

Promoting carbonization of polypropylene during combustion through synergistic catalysis of a trace of halogenated compounds and Ni₂O₃ for improving flame retardancy

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ABSTRACT

The effect of combination between a trace of halogenated compounds (such as ferric chloride and ammonium bromide) and Ni₂O₃ particles on the carbonization of polypropylene (PP) was investigated during combustion. The results showed a synergistic catalysis of combined halogenated compounds with Ni₂O₃ in promoting the formation of the residual char during combustion. The investigation on the promotion mechanism showed that halide radical releasing from halogen-containing additives worked as a catalyst to accelerate dehydrogenation–aromatization of degradation products of PP, which promote the degradation products to form the residual char catalyzed by nickel catalyst. The results of GC and GC/MS confirmed that halogenated compounds could accelerate dehydrogenation and aromatization of degradation products of PP. The morphological observation showed that longer fiber-like structure was formed in the residual char of PP/halogenated compound/Ni₂O₃ composites comparing with PP/Ni₂O₃ composite. As a result, the presence of a trace amount of halogenated compounds could significantly improve the flame retardancy of PP/Ni₂O₃ composites, which is proved by cone calorimeter tests.

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1. Introduction

Understanding how polymer materials respond to high temperatures has many important applications from developing thermal protection systems for spacecraft to improving fire-retardant materials for buildings, aircraft, etc. However, the combustion behavior of polymers depends on chemical structures of polymer chains. Typically, when thermally degradable polymers (non-charring materials) burn, such as polypropylene (PP), the resultant products are volatile fragments that combust when exposed to oxygen. Alternatively, a dense, relatively inert and insulating char can be formed in thermally crosslinked (charring materials) polymers, such as phenolic resin and polyimide, which locks up the fuel for further combustion and also provides insulation to inner layers for stopping further heating from the environment. Because char has the properties of less flammability, lower thermal conductivity and reflecting energy, it can serve as a physical barrier for heat flux from the flame and air to the polymer, as well as a barrier to inhibit

gaseous products from diffusing to and feeding the flame [1]. It is a reason why charring polymers usually show high flame retardancy compared to non-charring polymers. Therefore the goal of many efforts to design thermally protecting or fire resistant materials is to increase the char yield while suppressing the production of volatile species, especially in the case of non-charring polymers.

Among various methods for improving flame retardancy of polymers, forming carbonaceous protective layers during combustion has been proven to be an effective way [2–4]. The most used method is to add intumescent flame retardants (IFRs) into polymers (especially thermally degradable polymers) for forming carbonaceous protective layer [5–11]. Typically IFRs contain three components, namely, an acid source, a carbon source and a blowing source. The carbonaceous protective layer results from the carbonization of added carbon sources, not from polymers themselves. Similarly, carbon nanotubes (CNTs) as a flame retardant additive have been explored in recent years due to their highly elongated shape [12–16]. The most dominant mechanism is the in situ formation of a continuous, network structured protective layer from the CNTs, which is critical for significant reduction in heat release rate (HRR), because the layer thus acts as a thermal shield for energy feedback from the flame.

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Considering the limit of chemical structure of non-charring polymers (such as polyolefin), it is difficult to make these polymers carbonized efficiently during combustion. Selecting catalytic method may be alternative one. Recently our group has been exploring the method for increasing the char yield of polymer itself [17]. A combined catalytic method has been established to form CNTs [18,19] and improve the flame retardancy of polyolefin [20,21], in which the combination between nickel catalysts and solid acids could efficiently catalyze the carbonization of degradation products during combusting polyolefin/nickel catalyst/solid acid composites. As a result, a large amount of char, including CNTs, was in situ formed in the middle stage of combustion. In this case, the char results from the degradation products of the polymer itself, thus the amount of flammable volatiles evolved is reduced, and the flame retardancy of the polymer is also improved. This method is efficient to improve flame retardancy of polyolefin [21].

In this paper we aim to report a synergistic catalysis between halogenated compounds and Ni_2O_3 particles in increasing the char yield of non-charring polymers. Here PP is selected as an example, which is widely used due to its outstanding properties, such as good mechanical properties, low toxicity and good chemical resistance. However, one of the main drawbacks of PP is its inherent flammability, which restricts its application in many fields for safety consideration [22]. Therefore it is important issue to improve flame retardancy of PP. The results showed that the combination of a trace of halogenated compounds (including cuprous chloride, ferric chloride, nickel chloride, ammonium chloride and ammonium bromide) with Ni_2O_3 particles improved not only the yield of residual char but also the flame retardancy of PP comparing with pure PP and PP/ Ni_2O_3 composites. The mechanism of the synergistic effect between Ni_2O_3 and halogenated compounds in improving the flame retardancy has been studied. It was found that the addition of a trace of halogenated compounds could promote dehydrogenation and aromatization of degradation products of PP during combustion.

