

Effects of the addition of carbon black on the carbonization and flame retardancy of polypropylene in combination with nickel-molybdenum-magnesium catalysts

Rongjun Song, Zhengru Ren

Heilongjiang Key Laboratory of Molecular Design and Preparation of Flame-Retardant Materials, College of Science, Northeast Forestry University, Harbin 150040, People's Republic of China

Correspondence to: R. Song (E-mail: rongjunsong@nefu.edu.cn)

ABSTRACT: Carbon black particles were incorporated into the polypropylene (PP) in combination with Ni–Mo–Mg catalysts to investigate their influences on the carbonization and flame retardancy of PP. The results demonstrate that the carbon black exhibited a very positive effect on the char yield of PP in a pyrolyzation experiment with different temperatures. For pyrolyzation at 750 and 550°C, the PP/5% Ni–Mo–Mg/5% carbon black blends gave 56 and 37.1% char yields, respectively. Scanning electron microscopy, transmission electron microscopy results, and direct optical observations from designed experiments all demonstrated a combination of carbon black with growing carbon nanotubes (CNTs) for the generation of char with integrated and compact structures. Cone calorimeter and limited oxygen index tests confirmed that the integration of carbon black particles and CNTs led to a significant improvement in the flame retardancy of PP. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43034.

KEYWORDS: blends; degradation; flame retardance

Received 14 July 2015; accepted 11 October 2015

DOI: 10.1002/app.43034

INTRODUCTION

Polyolefin is presently the fastest growing plastic material for technical end uses, such as automobiles, housing, electronics, and electrical applications because of its essential features of a high tensile strength and low cost. However, the main drawback of the inherent flammability of polyolefin has posed a serious restriction for their application in many fields for safety considerations. Thus, a method for efficiently promoting the flame retardancy of polyolefin is urgently needed.^{1,2}

So far, considerable efforts have been dedicated the fabrication a polyolefin formulation with satisfying flame-retardant properties. Traditionally, halogen-containing species have been used as effective flame retardants of polyolefin.³ They typically work in the vapor phase to hinder the combustion reaction between radicals and oxygen by quickly triggering condensation and aromatization among radicals. However, a huge amount of dark smoke, including either the carbon black particles derived from radical condensation and aromatization or halogen acid in the form of halogen hydride from flame retardants themselves, inevitably results in the pollution of the environment and a threat to life. Metal hydrates are also capable of retarding the combustion of polyolefin, but they only work at high concentrations (normally 40–60 wt %) because of the simple flame-

retardant mechanisms of water release and heat absorption.^{4,5} Intumescent flame retardants (IFRs) used as flame retardants of polyolefin have gained emphasis again and have developed very quickly during the past decade.^{6–13} Their flame-retardant performances are attributed to the inhibition of a char barrier, which prevents further degradation and, hence, starves the flame of fuel. However, this protective char layer is totally derived from IFR itself; this obviously leads to a high level of IFR loading in the polyolefin matrix. In addition, some types of nanoscale inorganic additives, such as organic montmorillonites, carbon nanotubes (CNTs), and fullerenes, have been discovered to have the ability to promote the flame retardancy of polyolefin at a very low loading.^{14–16} These nanoscale additives in polyolefin can change the melting properties, assemble into a thin protective layer during combustion, and then reduce the combustion rate of polyolefin. However, with these nanoscale additives alone, polyolefin has never obtained a high limited oxygen index (LOI) value or passed a UL-94 rating. In brief, because of the structure of pure aliphatic hydrocarbon and its combustible properties, it has still been a big challenge to confer highly efficient and environmentally friendly flame-retardant properties on polyolefin thus far.

Encouragingly, Tang and his coworkers have found a method for producing CNTs largely from polyolefin by a pyrolysis or

combustion technique. Several combined catalysts, including solid acid/nickel catalysts,^{17–21} chlorinated compound/ Ni_2O_3 ,^{22,23} and activated carbon/ Ni_2O_3 ,²⁴ have been demonstrated to efficiently catalyze the carbonization of the degradation fragments of polyolefin during combustion. In our recent study,²⁵ a kind of Ni–Mo–Mg catalyst was prepared with a carbonization ability that was higher than those of the catalysts mentioned previously. Although this method of generating CNTs from polyolefin is dependent on the temperature of pyrolysis or combustion, these carbonization catalysts could only decrease the combustion intensity under certain forced-fire conditions. As for the improvement of the LOI value and the UL-94 ratings of polyolefin, the carbonization catalysts mentioned previously were basically deficient. We attributed this to the porous structures of CNTs and the temperature of carbonization.

