

Flame-retardancy properties of tris(2-hydroxyethyl) isocyanurate based charring agents on polypropylene

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ABSTRACT: Tris(2-hydroxyethyl) isocyanurate based charring agent (TBCA) was synthesized by melt polycondensation with tris(2-hydroxyethyl) isocyanurate (THEIC) and terephthalic acid as raw materials. It was characterized by Fourier transform infrared spectroscopy, elemental analysis, $^1\text{H-NMR}$, and thermogravimetric analysis (TGA). TBCA was blended with ammonium polyphosphate (APP) to form an intumescent flame retardant (IFR) for polypropylene (PP). The charring properties of TBCA was tested by flame retardancy in the PP/APP/TBCA (PP/IFR₂) composite and compared with that of the PP/APP/THEIC (PP/IFR₁) composite. The results show that PP/IFR₂ had lower flame-retardant properties but better water resistance than that of the PP/IFR₁ composite because PP/IFR₂ could still obtain a V-0 rating after it had been soaked in water at 70°C for 96 h, whereas PP/IFR₁ could not achieve any rating after 36 h. Their combustion performance was further evaluated by a cone calorimeter test, their thermal degradation processes were studied by TGA, and the morphology of the char residue was observed by scanning electron microscopy. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41810.

KEYWORDS: flame retardancy; properties and characterization; thermogravimetric analysis (TGA)

Received 9 September 2014; accepted 23 November 2014

DOI: 10.1002/app.41810

INTRODUCTION

Polypropylene (PP) is widely used in industry because of its excellent properties, including a good chemical resistance, ease of processing, and lower poison.^{1–5} However, the use of PP in electric and electronic applications, building, and transportation is strongly limited because of its flammability.^{6–11} Traditionally, halogen flame retardants have been added to improve the flame resistance of PP; however, toxic gases and corrosive fumes may be released during their combustion;^{12–14} this leads to a bad influence on people's safety. With the improvement of mankind's awareness on health, halogen-containing flame retardants are faced with prohibition.

In recent years, intumescent flame retardants (IFRs) have drawn much attention because of their environmentally friendly characteristics.^{9–11} Typically, an IFR system is composed of three ingredients: an acid source, a charring agent, and a blowing agent.^{5,15–18} Typical IFR systems containing ammonium polyphosphate (APP) and pentaerythritol (PER) have some shortcomings when it is used in plastics applications, such as lower flame retardant efficiency, lower thermal stability and lower water resistance.¹⁹ Many studies have been done to improve these disadvantages, for example, APP's thermal stability and water resistance can be enhanced through an increase in its degree of polymerization or by encapsulation,^{20–23} the flame-

retardant efficiency can be improved by the addition of synergistic agents, such as zeolites, metallic oxide, and layered minerals.^{7,12,24–27}

Until now, many attentions have been focused on acid sources; little has been paid to charring agents. PER has been used as a charring agent for many years; however, the accompanying problems have never been completely solved. One problem is that PER easily excludes the polymer surface during processing. Another is that PP/APP/PER composites are easily deliquescent in wet environments; this not only affects the appearance of products but also affects its flame-retardant durability. Therefore, new kinds of charring agents with better antideliquescent performances are needed.

In recent years, compounds with a triazine structure have been found to be effective in IFR systems. Li and Xu¹⁹ once reported a triazine-based char-forming agent, which was synthesized by cyanuric chloride, ethanolamine, and ethylenediamine. The IFR, consisting of a char-forming agent, APP, and 4A zeolite, showed very good flame-retardant efficiency on PP. Moreover, the flame-retarded composite had good water-resistance properties; a good V-0 rating could be obtained when it was soaked in water at 70°C for 168 h. However, these triazine-based charring agents were prepared from cyanuric chloride in the solvent system;^{28–32} the synthesized process will produce corrosive gases

