



# Synergistic effect of graphitic carbon nitride and ammonium polyphosphate for enhanced thermal and flame retardant properties of polystyrene



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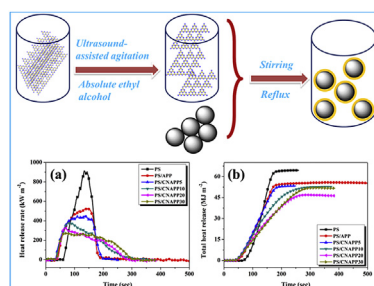
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## HIGHLIGHTS

- APP/g-C<sub>3</sub>N<sub>4</sub> hybrids were prepared for the first time.
- APP/g-C<sub>3</sub>N<sub>4</sub> hybrids showed the high residual content at high temperature.
- Both thermal stability and flame retardancy of PS/APP/g-C<sub>3</sub>N<sub>4</sub> composites were enhanced remarkably.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A series of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) wrapped ammonium polyphosphate (APP) (CNAPP) were firstly prepared, and then incorporated into polystyrene (PS). The results indicated the successful wrapping of APP by g-C<sub>3</sub>N<sub>4</sub>. The CNAPP exhibited the higher thermal stability than pure APP. Enhanced interfacial interactions between CNAPP and PS were obtained upon introduction of CNAPP. The thermal stability of PS/CNAPP composites was significantly improved, compared with that of PS containing an equal amount of APP. Moreover, cone results showed that the heat release rate and total heat release were reduced greatly for PS/CNAPP20. It was confirmed that the formation of P–O–C and P–N–C structures could remarkably improve the stability of char layer and thus result in the better flame retardancy of CNAPP, besides the enhanced thermal stability. The work provides a new paradigm for potential application of APP in polymeric materials.

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## 1. Introduction

Ammonium polyphosphate (APP) has attracted considerable attention in preparing flame-retardant materials because of its high phosphorus and nitrogen content, both of which are conducive to the flame retardancy of materials [1–3]. To date, APP has been

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extensively used as an efficient flame retardant for coatings, epoxy, and polyamide-6 (PA6), etc [4–6]. However, it is not an effective flame retardant for polystyrene (PS) upon being used individually [7]. This is mainly attributed to the explanation that combination of APP and PS cannot contribute to charring during the combustion. Therefore, it is very necessary to extend its utilization in the field of PS by combining APP with other flame-retardant additives.

At present, two conventional methods are adopted to expand applications of APP in PS. Charring agent (CA) is usually combined with APP through physical blending. The CA can participate in the charring during the combustion, and the formed char layer is of great importance for reducing the heat transfer between the flame and underlying polymer. Furthermore, it impedes mass transfer from the polymer towards the flame as well as the diffusion of oxygen into the material [8–11]. Watik et al. studied the fire-resistant polystyrene-butadiene/APP/pentaerythritol (PER)/talc systems, and found that limiting oxygen index (LOI) was increased with increased content of APP and PER and decreased loading of talc [12]. Wang et al. reported a combination of poly(1,3,5-triazin-2-aminoethanol diethylenetriamine) and APP for improving flame retardance and smoke suppression of PS [13]. The results indicated that the LOI value of 32.5% and UL-94 V-0 rating could be achieved when the content of APP and CA was 22.5 and 7.5 wt%, respectively. Moreover, heat release rate (HRR), the total heat release (THR) and total smoke production were reduced dramatically. On the other hand, combination of APP with micro(nano)-sized inorganic compounds is also an effective method for broadening the use of APP. Wilkie et al. investigated the influence of chemical interactions between APP and MgAl layered double hydroxide (MgAl-LDH) on fire resistance of PS, and the obtained results revealed the existence of synergism between APP and MgAl-LDH [1]. Lu et al. fabricated the PS/PA6/APP/clay composites, and observed the obviously improved fire retardance of PS by incorporation of APP and clay [14]. Unfortunately, based on the results aforementioned, it is concluded that excellent flame retardancy can be achieved at loading level surpassing 20 wt%. Therefore, it is better to enhance the application of APP in PS by modifying APP, and then the functionalized APP is used to flame retard PS alone.