2. Experimental section

2.1. Materials and preparation of samples

Polypropylene (PP) with melt flow index of 0.8 g/min was mixed with Ni_2O_3 (from Lingfeng Chemical Company of Shanghai) and halogenated compounds in a Brabender mixer at 100 rpm and 190 °C for 10 min. The concentration of Ni_2O_3 (5 wt%) was selected according to our previous reports [18,19]. Halogenated compounds included $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, CuCl , NH_4Cl and NH_4Br , and all compounds were of analytical grade quality used without further purification. An optimization study was conducted to establish the content of halogenated compounds. The resultant samples were designated as xMyNi. Here M and Ni denote halogenated compounds and Ni_2O_3 , respectively; and x and y denote the weight percentage of halogenated compounds and Ni_2O_3 , respectively. For example, 0.5FeCl₃5Ni means that the sample contains 0.5 wt% FeCl_3 and 5 wt% Ni_2O_3 .

2.2. Characterization

Morphologies of the composites were observed by means of transmission electron microscope (TEM, JEOL1011) at 100 kV accelerating voltage. Ultrathin sections were cryogenically cut using a Leica Ultracut and a glass knife at –80 °C. The samples were collected on carbon-coated copper TEM grids. The phase structures of the residues were analyzed by X-ray diffraction (XRD) using D8 advance X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The gas fraction of degradation products was analyzed by gas chromatograph (GC)

equipped with a flame ionization detector, using a GC–Alumina/ Na_2SO_4 (50 m × 0.53 mm ID), and the liquid fraction was examined by gas chromatography–mass spectrometry (GC–MS, AGILENT 5975MSD). The rheological properties of PP and its composites were measured on a controlled strain rate rheometer (ARES rheometer) in nitrogen atmosphere, and the size of samples measured was 25 mm in diameter, with a gap of 0.8 mm. Frequency sweeping was performed at 180 °C at a frequency from 0.05 to 100 s^{-1} , with a strain of 1% in order to make the materials be in linear viscoelastic response. Cone calorimeter tests were performed according to ISO5660-1 standard at a heat flux 35 kW/m^2 . Exhaust flow rate was 24 L/s and the spark was continuous until the sample ignited. The samples for the test of cone calorimeter were hot pressed by compression molding at 180 °C with the size of 100 × 100 × 6 mm square plaques. After cone calorimeter test, the residues were observed by field-emission scanning electron microscope (SEM, XL30ESEM–FEG) and TEM. The gasification processes of samples were studied by a radiant gasification apparatus designed and constructed at NIST. All experiments were conducted at 50 kW/m^2 and the detailed discussion of the gasification apparatus was given in the reference [23].

For testing the residual char in a imitative combustion experiment, a sample (~5 g) was placed in a crucible and burned at 700 °C until the tongue of flame disappeared; the residues were collected and weighted by analytical balance. The yield of carbonaceous residue was calculated by the amount of the residue after subtracting the amount of the residued catalysts divided by the amount of the sample.

3. Results and discussion

3.1. Effect of combined halogenated compounds/ Ni_2O_3 on the char yield of PP

Table 1 presents the results of the imitative combustion experiments. In the cases of PP and PP mixtures with halogenated compounds, the yields of residual char were zero or very low after combustion at 700 °C, meaning that halogenated compounds or their derivatives (HX, X = Cl or Br) could not catalyze carbonization of the degradation products under the experimental conditions. However, adding Ni_2O_3 into PP matrix leads to an increase in the yield of residual char. Very surprisingly, when a small amount of halogenated compounds was added into mixture of PP/ Ni_2O_3 , the yield of residual char was greatly promoted comparing with that from PP/ Ni_2O_3 composite. Thus the synergistic effect between halogenated compounds and Ni_2O_3 on the formation of residual char should be formed.