Table I. Flame Retardancy of the PP/IFR₁ and PP/IFR₂ Composites

| Sample | PP | APP | THEIC | TBCA | PER | LOI (%) | UL-94 | Dripping |
|--------|----|-----|-------|------|-----|---------|-------|----------|
| PP-0 | 70 | — | — | — | — | 17.8 | NR | Yes |
| PP-1 | 70 | 30 | — | — | — | 19.2 | NR | Yes |
| PP-2 | 70 | 27 | 3 | — | — | 30.8 | V-0 | No |
| PP-3 | 70 | 25 | 5 | — | — | 32.7 | V-0 | No |
| PP-4 | 70 | 20 | 10 | — | — | 34.8 | V-0 | No |
| PP-5 | 70 | 15 | 15 | — | — | 30.6 | V-0 | No |
| PP-6 | 70 | 10 | 20 | — | — | 24.8 | V-2 | Yes |
| PP-7 | 70 | 27 | — | 3 | — | 28.7 | V-0 | No |
| PP-8 | 70 | 25 | — | 5 | — | 29.8 | V-0 | No |
| PP-9 | 70 | 20 | — | 10 | — | 31.4 | V-0 | No |
| PP-10 | 70 | 15 | — | 15 | — | 30.0 | V-0 | No |
| PP-11 | 70 | 10 | — | 20 | — | 27.6 | V-0 | No |
| PP-12 | 70 | 20 | — | — | 10 | 31.6 | V-0 | No |

NR, no rating.

and waste solvents. Moreover, cyanuric chloride is chemically active, and the production of triazine-based charring agents from cyanuric chloride threaten workers' safety. These problems restrict the development of triazine-based charring agents. Recently, our group³³ found that tris(2-hydroxyethyl) isocyanurate (THEIC) is an effective charring agent, and it has good synergistic effects with APP. A new tris(2-hydroxyethyl) isocyanurate based charring agent (TBCA) was developed and used as a charring agent to flame-retard poly(lactic acid) resin.³⁴ The main concerns of our previous studies were to find new charring agents and to evaluate their charring behaviors with APP in different plastic fields. As a matter of fact, TBCA is derived from THEIC, and there are some structural similarities between them. However, the difference between TBCA and THEIC used as charring agents in IFR systems was ignored. In this study, TBCA was blended with APP to form an IFR for PP. The flame retardancy, thermal degradation, and combustion processes of the PP/APP/TBCA (PP/IFR₂) and PP/APP/THEIC (PP/IFR₁) composites were studied and compared, and the flame-retardant durability was emphasized.

EXPERIMENTAL

Materials

PP (T30s, melt-flow rate = 2.3 g/10 min) was supplied as pellets by SINOPEC Maoming Co. (China). APP of crystal form II with a polymerization degree of 1000 was kindly provided by Shandong Shi'an Chemical Co., Ltd. THEIC was purchased from Changzhou Lantian Chemical Co., Ltd. Others were purchased from Sinopharm Chemical Reagent Co., Ltd. All of the materials were used without further purification.

Synthesis of TBCA

An amount of 215.0 g of THEIC was added to a dry four-necked flask, which was equipped with a mechanical stirrer, thermometer, and reflux condenser. When THEIC was heated to 150°C, it turned into a melt state. Amounts of 1.2 g of 4-methylbenzenesulfonic acid and 94.0 g of terephthalic acid

(TPA) were added to the flask with constant stirring. This mixture was heated to 200°C and retained at this temperature for 8 h. Then, the melt was cooled and ground, and a white powder was obtained.

Preparation of the Samples

APP and TBCA were dried at 60°C *in vacuo* for 8 h before used. Pure PP was mixed at a rotation speed of 20 rpm at 180°C for 3 min with an internal mixer (SU70, Suyan Technology Co., China); then, APP and TBCA were introduced and mixed for 10 min. The composite was hot-pressed at 180°C into sheets of a suitable thickness and a size for further flame-properties tests. The formulations of all of the samples are listed in Table I.

Flame-Retardancy Test

The flame retardancy was characterized by limited oxygen index (LOI) and UL-94 methods. The LOI values were tested according to ASTM D 2863-97 with an oxygen index instrument (JF-3) produced by Jiangning Analysis Instrument Factory. UL-94 rating tests were conducted on a CZF-3 instrument (Jiangning, China) with sheet dimensions of 130 × 13 × 3 mm³ according to ASTM D 3801.