Recently, graphitic carbon nitride ( $g\text{-C}_3\text{N}_4$ ) has received increasing interest because of its fascinating thermal and chemical stability, photoelectrochemical and catalytic properties, etc [15–18]. There are uncondensed  $-\text{NH}_2$  and  $-\text{NH}$  groups existing on the surfaces of  $g\text{-C}_3\text{N}_4$  nanosheets, where these functional groups can provide a large number of anchoring sites. The  $g\text{-C}_3\text{N}_4$  and its derivatives have been widely applied in energy storage, catalysts, optoelectronic devices, and sensors, etc [18–23]. In addition,  $g\text{-C}_3\text{N}_4$  based polymer composites have been prepared for surface hydrophilicity, photocurrent generation and hydrogen evolution [24–26]. According to our previous work,  $g\text{-C}_3\text{N}_4$  alone or its nanohybrids could improve the mechanical properties and thermal stability, and reduce HRR, THR and toxic gas release of polymers [27–30]. To the best of our knowledge, scarcely any attention has been paid to the microencapsulation of APP by  $g\text{-C}_3\text{N}_4$  for reducing the fire hazards of PS. It is reported that  $\text{NH}_4^+$  on the APP can be successfully complexed with  $-\text{NH}$  or  $-\text{NH}_2$  from other compounds [31,32]. We expect that the  $g\text{-C}_3\text{N}_4$ /APP hybrids (CNAPP) can improve the thermal stability and flame retardancy of PS.

In the present work, CNAPP was successfully prepared from APP and  $g\text{-C}_3\text{N}_4$  by a simple solvent mixing approach, and subsequently introduced to fabricate flame retarded PS composites using melt blending method. The aim of this work was to reduce the fire hazards of PS by addition of CNAPP. The microstructure and morphology of CNAPP were characterized by X-ray diffraction

patterns, Fourier transform infrared spectra and scanning electron microscopy. The thermal properties of CNAPP and PS composites were evaluated by thermogravimetric analysis. The flame retardancy of PS composites was assessed by cone calorimeter. The interfacial interactions between PS and fillers, and morphology of char residues after cone calorimeter test were measured using scanning electron microscopy. The possible mechanisms to illustrate reduced fire hazards of PS were also discussed.

## 2. Experimental section

### 2.1. Raw materials

PS (158 K) was obtained from BASF-YPC Co., Ltd. (China). APP-II was provided by Shandong Chenxu Chemical Co., Ltd. (Shandong, China). Both urea and isopropanol (IPA) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were used as received without further purification.

### 2.2. Preparation of CNAPP

The bulk  $g\text{-C}_3\text{N}_4$  was synthesized according to published work [33]. The structural diagram of  $g\text{-C}_3\text{N}_4$  is presented in Scheme 1. A series of CNAPP were prepared by a simple mixing method. In a typical procedure, 1.00 g of as-synthesized  $g\text{-C}_3\text{N}_4$  was dispersed in 200 mL of IPA to obtain a homogeneous suspension under ultrasound-assisted agitation. After sonication for 4 h, 9.00 g of APP was introduced into the suspension above, followed by heated to 100 °C and further kept for 20 h. Then, the obtained precipitate was filtered, washed with absolute alcohol several times, and dried at 80 °C overnight. The dried product was labelled as CNAPP10. Furthermore, CNAPP5, CNAPP20 and CNAPP30, meaning the  $g\text{-C}_3\text{N}_4$  to APP of 5/95, 20/80 and 30/70 w/w, respectively, were fabricated by the same approach.

### 2.3. Preparation of flame retarded PS composites

Flame-retardant additives (20 wt% loading level in the work) were blended with PS in a Brabender-like apparatus at 180 °C for 20 min using a Rheomixer XSS-300 (Shanghai Kechuang Plastic Machinery Co., Ltd., China). After mixing, the samples were hot-pressed at 190 °C under 5 MPa for 5 min and additional 10 MPa for 10 min. The PS composites containing CNAPP5, CNAPP10, CNAPP20 and CNAPP30 were denoted as PS/CNAPP5, PS/CNAPP10, PS/CNAPP20 and PS/CNAPP30, respectively. For comparison, PS/APP composite was also fabricated via a similar process.

### 2.4. Characterization

X-ray diffraction (XRD) patterns were obtained by a Japan Rigaku Dmax X-ray diffractometer equipped with graphite monochromatized high-intensity  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Fourier transform infrared (FTIR) and real time infrared (RTIR) spectra were obtained using a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA) with scanning from 500 to 4000  $\text{cm}^{-1}$ . The RTIR spectrums of APP and CNAPP were carried out with a linear heating rate of 10 °C  $\text{min}^{-1}$  from room temperature to 600 °C. The morphology of APP and CNAPP was investigated by scanning electron microscopy (SEM) (AMRAY1000B, Beijing R&D Center of the Chinese Academy of Sciences, China). These samples were dispersed onto copper sheets for observation. The PS composites were cryogenically fractured in liquid nitrogen and then sputter-coated with a conductive layer. The morphology of char residues

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