Table 1
The Char Yield of PP Mixtures Burned in the Crucible at 700 °C.^a

Run	Yield of residual char (wt%)
PP	0
5Ni	14.0
0.5FeCl ₃	0
0.5FeCl ₃ 5Ni	48.8
0.5NiCl ₂	0.8
0.5NiCl ₂ 5Ni	46.2
0.06NH ₄ Cl	0
0.06NH ₄ Cl5Ni	26.2
0.1NH ₄ Br	0
0.1NH ₄ Br5Ni	50.3
0.9CuCl	0
0.9CuCl5Ni	46.4
0.4CuCl5Ni	42.7

^a After the flame disappeared, the residue was collected, in which the amounts of the residued catalysts were subtracted.

3.2. Effect of combined halogenated compounds/ Ni_2O_3 on microstructure of the residual char after combustion

In order to promote the dispersion of the additives in PP matrix, a small amount of trimethylolpropane triacrylate (TMPTA, 1 wt%) is added as a compatilizer [24]. In this case, on one hand, the carbonyl group in TMPTA can interact with Ni_2O_3 particles to prevent the aggregation of Ni_2O_3 ; on the other hand, the double bond of carbon–carbon in TMPTA can react with macromolecular radicals of PP. According to morphology observation, Ni_2O_3 could be well dispersed due to the compatibilization of TMPTA and when a chlorinated compound was added, the dispersion state of Ni_2O_3 had no obvious change.

Fig. 1 presents the morphologies of the residual chars. There are a lot of amorphous char accompanied by a small amount of fiber-like structure in the residual char from PP/ Ni_2O_3 composite (Fig. 1a). However, the residual char is mainly composed of short fiber-like structure in the case of 0.5FeCl₃5Ni composite (Fig. 1b). Interestingly a lot of long fiber-like structure is formed in the residual char from 0.1NH₄Br5Ni composite (Fig. 1c). Many physical entangled sites can be observed. TEM observation shows that most of the fiber-like char are multi-walled carbon nanotubes (MWCNTs) (Fig. 1d).

Fig. 2 shows XRD profiles of the samples before and after combustion. Compared to the XRD profiles of the original samples, the diffraction peaks of both graphite and metallic nickel appear in the residual chars, meanwhile the diffraction peaks of PP disappear completely, and the diffraction peaks of Ni_2O_3 become weak, especially in the cases containing halogenated compounds. These results show that the addition of halogenated compounds can promote the reduction of Ni_2O_3 and the formation of graphite structure during combustion. It can be clearly seen that the intensity ratio of diffraction peaks of the graphite to that of metallic nickel in the residual char from 0.1NH₄Br5Ni composite is the largest among three residual chars. Raman spectra showed that the ratio of D-band to G-band was almost the same in all the residual chars. This implies that the more residual char with graphitic structure is formed in the residual char from 0.1NH₄Br5Ni composite.

3.3. The mechanism for the formation of residual char with high yield based on the combination of halogen-containing additive and Ni_2O_3

In catalytic reforming, the presence of residual chlorine is known to have an impact on the degree of coking [25]. Chambers

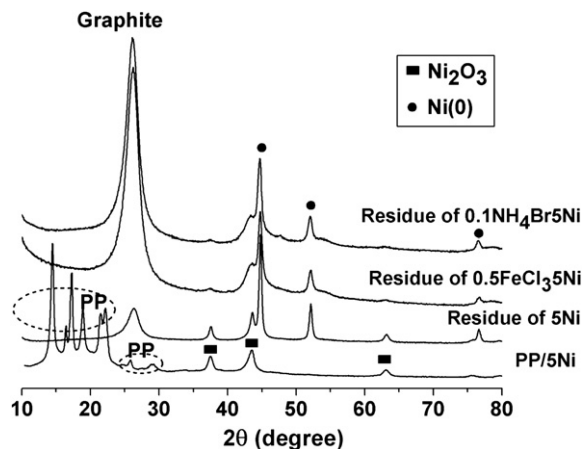


Fig. 2. XRD profiles for 5Ni and the residual chars of 5Ni, 0.5FeCl₃5Ni and 0.1NH₄Br5Ni.

and Baker [26] have noted that the presence of trace quantities of chlorine in an ethylene feed promoted the carbon deposition activity (at 673 K) of cobalt and iron powders. Keane et al. found that the presence of bromine could dramatically increase the yield of carbon filaments [27]. Recently, Qiu et al. found that halide was a crucial factor for selectively synthesizing high yield double-walled CNTs by arc discharge method [28]. However, the effect of halogen on the carbonization of polymers is more complicated. It is known that the carbon source ready to build residual char from PP should be the degradation products of PP. The presence of halogenated compounds probably affects not only the degradation of PP but also further reaction of degradation products, such as carbonization.