Characterization

The Fourier transform infrared (FTIR) spectrum was obtained with a Bruker Vertex 70 FTIR spectrometer in the range 400–4000 cm⁻¹ with the KBr disk method. The elemental analysis was performed by a Vario EL III CHN-O rapid elemental analyzer with acetanilide as the standard. The ¹H-NMR spectra were recorded at 400 MHz on an Avance 400 spectrometer (Bruker Co., Switzerland), and trichloromethane (CHCl₃) was used as a solvent. The combustion properties were evaluated with a cone calorimeter. All of the samples (100 × 100 × 3 mm³) were exposed to a Stanton Redcroft cone calorimeter under a heat flux of 50 kW/m² according to ISO-5660 standard procedure. The thermogravimetric analysis (TGA) tests were carried out on EXSTAR 6000 (Hitachi, Japan) at a heating rate

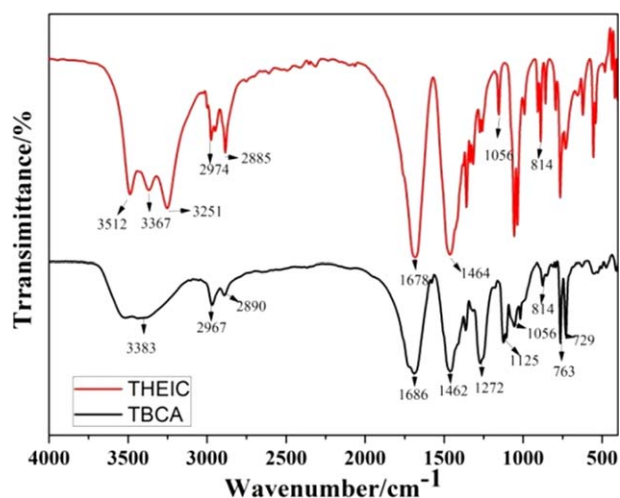


Figure 1. FTIR spectra of TBCA and THEIC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 10°C/min under an air atmosphere. The TGA data were collected from room temperature to 800°C, and the sample weight was kept within 10 mg. The morphology of the char residue was observed by a JSM-6360 scanning electron microscopy (SEM) instrument with an accelerating voltage of 15 kW.

RESULTS AND DISCUSSION

Characterization of TBCA

The FTIR spectra of THEIC and TBCA are shown in Figure 1. From the FTIR spectrum of THEIC shown in Figure 1. The absorption peaks at 3512, 3367, and 3251 cm^{-1} were attributed to O—H and hydrogen-bond vibrations. The absorptions at 2974 and 2949 cm^{-1} were assigned to the asymmetric stretching vibration of $-\text{CH}_2-$. The peak at 2885 cm^{-1} was attributed to $-\text{CH}_2-$ stretching vibrations. The band at 1464 cm^{-1} was caused by C=O stretching vibrations. The absorptions at 1056 and 1035 cm^{-1} were assigned to C—O vibrations. The area at 814 cm^{-1} was attributed to the skeleton vibration of the triazine ring.³³

From the spectra of TBCA in Figure 1, the absorption area at 3383 cm^{-1} was attributed to O—H vibrations, and the peak at

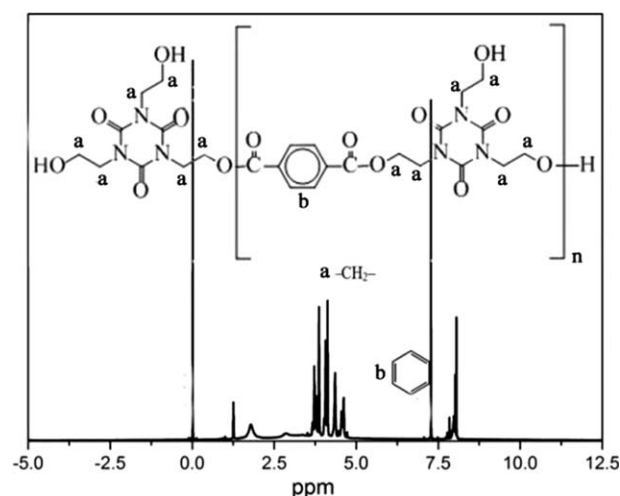


Figure 2. $^1\text{H-NMR}$ spectrum of TBCA.

Table II. Elemental Analysis of TBCA

| | Elemental content (%) | | |
|------|-----------------------|-------|------|
| | C | N | H |
| TBCA | 49.51 | 11.57 | 4.74 |

1125 cm^{-1} was caused by the vibrations of C—O—C. This was evidence of esterification bonding in TBCA. In the area from 3000 to 3550 cm^{-1} , three peaks in the THEIC spectra were very sharp; this was caused by a hydrogen-bond effect. However, the peak was flat in the TBCA spectra; this indicated that hydrogen bonding was weakened; this was possibly due to the esterification bonding.

