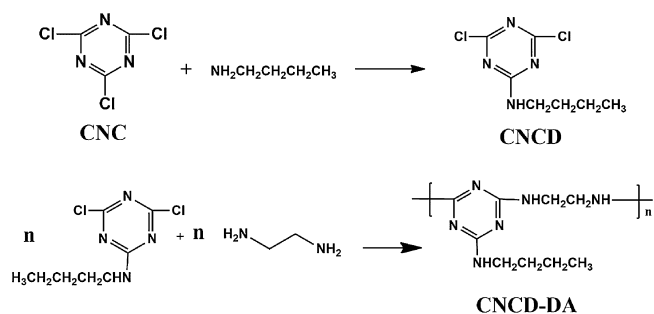
However, the traditional IFRs have some drawbacks, such as relatively lower water resistance, lower flame retardant efficiency, and lower thermal stability, compared with halogen-containing flame retardants. To solve these problems, researchers have made great efforts to develop new IFR systems [1,3,12–18]. In recent years, triazine derivatives have been proven to have excellent charring ability, due to the presence of the tertiary nitrogen in the triazine rings, and they have been used as efficient charring agents in IFR. However, because of their low water resistance ability, some of them are not suitable for charring agents of IFR systems [14,15].

In this work, a novel charring agent poly(4,6-dichloro-N-butyl-1,3,5-triazin-2-amine-ethylenediamine) (CNCD-DA) was designed and synthesized. It is an oligomeric triazine derivative, which is expected to have good char forming ability and thermal stability owing to the higher percentage of triazine rigid ring. And CNCD-DA contains butyl-group connected to triazine ring, which is expected to have good water resistance and better compatibility to PP [16,18,19]. The effects of the novel charring agent on flame

\* Corresponding authors.

E-mail addresses: [hjguang@139.com](mailto:hjguang@139.com) (J. Huang), [962651061@qq.com](mailto:962651061@qq.com) (H. Liu).

<sup>1</sup> The author contributed equally to this work and should be considered co-first author.



Scheme 1. Synthetic route of CNCD-DA.

retardant properties and mechanism of PP/IFR systems have also been investigated.

## 2. Experimental

### 2.1. Materials

Ammonium polyphosphate (APP) was provided by Shenzhen Anzheng Chemicals Company. Polypropylene (PP) resin (T30S, melt flow rate: 2–5 g/10 min) used in this work was purchased from Maoming Petroleum Chemical Company. Butylamine, ethylenediamine, acetonitrile and acetone were from Tianjin Hengda Chemical Reagent Factory. Cyanuric chloride (industrial) was manufactured by Yingkou Sanzheng Organic Chemical Industry Company. Antioxidant 1010 was produced by Ciba Specialty Chemicals, Switzerland.

### 2.2. Preparation

#### 2.2.1. Synthesis of CNCD-DA [16–19]

Acetone (100 ml) and cyanuric chloride (0.2 mol) were fed into a 500 ml four-neck flask which was equipped with two dropping funnels, a stirrer, and a thermometer. Butylamine (0.2 mol) and NaOH (0.2 mol) solution were added dropwise into the flask. The reaction was kept at about 0 °C for 2 h and a white solid (CNCD) (yield: 95.3%) was obtained.

CNCD (44.2 g, 0.2 mol) and 200 ml CH<sub>3</sub>CN were added into a 500 ml glass flask, which was equipped with a feeding funnel, stirrer, condenser, thermometer, and the mixture was stirred at room temperature, then diethylenetriamine (12.0 g, 0.2 mol) and triethylamine (40.4 g, 0.4 mol) were fed within 60 min. Thereafter, the mixture was heated to 120 °C by means of heating bath and refluxing for about 8 h. It was then cooled to room temperature. Followed by filtration, washing with distilled water, dried to a constant weight in vacuum at 70 °C for 24 h, a white solid (CNCD-DA) (yield: 96.0%) was obtained. The synthetic route of CNCD-DA was shown in Scheme 1.

