

Synthesis of Novel Triazine Charring Agent and Its Effect in Intumescent Flame-Retardant Polypropylene

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Received 17 March 2011; accepted 25 May 2011

DOI 10.1002/app.34993

Published online 6 September 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A novel charring agent (CNCA-DA) containing triazine and benzene ring, using cyanuric chloride, aniline, and ethylenediamine as raw materials, was synthesized and characterized. The effects of CNCA-DA on flame retardancy, thermal degradation, and flammability properties of polypropylene (PP) were investigated by limited oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA), and cone calorimeter test (CCT). The TGA results showed that CNCA-DA had a good char forming ability, and a high initial temperature of thermal degradation; the char residue of CNCA-DA reached 18.5% at 800°C; Ammonium polyphosphate (APP) could improve the char residue of APP/CNCA-DA system, the char residue reached 31.6% at 800°C. The results from LOI and UL-94 showed that the intumescent flame retardant (IFR) containing CNCA-DA and APP was very effective in flame retardancy

of PP. When the mass ratio of APP and CNCA-DA was 2 : 1, and the IFR loading was 30%, the IFR showed the best effect; the LOI value reached 35.6%. It was also found that when the IFR loading was only 20%, the flame retardancy of PP/IFR can still pass V-0 rating in UL-94 tests, and its LOI value reached 27.1%. The CCT results demonstrated that IFR could clearly change the decomposition behavior of PP and form a char layer on the surface of the composites, consequently resulting in efficient reduction of the flammability parameters, such as heat release rate (HRR), total heat release (THR), smoke production rate (SPR), total smoke production (TSP), and mass loss (ML). © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3208–3216, 2012

Key words: triazine charring agent; synthesis; thermal degradation; intumescent flame retardant; polypropylene

INTRODUCTION

Polypropylene is widely used in many fields such as automobiles, housing, electronic and electric materials, wires and cables for its excellent mechanical properties, low price and low density, ease-processing and good chemical resistance. However, its inherent flammability restricts its applications in the fields that required excellent flame-retardant properties. Thus researchers have made great efforts to improve the flame retardancy of polypropylene (PP).^{1–18} Traditionally, halogen-containing flame retardants and antimony trioxide are the most effective

ones and show a good ratio of property to price in flame retardancy of PP, especially bromine-containing flame retardants and antimony trioxide synergistic systems. However, the uses of these flame retardants have been limited, because halogen-containing flame retardants produce large amount of smoke and corrosive gases on burning.¹ Metal hydroxides, such as aluminum hydroxide and magnesium hydroxide, are other flame-retardant additives in PP. However, high loadings are needed to meet the same flame-retardant level in PP compared with halogen-containing retardants, and the mechanical properties of PP would be destroyed remarkably.^{2,3} Therefore, it is essential to develop the halogen-free flame-retardant PP owing to environmental and safety concerns.

Intumescent flame retardants (IFR) are well known as a new generation of flame retardants for PP, which are usually composed of three components, i.e., an acid source, a carbonization agent (or charring agent), and a blowing agent. Ammonium polyphosphate (APP)/pentaerythritol (PER)/melamine (MEL) system is the first used IFR system.⁴ Camino, Bourbigot and coworkers^{5–8} have done extensive studies on intumescent systems containing APP, PER and MEL, and the thermal degradation

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 50873116, 50773096, 50903096.

Contract grant sponsor: National 973 Program of China; contract grant number: 2011CB606100.

Contract grant sponsor: Department of Science Technology of Guangdong Province; contract grant number: 2008B090500196.

Contract grant sponsor: Fundamental Research Funds for the Central Universities.

mechanisms, charring processes and intumescent behaviors of IFR at molecular level were reported.^{9–11} However, the traditional IFR additives have some shortcomings, such as lower flame-retardant efficiency, lower thermal stability, and lower water resistance compared with bromine-containing flame retardants. To solve these problems, many research studies have been done.^{12–17} In recent years, triazine derivatives used as novel charring agents in IFR have been investigated. They are excellent charring agent, which can be attributed to the presence of the tertiary nitrogen in the triazine rings. However, owing to their low thermal stability and water resistance, some of them are not suitable for charring agents of IFR systems.^{14,15}

In this work, a novel charring agent was designed and synthesized. It is an oligomeric triazine derivative containing aniline, triazine rings and ethylenediamino groups, which is expected to have good thermal stability and char formation ability owing to the triazine and benzene rigid ring. The effects of the novel charring agent on thermal degradation and flame retardancy of PP/IFR systems have also been investigated.

EXPERIMENTAL

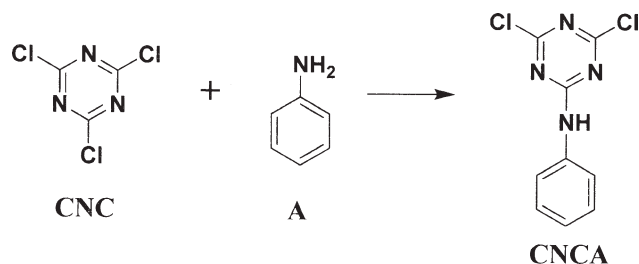
Materials

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

Preparation

Synthesis of 4,6-dichloro-N-phenyl-1,3,5-triazin-2-amine (CNCA)

Cyanuric chloride (0.2 mol) and acetone (100 mL) were fed into 500 mL three-neck flask provided with a magnetic stirrer, a thermometer and two dropping funnels. Both aniline and a solution of NaOH in water were simultaneously added dropwise to the flask, and the reaction temperature was kept at 0–5°C. The mixture was stirred for about 1 h until yellowish precipitate formed. Finally, the filtered product was washed chloride-free with cold water. The product was dried to a constant weight in vacuum at 50°C. A yellowish solid, yielded: 92.4%,



Scheme 1 Synthesis of CNCA.

was obtained. The synthesis route was shown in Scheme 1.