The $^1\text{H-NMR}$ spectrum of TBCA is shown in Figure 2. As shown in Figure 2, the signal of hydrogen in the benzene ring was found at 7.21–7.45, and the peaks from 3.64 to 4.61 were attributed to the hydrogen in the $-\text{CH}_2-$ group. It split to multiple peaks because of the complex chemical environment. The FTIR spectrum shown in Figure 1 provided the evidence of OH groups in TBCA. However, this hydrogen in the OH group belonged to active hydrogen, and it had no chemical shift in the $^1\text{H-NMR}$ spectrum. On the basis of the FTIR and $^1\text{H-NMR}$ spectra of TBCA, the chemical structure was determined and is shown in Figure 2. To fully characterize TBCA, elemental analysis was also conducted, and the results are listed in Table II. As shown in Table II, the experimental contents of C, H, and N in TBCA were 49.51, 11.57, and 4.74 wt %, respectively.

The thermal degradation curves of TBCA and THEIC are shown in Figure 3. As shown in Figure 3, THEIC decomposed in one step; this started at 259°C and ended at 293°C, with no char residue left. TBCA decomposed in three stages. The first stage was between 250 and 300°C. This stage was assumed to the loss of intermolecular water or the decomposition of the unstable groups in TBCA. The second stage was between 300 and 475°C. This stage was assumed to be degradation and volatilization.

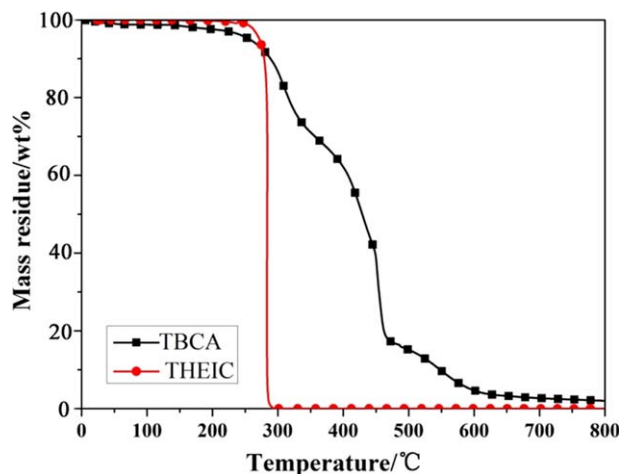


Figure 3. Thermogravimetry curves of TBCA and THEIC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Belsky *et al.*³⁵ once studied the decomposition process of the triazine ring; they found that the triazine ring in cyanuric acid tended to completely decompose into gaseous products of CO₂ and NH₃ when the temperature was higher than 300°C. This phenomenon supported the decomposition of the triazine ring in TBCA. Wang *et al.*³⁶ studied the decomposition mechanism of methylbenzene and calculated the stability of the product in possible decomposition paths. The benzene ring was rather stable, and the weight loss was mainly ascribed to volatilization. The third stage was between 470 and 600°C and was assumed to further the decomposition and volatilization of the product.

Flame Retardancy of the PP Composites

The charring ability of TBCA was tested and compared with that of THEIC. All of the flame-retardancy test results for the PP/IFR composites are listed in Table I.

Pure PP was easily flammable and accompanied with a droplet; its LOI value (PP-0) was only 17.8. The single addition of 30 wt % APP into PP had a low flame-retardant efficiency. The composite (PP-1) failed to achieve any V-rating in the UL-94 test; its LOI value was only 19.2. This result was similar to those of former reports.^{37,38} However, when APP and charring agent were both added to PP, the LOI values dramatically increased. The highest LOI values of the PP/IFR₂ composite (PP-4) and PP/IFR₁ composite (PP-9) were 34.8 and 31.4, respectively. PP-12 was a traditional formulation containing APP and PER; its LOI value was 31.6. This was the same as the LOI value of PP-9 but was lower than the LOI value of PP-4. This phenomenon indicated that the flame-retardant efficiency of TBCA was similar to that of PER but was lower than that of THEIC.