A possible reaction process for the formation of residual char from PP by the combined catalysis is shown in Fig. 3. As we know, halide radical (X^*) or HX ($X = \text{Cl}$ or Br) will be formed when heating halogenated compounds at high temperature. When PP is exposed to high temperature, it will degrade to form fragments including macromolecular species and small organic molecules. Generally, PP will degrade at high temperature, which forms radicals as reactive intermediates in the reaction system in spite of presence of X^* or HX. Breaking of C–C bond and C–H bond will form carbon radicals and hydrogen radical (H^*). In the presence of halogenated compounds, X^* will attack the hydrogen atom attached to carbons

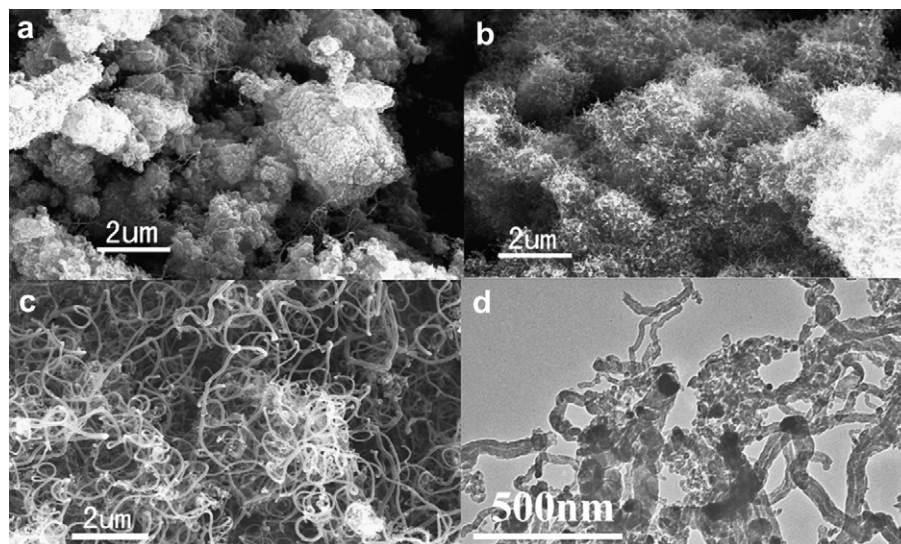


Fig. 1. SEM of the residues of composites (a) 5Ni, (b) 0.5FeCl₃5Ni, (c) 0.1NH₄Br5Ni and (d) TEM of the residues of 0.1NH₄Br5Ni.

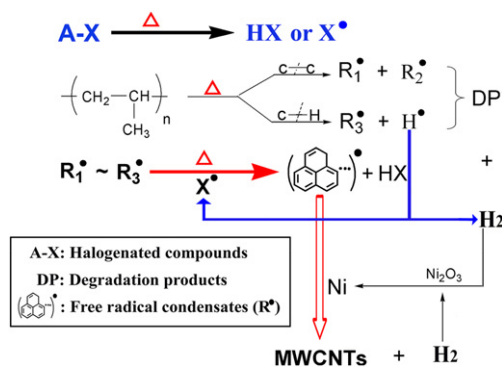


Fig. 3. Possible process of combined catalysis for formation of MWCNTs from PP during pyrolysis.

of degradation products of PP at high temperature, which easily leads to the formation of HX^* . Therefore dehydrogenation occurs after HX departs from the degradation products. Meanwhile X^* will be regenerated via the reaction of HX with H^* that results from breaking of $C-H$ bond. The above reactions take place repeatedly. Finally free radical condensates (R^* in Fig. 3) are formed in the reaction system. In fact, X^* acts as a catalyst for dehydrogenation of degradation products. In this case, the dehydrogenation will be accelerated. Owing to strong catalysis of X^* to the dehydrogenation of degradation products, hydrogen transfer, isomerization, cyclization and aromatization would take place during the degradation of PP, which leads to facile formation of more aromatic hydrocarbons in the degradation products. Simultaneously, Ni_2O_3 is in situ reduced to Ni, probably by H_2 and/or other degradation products of PP [18]. The free radical condensates (R^*) are catalyzed by Ni to form MWCNTs [29].