To resolve this problem, one commercial product of carbon black was selected as a synergistic additive of Ni–Mo–Mg catalysts to constitute a polypropylene (PP)/Ni–Mo–Mg/carbon black carbonization system. The carbon black is normally composed of a larger number of amorphous carbon structures, which can notably and effectively trap the formed radicals from PP during pyrolysis.²⁶ Because of the trapped radicals and mass amorphous carbon structures on their surface, these carbon black particles could participate in the growth of CNTs in this special carbonization system. In other words, it was very possible that these nanoscale carbon black particles could combine the growing CNTs together to generate a char with integrated and crosslinking structures. Thus, in this study, we systematically investigated the effects of carbon black on the char yield, char structures, and flame retardancy of PP blends with the addition of the carbon black into PP/Ni–Mo–Mg blends.

EXPERIMENTAL

Materials

PP powder with a melt flow index of 0.8 g/min was provided by Daqing Huake Co., Ltd. (China). The carbon black products, with a diameter of about 20 nm, were kindly supplied by Henan Yanxu Tanhei Co., Ltd. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was purchased from Tianjin Damao Chemical Reagent Factory. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was purchased from Tianjin Kaida Chemical Plant (the Fourth Chemical Reagent Factory), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was supplied from Tianjin Kemio Chemical Reagent Co., Ltd. (China).

Fabrication Procedure

The Ni–Mo–Mg catalysts were synthesized by a combustion method. A mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at a certain molar ratio (Ni/Mo/Mg = 7:0.7:1) was dissolved in poly(ethylene glycol) with a molecular weight of 200. The solution was heated at 600°C for 1 h in a muffle. Then, the product was obtained and ground into fine powder with a diameter of about 5 μm. The PP blends were prepared by the mixture of PP powders, Ni–Mo–Mg catalysts, and carbon black particles in a Brabender mixer at 100 rpm and 180 °C for 10 min. For comparison, pure PP was also subjected to the same mixing treatment. The blended PP materials were molded with a press-type molding machine to make the required shape. The obtained samples were labeled as PP/*x*% Ni–Mo–Mg/*y*% carbon black, where *x* and *y* represent

the weight percentages of Ni–Mo–Mg catalysts and carbon black in PP, respectively. For instance, PP/5% Ni–Mo–Mg/3% carbon black indicates that the weight concentrations of the Ni–Mo–Mg catalysts and carbon black particles were 5 and 3 wt % of PP, respectively.

Characterization

The charring experiments were carried out with two different methods. One was the pyrolysis of a piece of the blend (ca. 5 g) via a pyrolyzer under a nitrogen atmosphere, in which the blends were placed in a quartz tube and heated at a fixed temperature for 15 min. The other method was the heating of the blends with a muffle furnace, where a crucible containing the samples was heated at a fixed temperature in air. After the flame in the crucible disappeared, the black residual char was collected. The amount of residual char (*M*) was calculated by the subtraction of the weights of Ni–Mo–Mg catalysts and carbon black particles from the total residue (*R*):

$$M = R - (M_{\text{Ni-Mo-Mg}} + M_{\text{Carbon black}}) \quad (1)$$

The yield (*y*) of char was calculated from *M* divided by the amount of PP used in the sample (M_{PP}):

$$y(\%) = \frac{M}{M_{\text{PP}}} \times 100 \quad (2)$$

All of the samples were weighed with an analytical balance. Field emission scanning electron microscopy (SEM; FEI Quanta 200, United States) and transmission electron microscopy (TEM; JEM-1011, 100 kV) were used to characterize the morphologies of the residual char. The cone calorimetry tests (Fire Testing Technology, East Grinstead, United Kingdom) were performed according to ISO5660, namely, at a heat flux of 50 kW/m² (750°C) with a 1.24 L/s exhaust flow rate, and the spark was continuous until the sample was ignited. The samples to be tested in the cone calorimeter were prepared by compression molding at 180°C with 100 × 100 × 6 mm³ square plaques. The LOI value was measured on a JF-3 oxygen index meter (Jiangning, China) with sheet dimensions of 130 × 6.5 × 3 mm³, according to ISO4589-1984. UL-94 ratings of all of the samples were measured on a CZF-2 instrument produced by Jiangning Analysis Instrument Factory (China).