The UL-94 test results are also listed in Table I. When IFR was added to PP, all of the samples achieved a V-0 rating except PP-6. This indicated that the flame retardancy was closely related to the mass proportion of APP to the charring agent; there was a synergistic effect between them.

To fully compare the flame retardancy of THEIC and TBCA, the LOI values of different mass ratios of APP/THEIC or APP/TBCA in the IFRs were studied. The results are shown in Figure 4. As shown in Figure 4, the LOI variation tendency of PP/IFR₁ and PP/IFR₂ was similar. When the mass ratio of APP/THEIC and APP/TBCA were 9:1, the LOI values of PP-2 and PP-7 were 30.8 and 28.7, respectively. With the raise of charring agent in the IFR system, the LOI values simultaneously increased for the two systems. When the mass ratio of APP to the charring agent was 2:1, both composites obtained the highest LOI values at the same time. After that, with decreasing APP, the LOI values decreased. The results indicate that the synergistic effect between THEIC and APP was similar to the synergistic effect between TBCA and APP. However, the LOI values of the PP/IFR₁ composites were a little higher than those of PP/IFR₂ at the same proportion of IFR; this indicated that the synergistic efficiency of THEIC was better than that of TBCA.

Water Resistance of the PP/IFR₁ and PP/IFR₂ Composites

According to results of the LOI tests, the best flame-retardant formulations were selected as PP-4 and PP-9. The PP-IFR composites contained 70 wt % PP, 20 wt % APP, and 10 wt % char-

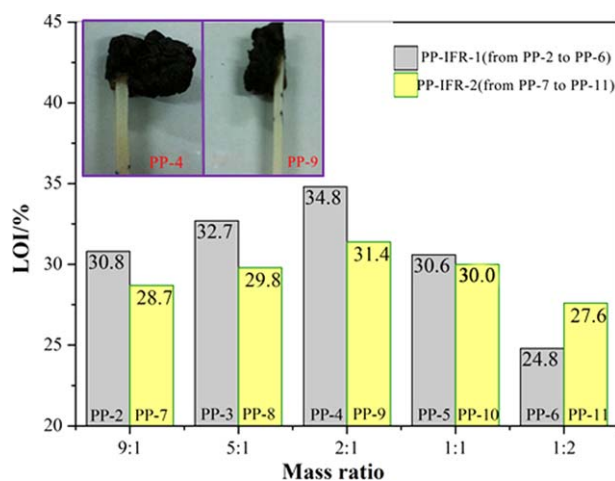


Figure 4. LOI values for different APP/THEIC and APP/TBCA mass ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ring agent, respectively. The samples were soaked in water at 70°C for different times, and their flame-retardancy properties were tested, including LOI and UL-94 tests. The results are listed in Table III. Table III shows that both PP-4 and PP-9 achieved a V-0 rating after it soaked in water at 70°C for 12 h. However, PP-4 only obtained a V-2 rating after 24 h, with melt dripping occurring during the combustion process. After 36 h, no rating was obtained for PP-4. However, PP-9 still obtained a V-0 rating after 96 h of soaking. PP-4's LOI value dropped from 34.8 to 26.9 after 96 h, a decrease of 22.7%. Nevertheless, PP-9's LOI value dropped from 31.4 to 29.7, a decrease of only 6.68%. The results indicate that APP/TBCA had good water-resistance properties. PP/IFR₂ had a better flame-retardant durability than the PP/IFR₁ composite. We explained this by the molecular structure of TBCA and THEIC. THEIC is a small molecule with three OH groups; it tends to be hydrophilic. As a result, the water-resistance properties of PP/IFR₁ was not perfect. Compared with THEIC, TBCA's molecular weight was higher because of the esterification of THEIC, and TPA, a large proportion of hydrophilic OH groups in THEIC, was replaced by a nonhydrophilic

Table III. UL-94 and LOI Test Results for PP-4 and PP-9 after Treatment with 70°C Water for Different Times

| | Sample | |
|----------------|--------|------|
| | PP-4 | PP-9 |
| Treatment time | | |
| 12 h | V-0 | V-0 |
| 24 h | V-2 | V-0 |
| 36 h | NR | V-0 |
| 48 h | NR | V-0 |
| 96 h | NR | V-0 |
| LOI | | |
| After 0 h | 34.8 | 31.4 |
| After 24 h | 30.2 | 30.5 |
| After 96 h | 26.9 | 29.7 |