Synthesis of CNCA-DA

In a 500-mL glass flask, equipped with a stirrer, thermometer, feeding funnel, condenser, and heating bath, CNCA (48.2 g, 0.2 mol) and 250 mL CH₃CN were added; the mixture was then 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 100°C 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 80°C for 24 h a light yellowish solid (yield: 95.0%) was obtained. The synthesis route was shown in Scheme 2.

Preparation of intumescent flame-retardant polypropylene composites

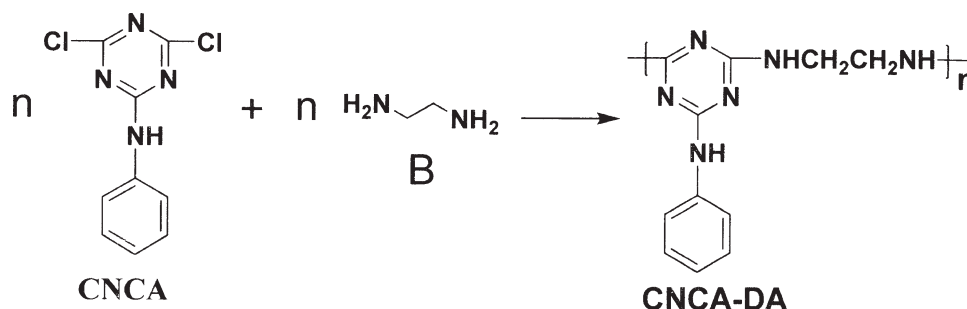
All samples were prepared by mixing PP, APP, CNCA-DA, and antioxidant 1010 on a two-roll mill at a temperature range of 170–180°C for 8 min, then pressed on a curing machine for 4 min to produce various thick sheets, which were used to produce various dimension sheets in all tests.

Characterization

The Fourier transform infrared (FTIR) spectra were obtained with a Nicolet FTIR 6700 infrared spectrophotometer, where the samples were prepared with KBr pellets. ¹H-NMR spectra were measured on a Mercury-Plus 300 spectrometer, using DMSO as solvent and tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were measured on a Thermo MAT95XP-HRMS spectrometer.

Flame-retardancy test

The flame retardancy of all samples was characterized by limited oxygen index (LOI) and UL-94 methods. LOI data of all the samples were obtained at room temperature on an oxygen index instrument



Scheme 2 Synthesis of CNCA-DA.

(DRK304B) produced by Jinan Deruik Instrument Factory, according to ISO 4589-1984 standard. The dimensions of all samples are $130 \times 10 \times 4 \text{ mm}^3$. Vertical burning rates of all samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory, with the sample dimensions of $125 \times 12.5 \times 3.2 \text{ mm}^3$ according to the American National Standard UL-94 standard. UL-94 test results are classified by burning ratings V-0, V-1 or V-2. V-0 rating indicates polymeric materials with the best flame retardancy.

Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was performed on a TA Q500 thermogravimetric analyzer at a heating rate of $10^\circ\text{C}/\text{min}$. The 4–5 mg sample was examined under a N_2 flowing rate of $40 \text{ mL}/\text{min}$ at temperature ranging from ambient to 800°C . All thermal degradation data were obtained from TG and DTG curves.

Cone calorimeter test

All CONE data were taken from Cone Calorimeter (manufactured by Fire Testing Technology) at a heat flux of 35 kW m^{-2} according to ISO 5660-1 standard.

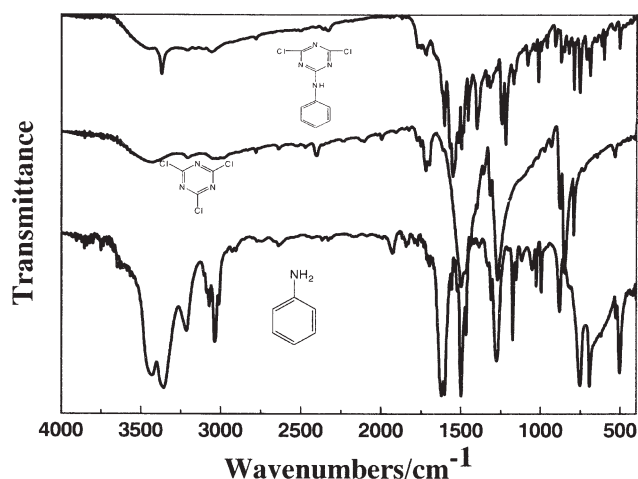


Figure 1 FTIR spectrum of CNCA.

All samples ($100 \times 100 \times 4 \text{ mm}^3$) were laid on a horizontal sample holder.