RESULTS AND DISCUSSION

Effects of the Addition of Carbon Black on PP/Ni–Mo–Mg Blends on the Char Yield and Char Structures with Pyrolyzation at 750°C

Generally speaking, when carbonaceous substances form on the combustion surface of the polymer, an obvious reduction in the flammability of the polymer will be observed because of the low flammability and high reflecting properties of the carbonaceous substances. Although the reduced ability of a char material generally depends on three factors, namely, the char yield, char morphology, and temperature required for its formation, a temperature of 750°C as the representative temperature in a middle-sized fire was first chosen to investigate the effects of carbon black addition to the PP/Ni–Mo–Mg blends on the char yield and char structures. The char yield in both charring experiments was almost equal for a blend; this indicated same charring ability of the sample in air and in nitrogen.

Table I. PP Compositions and Corresponding Char Yields by Pyrolyzation at 750°C

Sample	PP (wt %)	Ni-Mo-Mg (wt %)	Carbon black (wt %)	Char yield (%)
1	100	0	0	0
4	97	3	0	16.7
5	95	5	0	35
6	92	5	3	42.9
8	90	5	5	56
9	88	5	7	45.6

Table I lists the composition of the PP blends and their corresponding char yields via pyrolyzation at 750°C. In the case of pure PP, the yield of the residual char was zero; this indicated the noncharring properties of pure PP. Similar to our previous results,²⁵ the PP/Ni-Mo-Mg blends left a large number of char materials after pyrolyzation. Char yields of 16.7 and 35% were found for the PP/3% Ni-Mo-Mg and PP/5% Ni-Mo-Mg blends, respectively. It was previously demonstrated that the char residue mostly comprised the CNT structures.²⁵ Subsequently, carbon black was introduced into the PP/5% Ni-Mo-Mg blends to investigate its effect on the char yield. Surprisingly, the presence of carbon black had a further positive influence on the char yield, as shown in Table I. In particular, when the content of carbon black was less than 5 wt %, the char yield increased dramatically with its addition. When the content of

carbon black in the PP/5% Ni-Mo-Mg blends was increased further, the char yield underwent a decreasing trend. Nevertheless, the content of carbon black of 5 wt % led to a maximum char yield of 56%. The synergistic effect of carbon black was tentatively attributed to its influence on the char structure. We estimated that the carbon black particles in the matrix could integrate the growing CNTs to form a char layer with more continuous structures; this served as a barrier to the volatilization of organic fragments and led to the enhancement of char yield.

SEM and TEM techniques were applied to examine the structure of the char residue. As shown in Figure 1(a), the large presence of fibrous structures further confirmed the carbonization ability of Ni-Mo-Mg catalysts in PP. Clearly, this char structure had a weak ability to bar heat and mass transportation. As a comparison, the char residue of PP/5% carbon black is also shown in Figure 1(b), in which only numerous islands of amorphous carbon are shown. We attributed this to the combination of carbon black particles themselves during the pyrolyzation of the PP blends. Then, the influence of carbon black on the char structure of the PP/5% Ni-Mo-Mg blends were studied. As shown in Figure 1(c), a relatively integrated char structure was observed, even with contents of carbon black as low as 1 wt %. When the content of carbon black was increased further to 3 or 5 wt % in the PP/5% Ni-Mo-Mg blends, more integrated char structures were formed [Figure 1(d,e)], and almost no CNT structures were detected. However, when the content of carbon black was increased up to 7 wt %, the