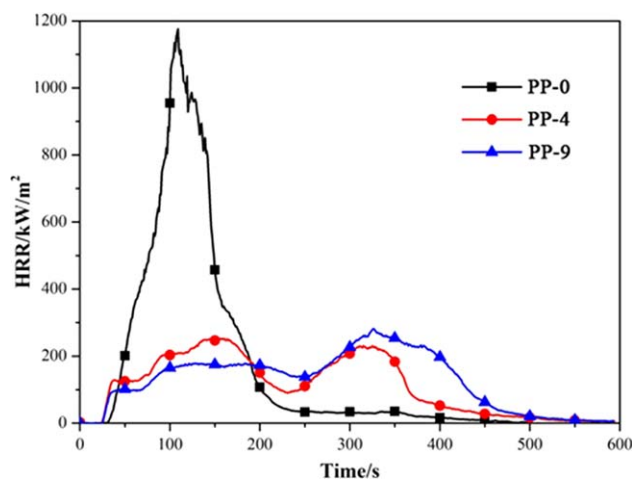


Figure 5. HRR curves of PP-0, PP-4, and PP-9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

—C—O—C—group. Therefore, the water-resistance properties of PP/IFR₂ were better than those of PP/IFR₁.

Cone Calorimetry Testing

Cone calorimetry is a small-scale test, but it has a good correlation with real fire disasters and is commonly used to predict the combustion behavior of materials in real fires. The heat release rate (HRR) is recognized as the most important parameter for evaluating the developing, spreading, and intensity of fires. The effects of APP/THEIC and APP/TBCA on the HRR of PP are shown in Figure 5.

When APP/THEIC or APP/TBCA was added to PP, the peak heat release rate (PHRR) decreased remarkably. The PHRRs of PP-4 and PP-9 were 251.92 and 280.96 kW/m². Decreases of 78.57 and 76.10% in comparison with PP-0, respectively. PP-4 had a lower PHRR value; this indicated that THEIC had better char-forming properties than TBCA. The formed char layer effectively reduced the heat and mass transmission. There are two peaks in the PHRR curves in Figure 5 of the two composites. This can be explained as follows:³¹ First, the APP/THEIC

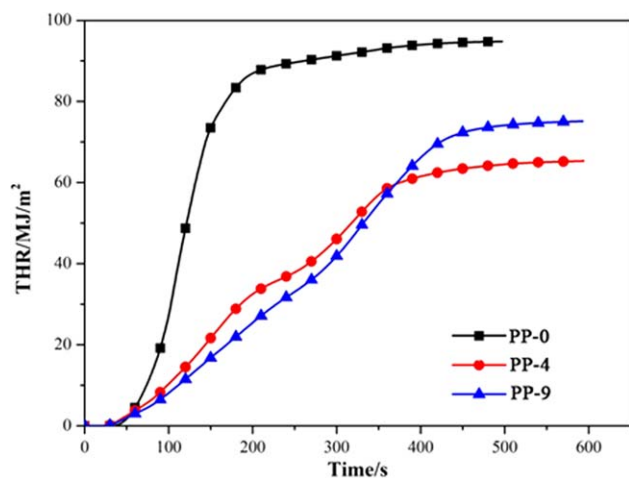


Figure 6. THR curves of PP-0, PP-4, and PP-9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

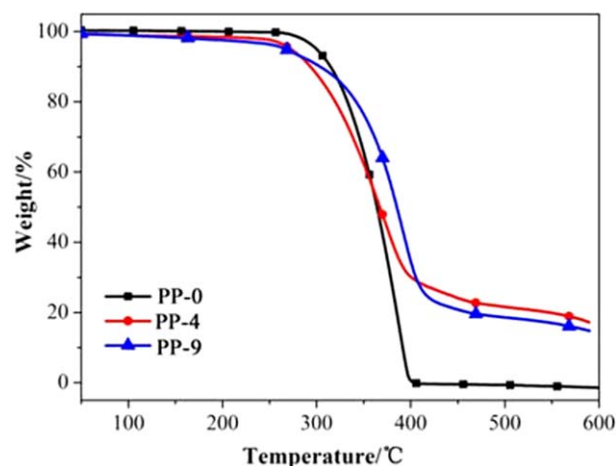


Figure 7. Thermogravimetry curves of PP-0, PP-4, and PP-9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and APP/TBCA degraded, and an intumescent shield forms. Second, this shield degraded when it faced massive heat. Consequently, the residual materials degraded and formed a new intumescent filed. The further degradation of the inner PP was prevented because of the formation of a protective char; this char effectively decreased the amount of heat and gas to transfer from the burning area to the inner matrix. Thus, the flame retardancy was achieved.