RESULTS AND DISCUSSION

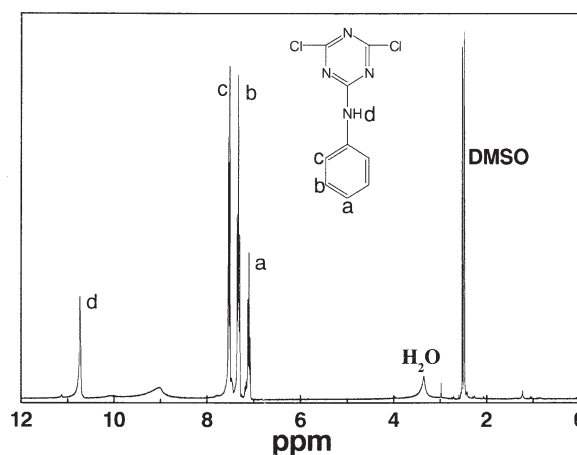
Characterization of CNCA

Figure 1 shows the FTIR spectra of CNCA. In this spectra, the absorption peaks at 3369 cm^{-1} can be attributed to $\nu_{\text{N-H}}$, the absorption band at 3054 cm^{-1} corresponds to $\nu_{\text{C-H}}$ of benzene ring, 1551 and 1400 cm^{-1} can be assigned to $\nu_{\text{C=N}}$ of triazine ring, 1605 , 1497 , and 1456 cm^{-1} can be assigned to $\nu_{\text{C=C}}$ of benzene ring. The appearance of characteristic absorption bands of triazine and benzene rings indicate the successful incorporation of aniline to cyanuric chloride.^{17,18}

Figure 2 shows the $^1\text{H-NMR}$ spectrum of CNCA. $^1\text{H-NMR}$ (300 MHz, DMSO) d (ppm): 10.73 (s, 1H), 7.52 (d, 2H), 7.33 (t, 2H), 7.10 (t, 1H). MS $[\text{M}-1]^+ : m/z$ 239. All these above facts allow us to conclude that the target product (CNCA) was successfully synthesized.

Characterization of CNCA-DA

Figure 3 shows the FTIR spectrum of CNCA-DA. In these spectra, the absorption peaks at 3370 and 3278

Figure 2 $^1\text{H-NMR}$ spectrum of CNCA.

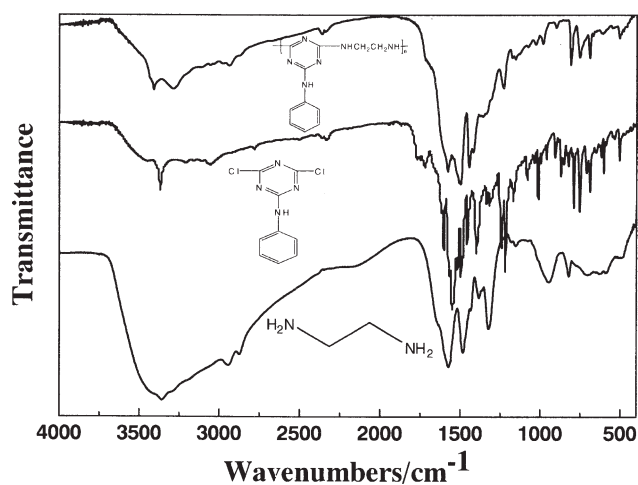


Figure 3 FTIR spectra of CNCA-DA.

cm^{-1} can be attributed to $\nu_{\text{N-H}}$; the absorption band at 3057 cm^{-1} corresponds to $\nu_{\text{C-H}}$ of benzene ring; those at 2935 and 2867 cm^{-1} can be assigned to $\nu_{\text{C-H}}$ in $-\text{CH}_2\text{CH}_2-$; those at 1578 and 1420 cm^{-1} can be assigned to $\nu_{\text{C=N}}$ of triazine ring, and at 1611 , 1498 , and 1445 cm^{-1} can be assigned to C=C of benzene ring. The appearance of characteristic absorp-

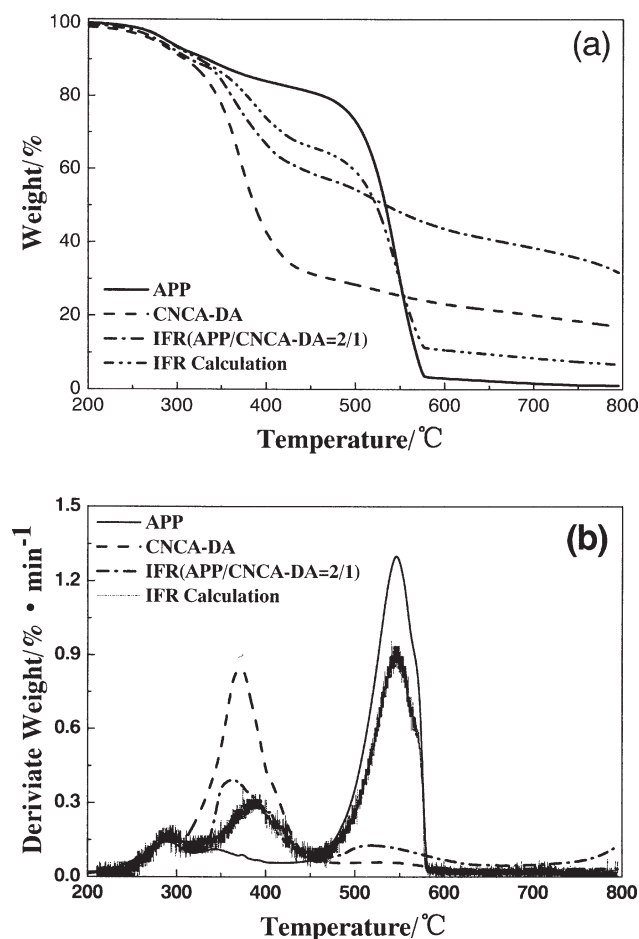


Figure 4 TGA (a) and DTG (b) curves of IFRs.