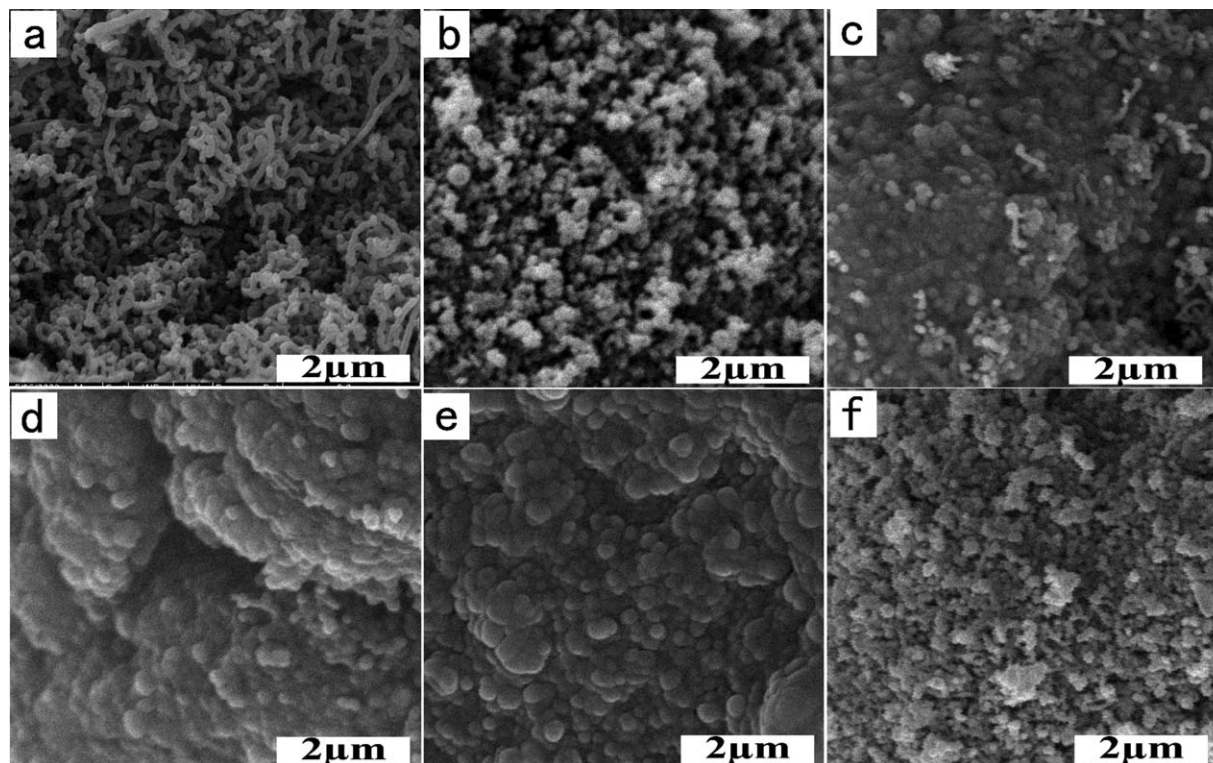


Figure 1. Typical SEM images of the residual chars from the PP/*x*% Ni-Mo-Mg/*y*% carbon black blends by pyrolyzation at 750°C: (a) PP/5% Ni-Mo-Mg, (b) PP/5% carbon black, (c) PP/5% Ni-Mo-Mg/1% carbon black, (d) PP/5% Ni-Mo-Mg/3% carbon black, (e) PP/5% Ni-Mo-Mg/5% carbon black, and (f) PP/5% Ni-Mo-Mg/7% carbon black.