The total heat release (THR) values of PP-0, PP-4, and PP-9 are shown in Figure 6. As shown in Figure 6, THR of the pure PP (PP-0) was 94.79 MJ/m². When IFRs were added to the pure PP, the THR values of PP-4 and PP-9 dropped to 65.33 and 75.13 MJ/m², respectively. Relatively, the THR of PP-4 was still lower than that of PP-9; this indicated that APP/THEIC had a better flame retardancy than APP/TBCA.

Thermal Stability

TGA is a common technique for the rapid evaluation of the thermal stabilities of different materials; it also reveals the decomposition of polymers at various temperatures. To

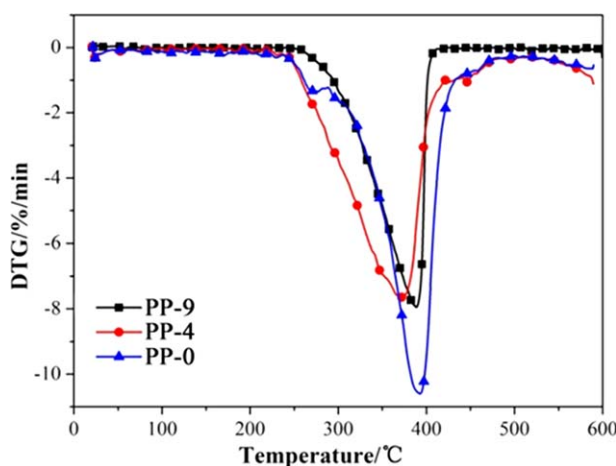


Figure 8. DTG curves of PP-0, PP-4, and PP-9. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Thermal Degradation Data for PP-0, PP-4, and PP-9

| Sample | T_{onset} (°C) | T_{max} (°C) | T_{max} (%/min) | Char residue (%) | | |
|--------|-------------------------|-----------------------|-----------------------------|------------------|-------|-------|
| | | | | 400°C | 500°C | 600°C |
| PP-0 | 300.00 | 391.76 | 10.59 | 0.57 | 0 | 0 |
| PP-4 | 272.54 | 371.70 | 7.63 | 30.12 | 21.58 | 16.06 |
| PP-9 | 266.95 | 388.53 | 7.94 | 34.33 | 18.60 | 14.69 |

understand the effects of TBCA and THEIC on the IFR–PP system, we compared the thermal degradation process and residual char obtained from the TGA tests. The onset thermal degradation temperature (T_{onset}) is defined as the temperature when 5 wt % mass loss occurs; T_{max} is defined as the maximum-rate decomposition temperature. The TGA and derivative thermogravimetry (DTG) curves of PP-0, PP-4, and PP-9 are shown in Figures 7 and 8.

As shown in Figures 7 and 8, all of the samples decomposed in one step. Pure PP decomposed rapidly from 300 to 400°C. The addition of the IFR decreased the T_{onset} values of PP-4 and PP-9; the T_{onset} values of PP-4 and PP-9 were 273.54 and 266.95°C, respectively; these values were lower than that of PP-0 (300°C). Song *et al.*³⁹ were the same as ours; he found the incorporation of IFR into PP resulted in a decrease in T_{onset} . It seemed the larger the IFR loading in PP was, the lower the T_{onset} values were. The T_{onset} value of PP-9 was lower than that of PP-4; this indicated that the mixture of APP/TBCA was inclined to decompose at a lower temperature than APP/THEIC.

The thermal degradation data of PP-0, PP-4, and PP-9 are listed in Table IV. As shown in Table IV, the maximum decomposition rate of PP-0 was the biggest, about 10.60%/min. With addition of IFR, both PP-4 and PP-9's maximum decomposition rate decreased to 7.63 and 7.94%/min, respectively. The char residue of PP-0 was zero when the temperature was higher than 450°C. However, PP-4's char residue was 30.12% at 400°C, 21.58% at 500°C, and 16.06% at 600°C, respectively. PP-9's char residue was 34.33% at 400°C, 18.61% at 500°C, and 14.69% at 600°C, respectively. PP-4's char residue was higher than PP-9 when the temperature was higher than 450°C; the higher char residue indicated a better flame retardancy and higher LOI value; thus, the flame retardancy of PP4 was better.