#### 2.2.2. Preparation of polypropylene composites

APP and CNCD-DA were dried in a vacuum oven at 60–70 °C overnight before use. All the samples with PP, APP, CNCD-DA and antioxidant 1010 were prepared by a two-roll mill at a temperature range of 170–180 °C for 8 min, and the roller speed was 60 rpm, then pressed on a curing machine for about 1 min to produce various thick sheets, which were used to produce various dimension sheets for LOI, UL and cone calorimeter tests.

### 2.3. Characterization

#### 2.3.1. FTIR analysis

The sample was mixed with KBr powder, and then pressed into a tablet. The Fourier transform infrared (FTIR) spectra were obtained

with a Nicolet FTIR 6700 infrared spectrophotometer by averaging 32 scans at a resolution of 4 cm<sup>-1</sup>. The measurement was carried out in the optical range of 4000–400 cm<sup>-1</sup>.

#### 2.3.2. LOI test

The LOI data of all the samples were obtained at the room temperature from an oxygen index instrument (DRK304B) produced by Jinan Deruik Instrument Factory in accordance with the ISO 4589 standard. The dimensions of all the samples were 130 mm × 10 mm × 4 mm.

#### 2.3.3. Vertical burning test (UL-94 rating)

The vertical burning tests of all the samples were measured by a CZF-2 instrument produced by Jiangning Analysis Instrument Factory with the sample dimensions of 125 mm × 12.5 mm × 3.2 mm in accordance with the American National Standard UL-94 standard. UL-94 test results are classified by burning ratings V-0, V-1 and V-2. V-0 rating indicates the best flame retardancy of composites.

#### 2.3.4. Cone calorimeter test (CCT)

The CCT was carried out by using a cone calorimeter (Fire Testing Technology Co., UK) according to ISO 5660-1. Each specimen, with the dimensions of (100 mm × 100 mm × 4 mm), was wrapped in aluminum foil and exposed horizontally to an external heat flux of 35 kW/m<sup>2</sup>. All samples were run in duplicate and the average value was reported. The experimental error for all the mentioned parameters is ±10%. The residues of the samples after the cone calorimetric test were pursued for further analysis.

#### 2.3.5. Thermogravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was carried out with a TA Q500 thermogravimetric analyzer at a heating rate of 10 °C/min under N<sub>2</sub> or air atmosphere of 40 ml/min at the temperature ranging from room temperature to 800 °C. The 4–5 mg sample was examined by using an alumina crucible under a N<sub>2</sub> or air flowing rate. All the thermal degradation data were obtained from TG and DTG curves.

#### 2.3.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed by using a Hitachi SU80100 SEM, whose accelerating voltage was 2 kV without platinum sputter-coating before examination, to examine the morphology of the char residue obtained after heated at 500 °C for 5 min. High magnification (≥5000 times) micrographs were obtained with the accelerating voltage of 1.5 kV with Deceleration mode.

#### 2.3.7. Laser Raman spectroscopy analysis

The laser Raman spectroscopy (LRS) measurements were measured at the room temperature by using of a Raman microspectrometer (Renishaw inVia, UK) with excitation by a 514.5 nm helium–neon laser line focusing with a micrometer spot on the sample surface, and scanning in the 50–4000 cm<sup>-1</sup> region. To avoid sample heating, the power was kept below 4 mW. A subsequent visual examination of the surface was made systematically in order to ensure that no alteration happened around the focal point.

## 3. Results and discussion

### 3.1. Thermal analysis of CNCD-DA

Fig. 3 showed the thermogravimetric analysis curves of CNCD-DA under N<sub>2</sub> and air, and the results were presented in Table 1. As can be seen, the thermal degradation processes of CNCD-DA under N<sub>2</sub> and air were similar, but the DTG curve under air has one more peak than that under N<sub>2</sub>. The TGA curve under N<sub>2</sub> could be divided

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