tion bands of triazine and benzene rings and $-\text{CH}_2\text{CH}_2-$ indicate the successful synthesis of CNCA-DA.

Thermal stability of CNCA-DA, APP, and APP/CNCA-DA systems

The thermal stability of APP/CNCA-DA systems was measured by TGA, and the degradation curves are shown in Figure 4. Table I gives thermogravimetric analysis data. APP is a very important component in IFR system, which can catalyze dehydration and crosslinking reaction of charring agents in IFR, served as acid source and gas source.^{1,19} From Table I and Figure 4, APP shows good thermal stability, its initial decomposing temperature was 289.2°C , based on 5% mass loss. It was found that thermal degradation process of APP was classified into two steps. The peak of step one is 286.4°C , which releases the water and ammonia; and the other one is 546.2°C , which can be assigned to the scission of phosphate ester.¹⁹

As can be seen in Table I, CNCA-DA shows high thermal stability. Its initial decomposing temperature was 288.5°C , based on 5% mass loss. It was revealed that thermal degradation of CNCA-DA was also classified in two steps. The first one at 293.9°C was the release of ammonia,^{1,14} and the second one at 390.0°C was the decomposition and char-forming of CNCA-DA. CNCA-DA shows a very effective char-forming ability according to the char residue results in Table I. The char residue of CNCA-DA was 26.1% at 600°C , 22.5% at 700°C , and 18.5% at 800°C . These results are attributed to the presence of benzene ring and six-membered rings containing tertiary amino groups within the macromolecular chain of CNCA-DA.

TABLE I
Thermal Properties of IFRs

	APP	CNCA-DA	IFR ^c	IFR-calculation ^e
^a $T_{1\%}/^\circ\text{C}$	246.0	246.8	228.2	246.1
^a $T_{5\%}/^\circ\text{C}$	289.2	288.5	280.2	288.9
^a $T_{10\%}/^\circ\text{C}$	333.3	315.3	314.3	324.7
^a $T_{50\%}/^\circ\text{C}$	533.4	406.1	534.2	523.1
^b $T_p/^\circ\text{C}$	546.2	390.0	363.7	540.7
^d $W_{600^\circ\text{C}}/\%$	3.0	26.1	43.8	10.7
^d $W_{700^\circ\text{C}}/\%$	1.6	22.5	38.4	8.6
^d $W_{800^\circ\text{C}}/\%$	0.98	18.5	31.6	6.8

^a $T_{1\%}$, $T_{5\%}$, $T_{10\%}$, and $T_{50\%}$ were the temperature at which 1 and 5% and 10 and 50% weight loss occurred, respectively.

^b T_p was the temperature at which the maximum of weight loss rate took place.

^c The ratio of APP : CNCA-DA is 2 : 1.

^d $W_{600^\circ\text{C}}/\%$, $W_{700^\circ\text{C}}/\%$ and $W_{800^\circ\text{C}}/\%$ were the residue of materials at 600, 700, and 800°C .

^e $W_{\text{calculation}} = W_{\text{APP}} \times 66.7\% + W_{\text{CNCA-DA}} \times 33.3\%$ (1).

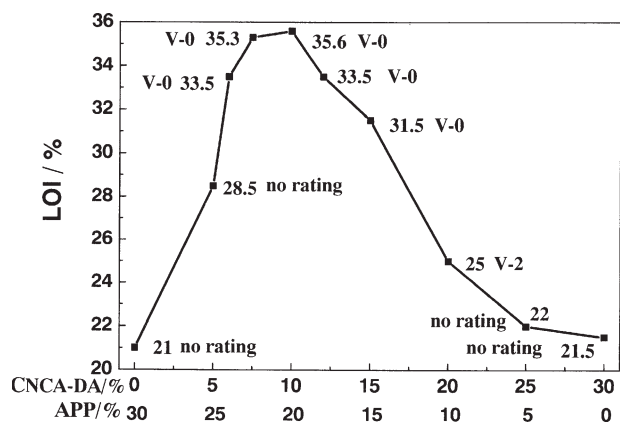


Figure 5 Effect of CNCA-DA on flame retardancy of PP/IFR systems.

In Figure 4, Curve IFR calculation is the result calculated from the experimental results of APP and CNCA-DA based on their percentage in IFR system according to formula (1). Curve IFR is the experimental result. According to Figure 4 and Table I, the initial decomposition temperature of IFR system was lower than that of APP and CNCA-DA. Compared with the theoretical calculation value, the experimental result of the main degradation peak of IFR (363.7°C) is much lower than that of theoretical value (540.7°C). This result revealed that incorporation of APP into CNCA-DA, the thermal degradation behaviors of APP and CNCA-DA changed. APP can improve the char formation property of CNCA-DA; the char residue at 800 was 31.6%, while it was only 6.8% based on the calculation result.