In order to confirm the influence of halogenated compounds on the degradation of PP, GC and GC-MS were used to analyze the composition of the degradation products from PP and PP/ NH_4Cl mixture at 700 °C. Gas and liquid fractions of the degradation products from the above systems were collected, respectively. There were H_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 and C_3H_6 in the gaseous fractions of degradation products of PP and PP/ NH_4Cl mixtures. But the quantity of gaseous fraction from the latter case was higher than that from the former case. GC measurements showed that the content of H_2 in the gaseous fraction of PP/ NH_4Cl mixture was three times as that of PP. Fig. 4 shows GC-MS profiles of liquid fractions in the degradation products of PP and PP/ NH_4Cl mixture. The content of aromatic compounds (such as styrene, toluene, ethylbenzene and xylene) in the degradation products of PP/ NH_4Cl mixture was much higher than that in the degradation products of PP. The total content of aromatic hydrocarbons in the liquid fraction of the degradation products of PP/ NH_4Cl mixture (Fig. 4b) was two times as that of PP (Fig. 4a). The above results confirm that the presence of halogenated compounds can promote dehydrogenation and aromatization during the degradation of PP. This can explain why the more Ni_2O_3 was reduced to metallic nickel and the char yield of PP was high in the presence of halogenated compounds (Fig. 2 and Table 1).

In the above reaction mechanism, the presence of HX in the PP matrix is a key factor to the efficient carbonization of PP. However, it is an interesting question why HX does not volatilize quickly from the PP matrix during combustion. The main reason is physical barrier of PP matrix, which is confirmed by the following comparative experiments. A sample is put into a tube-like pyrolyzer for pyrolyzing under N_2 atmosphere or put into a crucible for burning. In the former experiment, it is observed that the sample melts and spreads out on the bottom surface of the pyrolyzer. In this case, the thin layer of the sample is formed. As a result, the

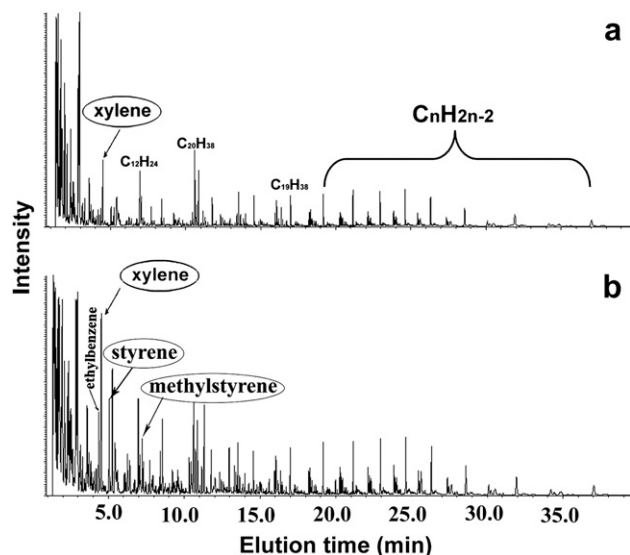
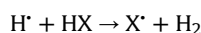


Fig. 4. GC-MS profiles of the collected liquid fractions of the degradation products from PP (a) and PP/ NH_4Cl mixture (b).

physical barrier of PP matrix for HX is weaker than that in the case of crucible. Furthermore the flow of nitrogen can blow HX away easily in the pyrolyzer. The yield of residual char from PP/ Ni_2O_3 composite in the tube-like pyrolyzer is the same as that in the crucible (Table 2). In contrast, although the addition of NH_4Br leads to the increase in the yield of residual char, the yield of residual char from PP/ Ni_2O_3 /halogenated compound composites in a tube-like pyrolyzer is much lower than that in the crucible (Table 2). This means that the good physical barrier of PP matrix prevents quick release of HX from the sample in the case of crucible, as a result, the formation of residual char is promoted.

Interestingly, although the molar percentages of NH_4Cl and NH_4Br are the same in the composites, the yield of residual char in 0.1 NH_4Br 5Ni composite is much higher than that of 0.06 NH_4Cl 5Ni composite (Table 1). This should be attributed to different reactive trend of the following reaction:



Generally the equilibrium constant for the reaction between HBr and hydrogen radical is higher than that between HCl and hydrogen radical. At 700 °C, the equilibrium constants of HBr and HCl are 2.97 and 0.67, respectively [30]. So HBr from the decomposition of NH_4Br is more efficient than HCl to form more X^* radicals and promote the formation of residual char.

3.4. Effect of combined halogenated compounds/ Ni_2O_3 on the flammability of PP

The influences of halogenated compounds and Ni_2O_3 on the flame retardancy of PP matrix were investigated by means of cone calorimeter. Heat release rate (HRR) is an important parameter

Table 2
Comparison of the Char Yield Based on Different Atmosphere.