Morphology of the Char

Figure 9 displays the SEM images of the residual char; these were obtained after LOI tests. As shown in Figure 9(a,c), there were a lot of holes and fiberlike sheets in PP-4's residue char. These resulted from gases released from the degradation of APP and THEIC. In contrast, there were little bubbles, as shown in

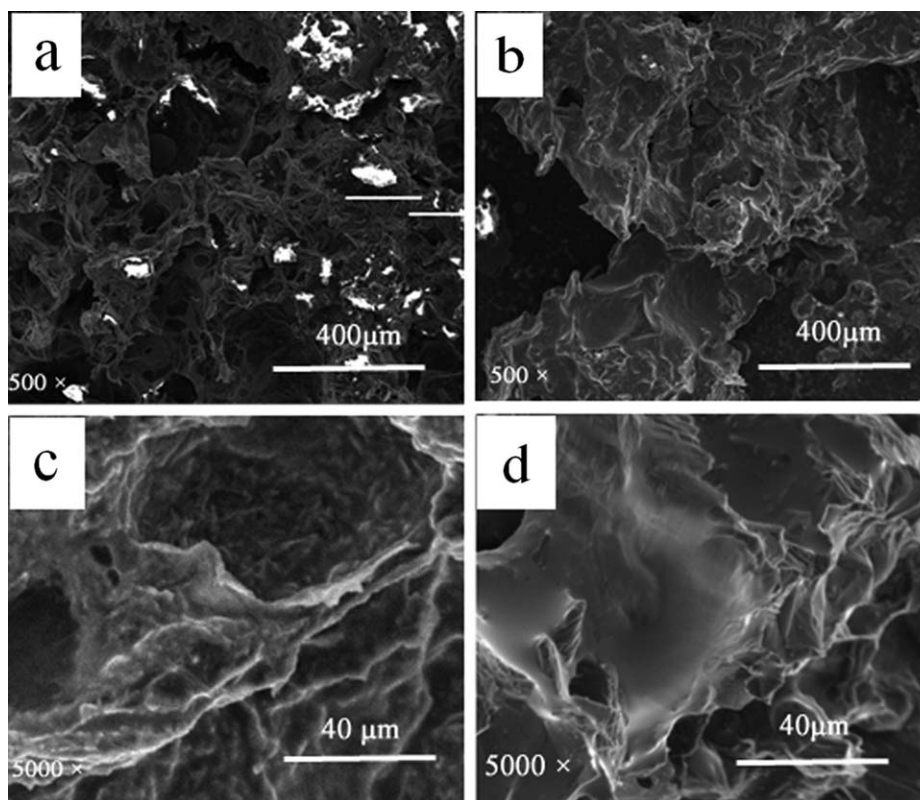
**Figure 9.** SEM images of the residual char: (a,c) PP-4 and (b,d) PP-9.

Figure 9(b,d), in PP-9's residual char. The residual char surface was smooth. This indicated that few gases were released from the degradation of APP and TBCA. Moreover, PP-9's residual char surface, with a flake shape, was thin. It was not as compact as PP-4's. The mechanism of IFR was based on a char layer; this slowed down the heat and mass transfer between the gas and condense phase. The thick char played a dominant role in the flame retardancy. PP-4's residual char was more compact, and this led to a better flame retardancy than that of PP-9.

CONCLUSIONS

A new kind of TBCA was synthesized, and its chemical structure was confirmed by FTIR spectroscopy, ¹H-NMR, and elemental analysis. Because of the esterification with TPA in THIEC's molecule, TBCA had better compatibility and hydrophobicity than THEIC. The PP/IFR₂ composite achieved a V-0 rating after it was soaked in water at 70°C for 96 h. However, its flame retardancy was not better than that of the PP/IFR₁ composite. The results indicate that TBCA's char-forming ability decreased because of esterification, but its compatibility and water-resistant properties were improved. The cone test, TGA, and SEM further proved this conclusion.

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