Flame retardancy

The novel triazine oligomer synthesized in this work was used as both a charring agent and a foaming agent in intumescent flame retardants, named as a novel charring agent (CNCA-DA). CNCA-DA was mixed with ammonium polyphosphate (APP) to produce a new intumescent flame retardant (IFR). This intumescent flame retardant was used in PP to obtain the PP/IFR systems. It has been suggested that a suitable acid source/charring agent/foaming agent ratio in the IFR system is very important to its flame retardancy.^{12–16} LOI is a parameter for evaluating flame retardancy and flammability of polymeric materials in the same condition. It denotes the lowest volume concentration of oxygen sustaining candle burning of materials in mixing gases of nitrogen and oxygen. Whereas UL test provides only a qualitative classification of the samples, and the results are classified by V-0, V-1, or V-2 ratings, where V-0 rating is the highest flame-retardant rating for materials, corresponding to prevention of flame spread vertically upwards, and without sam-

ple dripping, the V-1 rating allows nonflaming drips and V-2 allows flaming drips.

Figure 5 lists the LOI values and vertical burning rates for the PP/IFR systems with a total loading of the APP and CNCA-DA additives of 30 wt %. PP is an easily flammable polymeric material, and its LOI value is only 17.5%. Single additive of APP or CNCA-DA show little effect on the flame retardancy of PP, as the LOI value of PP composites containing 30% of APP or CNCA-DA is only about 21% and 21.5%. When CNCA-DA and APP are combined together, the LOI value of PP composites increased remarkably with the increasing of CNCA-DA content. When the weight ratio of APP and CNCA-DA increased to 2 : 1, the LOI value of PP/IFR composite reached the largest value, which is 35.6%. When the ratio of CNCA-DA and APP continued to increase, the LOI value decreased. It showed that When CNCA-DA and APP were mixed in a certain proportion, LOI values of PP/IFR systems were remarkably enhanced and exceeded 30%. The experimental results of vertical testing showed that all of PP/IFR system could reach V-0 rating when the weight ratio of APP and CNCA-DA is between 1 : 1 and 4 : 1.

Table II gives LOI value and UL rating of PP/IFR systems with different loading of IFR, where the weight ratio of APP and CNCA-DA is 2 : 1. With the increasing loading of IFR, the LOI value of PP/IFR system increased. When 20% of IFR was added, the LOI value of PP/IFR could reach 27.1%, and pass the UL-94 V-0 rating. When the loading of IFR is below 20%, it can't pass any rating with heavily dripping, named no rating. These experimental results further demonstrated that the novel IFR system is effective in PP.

TGA of PP/IFR system

Figure 6 and Table III give the TGA analysis curves and data of PP, PP/APP, PP/CNCA-DA, PP/IFR, and PP/IFR calculation in nitrogen, loading of APP, CNCA-DA, or IFR is 30%. The thermal degradation behavior of PP showed one decomposition peak at 446.7°C, and only 0.22% residue at 600°C. Compared with pure PP, PP/APP, PP/CNCA-DA, and PP/IFR

TABLE II
Effect of IFR Addition on Flame Retardancy of PP

PP/%	IFR/%	LOI/%	UL-94
100	0	17.5	no rating
85	15	23	no rating
82	18	25.1	no rating
80	20	27.1	V-0
78	22	28.5	V-0
70	30	35.6	V-0

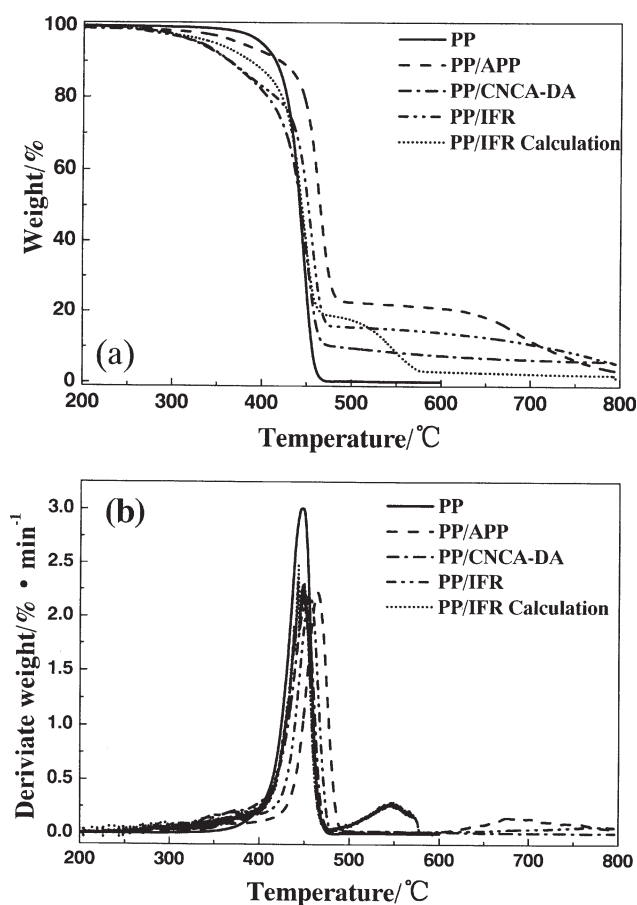


Figure 6 TGA (a) and DTG (b) curves of flame retardant PP in N_2 .