Run	NH_4Br (wt%)	Ni_2O_3 (wt%)	PP(wt%)	Char yield(%)
1 ^a	0	5	95	14.0
2 ^b	0	5	95	14.2
3 ^a	0.1	5	94.9	50.3
4 ^b	0.1	5	94.9	23.1

^a Combusting in the crucible at 700 °C.

^b Pyrolyzing under nitrogen at 700 °C.

related to the flame retardancy of a material during combustion. Fig. 5 shows HRR plots for PP, PP/Ni₂O₃, PP/halogenated compounds and PP/halogenated compounds/Ni₂O₃ composites at a 35 kW/m² heat flux. The peak value (PHRR) in the HRR plots of the PP/halogenated compound mixtures changes slightly compared to that of PP (Fig. 5a and Table 3), indicating that the flammability is not influenced strongly by adding halogenated compounds alone in the PP matrix. An approximate 58% reduction in the PHRR of PP/Ni₂O₃ = 95/5 (by weight) composite (curve-5Ni in Fig. 5b) compared to PP may be attributed to the carbonization reaction of the degradation products from PP catalyzed by Ni₂O₃ [21]. When the combination of halogenated compound and Ni₂O₃ is applied, the PHRR of PP composites shows a further reduction compared to that of PP/Ni₂O₃ composite (Fig. 5b and Table 3), suggesting a synergistic effect of halogenated compounds with Ni₂O₃. It is noteworthy that the HRR of 0.06NH₄Cl5Ni composite (Fig. 5b) shows the lowest peak value and reduces further after the peak, and stays at a low level throughout. Comparing the structures of the residual chars from 0.5FeCl₃5Ni and 0.1NH₄Br5Ni composites (Fig. 1), the residual chars from 0.1NH₄Br5Ni included a lot of longer and more tangled fiber-like structure, which can make the residue of 0.1NH₄Br5Ni serve as a better barrier. Thus we can understand why the HRR of 0.1NH₄Br5Ni is lower than that of 0.5FeCl₃5Ni although the yield of the residual char is almost the same in the two cases. In addition, total heat release (THR) of PP/halogenated compounds/Ni₂O₃ composites with reasonable composition reduces 20~25% compared to that of pure PP. In contrast, the THR

Table 3

Summary of the Cone Calorimetric Results (Fig. 5) for PP and Its Composites.

Run	PHRR(kW/m ²)	THR(MJ/m ²)
PP	1283	214
PP/TMPTA	1248	217
5Ni	531	202
0.06NH ₄ Cl	1290	201
0.06NH ₄ Cl5Ni	411	158
1NH ₄ Cl5Ni	511	171
0.1NH ₄ Br	1382	202
0.1NH ₄ Br5Ni	440	156
0.4NH ₄ Br5Ni	711	195
0.5FeCl ₃	1176	211
0.5FeCl ₃ 5Ni	468	172
0.5NiCl ₂	1325	217
0.5NiCl ₂ 5Ni	483	168
0.9CuCl	1310	213
0.4CuCl5Ni	478	170
0.9 CuCl5Ni	457	177

of PP/Ni₂O₃ composites just reduced a little compared to that of pure PP.

Furthermore, the shape of HRR curves is different when adding Ni₂O₃ or its combination with halogenated compounds into PP matrix, meaning that the combustion behavior of PP has been changed besides the change in PHRR and THR values. In the cases of the samples containing both halogenated compounds and Ni₂O₃, there are two PHRR in the HRR plots. This behavior is similar to some thermally thick charring materials, such as IFRs and wood, which tend to show the first HRR peak at the beginning, prior to charring, and the second HRR peak at the end of the measurements [8,31]. The second peak may be caused by cracking char or increase in the effective pyrolysis, as observed with the thick non-charring materials.