systems have poor thermal stability before 450°C , because of the degradation of APP, CNCA-DA, and the interaction between APP and CNCA-DA to form char layer. Curve PP/IFR calculation is the calculated results based on formula (2). By comparing with the experimental and calculated results, it was

found that IFR could increase the maximum decomposition temperature of PP. The main decomposition peak of PP/IFR system appeared at 455.5°C , while that of PP/IFR calculation appeared at 443.0°C . The results indicated the interaction between PP and IFR during the thermal degradation. The char residue of PP/IFR system showed a clear increase at 600, 700, and 800°C compared with the calculated results. The reason can be attributed to the char layer formed by IFR system which could prevent heat from transferring inside of PP/IFR system.

Cone calorimeter study

Cone calorimetric analysis has been widely used to evaluate the flame-retardant characteristics of flame-retardant materials. It has good correlation with real fire disaster and can provide a wealth of information on combustion behavior.^{16,17} Various parameters could be obtained from cone calorimetry, including the heat release rate (HRR), the peak heat release rate (PHRR), the total heat release (THR), mass loss (ML), smoke produce rate (SPR), and total smoke produce (TSP). Figure 7–9 and Table IV clearly demonstrates the plots and data for PP and PP/20%IFR obtained from the cone calorimeter test at a heat flux of 35 kW m^{-2} .

The heat release rate (HRR) is recognized to be the most important parameter to evaluate the intensity of fire. Normally, an effective flame-retardant system shows a low HRR value. Figure 7 presents the HRR curves of PP and PP/20%IFR at a heat flux of 35 kW m^{-2} . Pure PP burned very fast after ignition and a sharp peak appeared, evolved a large amount of heat release with a PHRR of 816.56 kW m^{-2} . When 20% of IFR was incorporated into PP, the HRR peak of PP composite decreased remarkably. The reduction in peak of HRR was nearly 81%,

TABLE III
TGA Data of Flame Retardant PP in N_2

	PP	PP/APP	PP/CNCA-DA	PP/IFR	PP/IFR calculation ^d
^a $T_{1\%}/^\circ\text{C}$	358.4	279.5	256.6	257.4	209.1
^a $T_{5\%}/^\circ\text{C}$	399.5	376.2	329.7	331.9	355.0
^a $T_{10\%}/^\circ\text{C}$	414.5	420.0	363.0	363.8	393.6
^a $T_{50\%}/^\circ\text{C}$	442.0	464.6	442.9	451.4	444.3
^b $T_p/^\circ\text{C}$	446.7	464.0	450.4	455.5	443.0
^c $W_{600^\circ\text{C}}/\%$	0.22	21.04	7.63	14.12	3.37
^c $W_{700^\circ\text{C}}/\%$	–	12.00	6.53	11.97	2.73
^c $W_{800^\circ\text{C}}/\%$	–	3.34	5.89	5.54	0.35

^a $T_{1\%}$ and $T_{5\%}$ and $T_{10\%}$ and $T_{50\%}$ were the temperature at which 1 and 5% and 10 and 50% weight loss occurred, respectively.

^b T_p was the temperature at which the maximum of weight loss rate took place.

^c $W_{600^\circ\text{C}}/\%$, $W_{700^\circ\text{C}}/\%$, and $W_{800^\circ\text{C}}/\%$ were the residue of materials at 600, 700, and 800°C .

^d $W_{\text{calculation}} = W_{\text{PP}} \times 70\% + W_{\text{APP}} \times 20\% + W_{\text{CNCA-DA}} \times 10\%$ (2).

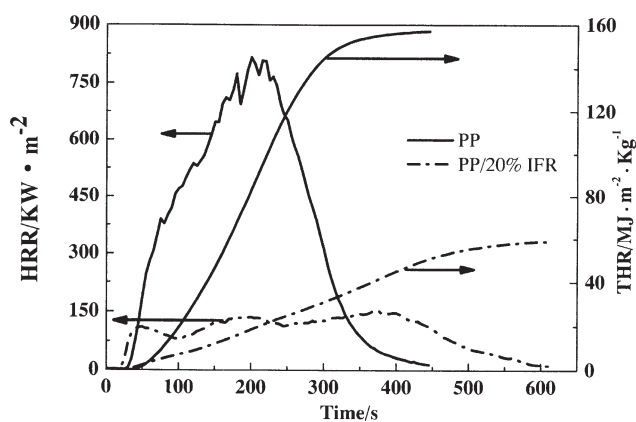


Figure 7 The HRR and THR curves of PP and PP/20%IFR.

and the PHRR decreased from 816.56 kW m^{-2} to 153.64 kW m^{-2} . Moreover, the burning time of PP composite is about 200 s longer than that of pure PP. The HRR curve of PP/20%IFR system showed three peaks. The reason can be explained as followed: first, IFR degrades and intumescent shield forms; second, the intumescent coating formed at first step is not strong enough to resist heat from cone calorimeter and degrades, consequently a new intumescent shield forms; and third, the residual char formed at second step is still not strong and oxidized, and then forms a much stronger intumescent char.

Figure 7 also presents the total heat release rate (THR) curves of PP and PP/20%IFR, and the slope of the THR curves is assumed as representative of fire spread rate. The largest value of THR for pure PP is $157.14 \text{ MJ m}^{-2} \text{ kg}$. In contrast, the curve of PP/20%IFR composite shows much lower value in THR plot, which is about $59.05 \text{ MJ m}^{-2} \text{ kg}$. This significant decrease in THR of PP/20%IFR system indicates that parts of PP/IFR composite was not burn completely. This is because the intumescent char

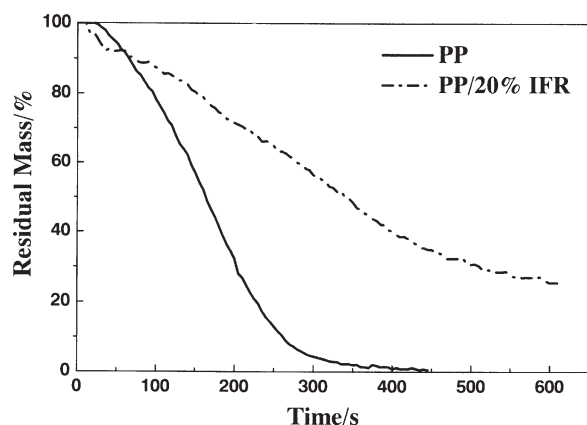


Figure 8 The Residual Mass curves of PP and PP/20%IFR.

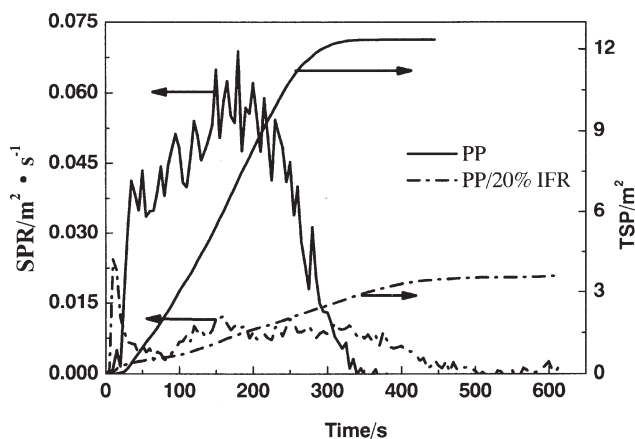


Figure 9 The SPR and TSP curves of PP and PP/20%IFR.

formed on the surface of matrix while PP/IFR composite combustion, which served as thermal insulator and prevented combustible gas from feeding the flame, protected the underlying matrix from further burning and retarded pyrolysis of the polymer.

Figure 8 presents the dynamic curves of mass versus time for PP and PP/20%IFR during combustion. It can be seen that pure PP lost its mass faster than the PP/20%IFR system. After combustion, the residual mass of PP/IFR composite was 34.90%, while nothing left for the pure PP, which agrees well with the results of TGA. This means that the compact char layer decrease the evolution of combustible gas during the combustion process.

The smoke production along with the HRR also plays a critical part in fire. The smoke production rate (SPR) and total smoke production (TSP) curves of the two samples are showed in Figure 9. It can be seen that the curve and the value of PP/IFR are far lower than those of PP, similar to HRR curves. This result can also be attributed to the stable char layer covering on the surface of matrix. The peak of SPR for PP/20%IFR appears earlier. That is because at

TABLE IV
Cone Results of Materials

Properties	PP	PP/20%IFR
Peak1-HRR/ KW m^{-2}	816.56	110.74
$t_{\text{peak1-HRR/s}}$	200	50
Peak2-HRR/ KW m^{-2}	—	136.26
$t_{\text{peak2-HRR/s}}$	—	200
Peak3-HRR/ KW m^{-2}	—	153.64
$t_{\text{peak3-HRR/s}}$	—	375
AHRR/ KW m^{-2}	369.75	97.58
THR/ $\text{MJ}\cdot\text{m}^{-2}\cdot\text{kg}$	157.14	59.05
Peak1-SPR/ $\text{m}^2\text{ s}^{-1}$	0.069	0.024
$t_{\text{peak1-SPR/s}}$	180	10
Peak2-SPR/ $\text{m}^2\text{ s}^{-1}$	—	0.012
$t_{\text{peak2-SPR/s}}$	—	160
TSP/ m^2	12.32	3.60
Char residue at 450s/%	0	34.90

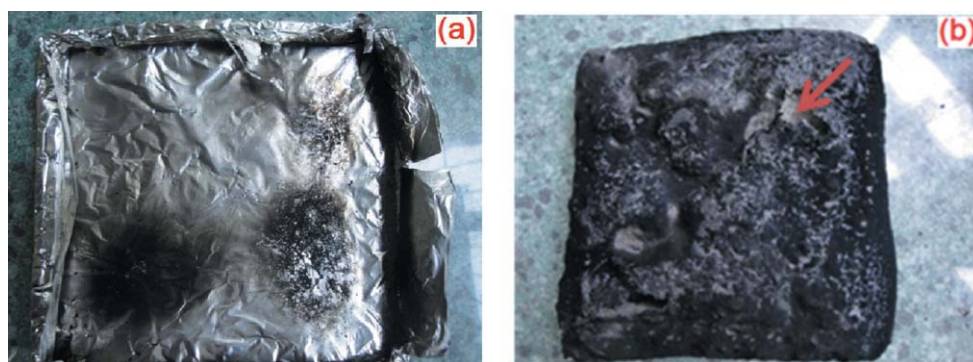


Figure 10 Photographs of the specimens after cone calorimeter test of (a) PP and (b) PP/20%IFR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the initial stage of heating, the surface temperature of PP/20%IFR system raises quickly, resulting in the rapid decomposition of IFR on the surface of PP/20%IFR.