Fig. 6 shows the change of the residual mass of the samples with combustion time. Addition of halogenated compounds in PP matrix does not significantly affect the mass loss rate (MLR) comparing with that of PP matrix alone. In contrast, adding Ni₂O₃ into PP matrix leads to a dramatic decrease of the MLR in the later stage of combustion. Addition of both halogenated compounds and Ni₂O₃ into PP matrix leads to a dramatic increase in the residual mass during combustion for more than 300 s (Fig. 6), especially in the case of 0.1NH₄Br5Ni. These results are similar to those shown in Table 1. This means that there are relatively fewer pyrolytic flammable gases to volatilize during combustion in these cases. As

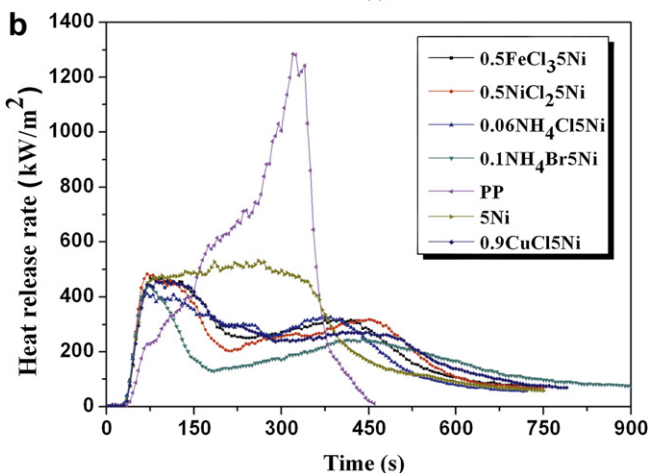
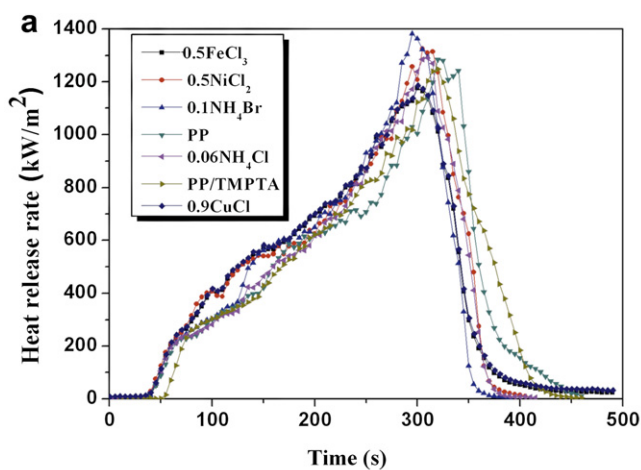


Fig. 5. Comparison of heat release rate plots for PP and PP composites (measured by cone calorimeter at an external radiant flux of 35 kW/m²).

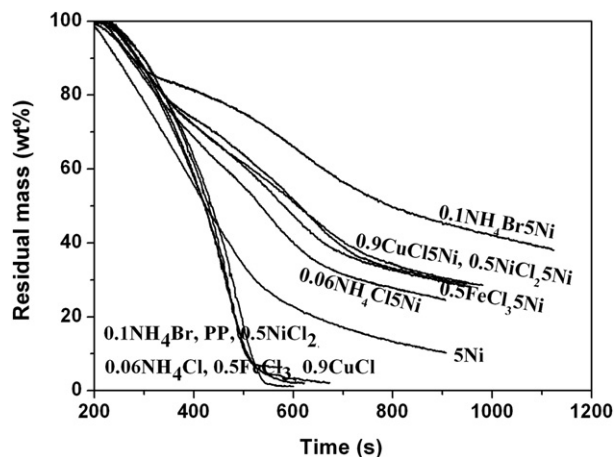


Fig. 6. Mass loss curves of PP and its composites measured by cone calorimeter at an external radiant flux of 35 kW/m².

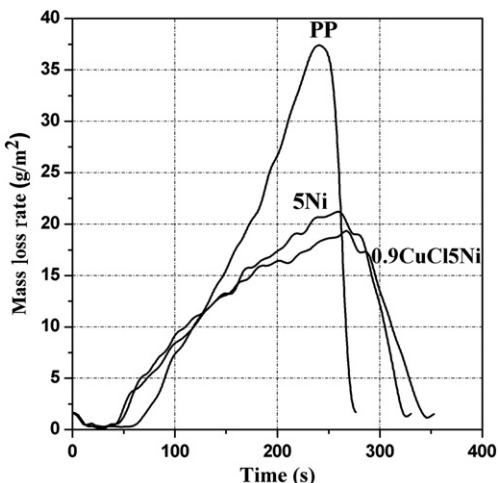


Fig. 7. Mass loss rate plots of PP and PP composites at 50 kW/m² in nitrogen.

a result, the HRR of PP/halogenated compounds/Ni₂O₃ composites can be further reduced comparing with that of PP/Ni₂O₃ composite. A similar phenomenon was observed when the above samples were tested using cone calorimeter at an external radiant flux of 50 kW/m². Here the samples are round plates with 5 mm thickness. Although the shapes of combustion curves obtained at the testing conditions of 35 and 50 kW/m² are different, the change trend of the PHRR is similar after adding Ni₂O₃ and halogenated compounds.