Figure 9 also gives the TSP curves of PP and PP/20%IFR. Similar to the THR curves, the PP/IFR composites could significantly reduce the values of TSP, as compared with the pure PP. The value of TSP reduces from 12.32 m² to 3.60 m². Comprehensively, all the above data and curves (HRR, THR, Mass loss, SPR, and TSP) indicate that APP/CNCA-DA system can form compact and continuous char layer and perform excellent flame retardancy and smoke suppression function.

Morphology of burnt composites

Figure 10 displays photographs of the specimens after cone calorimeter tests for PP and PP/20%IFR. For pure PP, it was almost burnt out, and no char left after test. Although for the PP composite with 20% of IFR, a thick, continuous, and impact char layer with some small holes on the char surface was

formed, which prevented heat and mass from transferring between the flame zone and the burning substrate. The char layer is strong enough to protect the underlying materials from further burning and retarding the pyrolysis of materials, as shown in Figure 10(b) (pointed out by the red arrow) and Figure 11.

CONCLUSIONS

A novel charring agent with benzene and triazine ring (CNCA-DA) has been successfully synthesized and characterized. It can be used as a charring agent and a foaming agent in intumescent flame retardant. TGA results showed that CNCA-DA had good thermal stability and ability of char formation. APP could promote char formation ability of APP/CNCA-DA IFR system.

The combination of APP and CNCA-DA can form an effective intumescent flame-retardant (IFR) system. When the mass ratio of APP and CNCA-DA is 2 : 1, it showed the most effective flame retardancy. When the IFR loading was 20% in PP, LOI value of PP/IFR system reached 27.1%, and passed the V-0 rating in UL-94 tests.

Comparing the experimental results and the theoretically calculated value, the TGA results showed that IFR could change the thermal degradation behavior of PP, and promote PP to form char, enhancing the temperature of the maximum decomposition rate of PP.

According to cone calorimeter studies, the addition of IFR reduces the value of HRR, THR, SPR, TSP, and mass loss significantly, which confirm that the IFR system acts as effective flame retardant and smoke suppressant in PP.

References

1. Chiang, W. Y.; Hu, C. H. *Eur Polym Mater* 1996, 32, 385.
2. Rothon, R. N.; Hornsby, P. R.; *Polym Degrad Stab* 1996, 54, 383.



Figure 11 Photograph of residue under char of PP/20%IFR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3. Hornsby, P. R. *Fire Mater* 1994, 18, 269.
4. Camino, G.; Grassie, N.; McNeill, I. C. *J Polym Sci Polym Chem Ed* 1978, 16, 95.
5. Bourbigot, S.; Le Bras, M. *Carbon* 1995, 33, 283.
6. Chiu, S. H.; Wang, W. K. *Polymer* 1998, 39, 39.
7. Camino, G.; Costa, L.; Trossarelli, L. *Polym Degrad Stab* 1985, 12, 213.
8. Riva, A.; Camino, G.; Fomperie, L.; Amigouet, P. *Polym Degrad Stab* 2003, 82, 341.
9. Camino, G.; Costa, L.; Trossarelli, L. *Polym Degrad Stab* 1984, 6, 243.
10. Camino, G.; Costa, L.; Trossarelli, L. *Polym Degrad Stab* 1985, 12, 203.
11. Camino, G.; Martinasso, G.; Costa, L. *Polym Degrad Stab* 1990, 27, 285.
12. Li, B.; Xu, M. *J Polym Degrad Stab* 2006, 91, 1380.
13. Lv, P.; Wang, Z. Z.; Hu, K. L.; Fan, W. C. *Polym Degrad Stab* 2005, 90, 523.
14. Dai, J. F.; Li, B. *J App Polym Sci* 2010, 116, 2157.
15. Hu, X. P.; Li, W. Y.; Wang, Y. Z. *J App Polym Sci* 2004, 94, 1556.
16. Hu, X. P.; Li, Y. L.; Wang, Y. Z. *Macromol Mater Eng* 2004, 289, 208.
17. Nie, S. B.; Hu, Y.; Song, L.; He, Q. L.; Yang, D. D.; Chen, H. *Polym Adv Technol* 2008, 19, 1077.
18. Song, P. A.; Fang, Z. P.; Tong, L. F.; Jin, Y. M.; Lu, F. Z. *J Anal Appl Pyrol* 2008, 82, 286.
19. Samyn, F.; Bourbigot, S.; Duquesne, S.; Delobel, R. *Thermo-chim Acta* 2007, 456, 134.