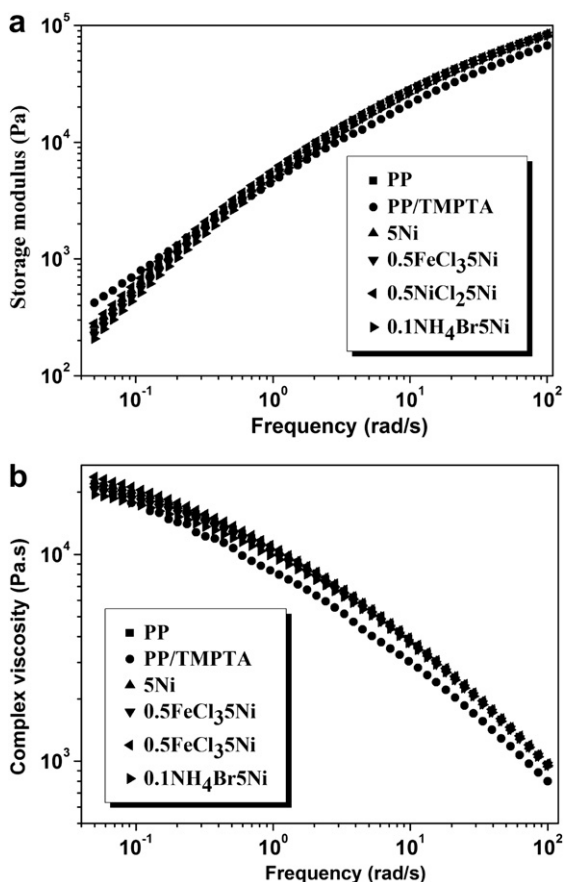


Fig. 8. Rheological curves of PP and PP composites. (a) Storage modulus; (b) Complex viscosity.

This means that the improvement in the flame retardancy of PP, which is originated from the char formation, is still effective at higher temperature environments. Fig. 7 shows MLR plots of the samples obtained from the gasification apparatus under nitrogen atmosphere. Compared to PP, the MLR of 5Ni was reduced greatly. However, the MLR of the sample containing the combination of halogenated compound and Ni₂O₃ (curve 0.9CuCl₅Ni) was slightly lower than that of PP/Ni₂O₃ composites (curve 5Ni). This should result from a smaller difference in the residual chars of the samples containing the combined catalysts and the one containing only Ni₂O₃ under nitrogen atmosphere compared to that under the combustion conditions, as shown in Table 2.

Some previous reports have shown that the formation of network-like structure of fillers in polymer composites is profitable to the improvements of the flame retardancy [14,32]. The presence of a filler network can be demonstrated by the change of dynamic melt rheological properties. Fig. 8 shows the storage modulus (G') and complex viscosity (η) of the samples at 180 °C. The rheological properties in the low frequency (ω) regime reflect the relaxation and motion of the whole polymer chains. From the results of Fig. 8a, it is observed that the terminal slope of G' - ω curves almost does not change after adding Ni₂O₃ and halogenated compounds comparing with pure PP, indicating no the formation of filler network in PP matrix. Thus the improvements in the flame retardancy of PP should result from the formation of a large amount of residual char from the degradation products during combustion.

4. Conclusions

A novel combined catalytic method for promoting carbonization of PP has been found. This method is based on a synergistic catalysis of a trace of halogen-containing additives with Ni₂O₃ in promoting the formation of residual char from PP during combustion. Here the char resulted from the degradation products of PP itself exposed to fire conditions, thus the amount of flammable volatiles evolved was reduced, and the flame retardancy of PP was also improved. Halogen-containing additives provided halide radical (X^*) via thermal decomposition in the reaction system. X^* influenced the degradation of PP and the carbonization behavior of the degradation products, particularly dehydrogenation and aromatization, and strongly promoted the growth of residual char (such as carbon nanotubes) catalyzed by Ni catalyst formed in situ from the reduction of Ni₂O₃. More investigation will be needed to further improve the catalytic efficiency. It is believed that the combined catalytic method is possible to promote the carbonization of other non-charring polymer and improve their fire retardancy through carefully selecting the combined catalysts.

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