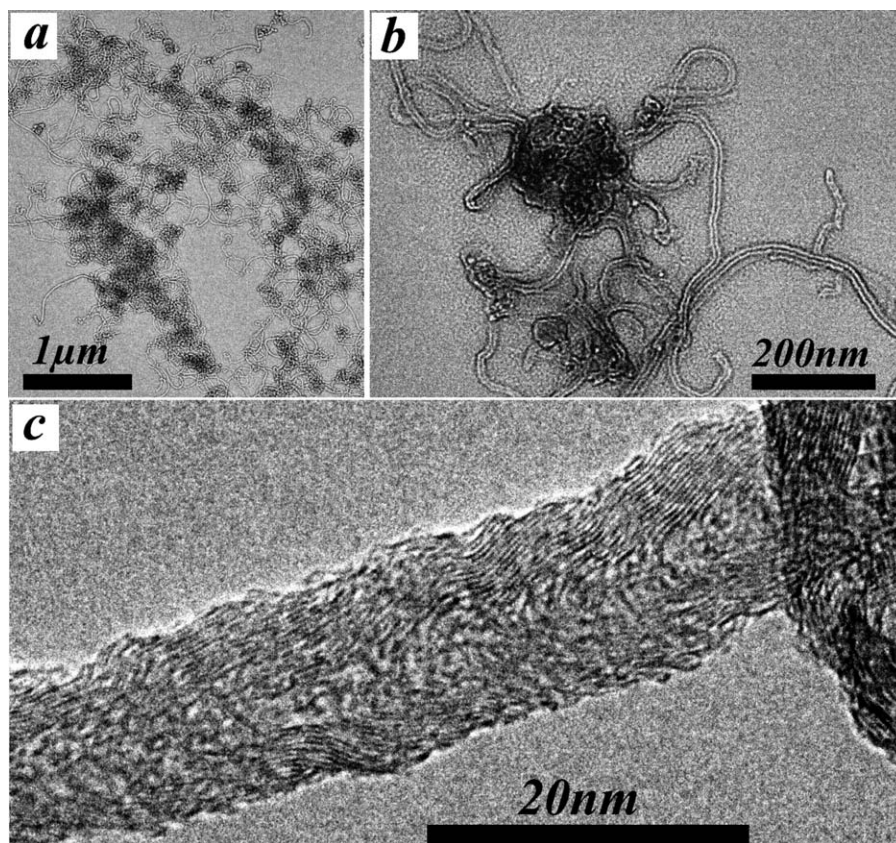


Figure 2. Typical TEM images of the residual chars from the PP/5% Ni–Mo–Mg/5% carbon black blends by pyrolyzation at 750°C: (a,b) low-resolution and (c) high-resolution TEM images.

integration degree of the char seemed to decrease [Figure 1(f)]. From previous observations, we verified that the incorporation of carbon black led to char formation with continuous and integrated char structures, and we assumed that the carbon black with an appropriate concentration in PP/5% Ni–Mo–Mg could combine growing CNTs.

To further confirm the effects of carbon black on the structure of the residual char, the TEM technique was used. After immersion in HCl for 24 h, some of the amorphous carbon in the char residue was removed. Figure 2 shows typical images of the treated char obtained from the PP/5% Ni–Mo–Mg/5% carbon black blends. It was very interesting that the integrated char was transformed to a net structure with many knots and nanosized fibers [Figure 2(a,b)]. Moreover, the nanosized fibers in the treated char were revealed to be CNTs with multiwalled structures [Figure 2(c)], although these structures could not be found in its corresponding SEM measurements. The change in the char structures before and after treatment could be reasonably explained by the combination of carbon black. During pyrolyzation, these carbon black particles could combine growing CNTs together, and this led to an integrated and continuous char structure. After treatment with HCl, lots of combination points and a CNT network were displayed, as demonstrated by TEM.

Cone Calorimeter Studies

The cone calorimetry device was first selected to characterize the influence of carbon black on the flame retardancy of the

PP/5% Ni–Mo–Mg blends with an external heating of 50 kW/m² (~750°C). As one of the most effective medium-sized fire-behavior tests, cone calorimetry provides comprehensive insight into fire risk via parameters that include the heat release rate (HRR), the peak heat release rate (PHRR), and the mass loss rate (MLR).

The HRR curves reflected the combustion speed and intensity of materials under certain forced-fire conditions. Figure 3 displays the HRR plots of PP and the PP/Ni–Mo–Mg, PP/carbon black, and PP/Ni–Mo–Mg/carbon black blends. The HRR of pure PP increased very fast after ignition up to a PHRR of 1175 kW/m² and then underwent a vertical drop. Obviously, the pure PP burned very quickly and intensively under these conditions. As for the PP with the Ni–Mo–Mg catalyst alone, an obvious reduction in HRR was obtained. Compared with the pure PP, the PP/5% Ni–Mo–Mg blends showed an approximate decrease of 49.0% in PHRR. Meanwhile, the HRR curve stayed at a long, stable, and low-combustion rate stage after 150 s; this implied that the formed char protected the polymer matrix from decomposition to some extent. As a comparison, the PP/5% carbon black blends were also measured. A totally different HRR curve appeared, as no obvious PHRRs were observed, but a long PHRR platform occurred at about 410 kW/m² for about 300 s. This looked very similar to the HRR results of some PP nanocomposites^{14–16} and indicated that the carbon black alone could only suppress the combustion speed and intensity of PP by means of a physical barrier instead of through catalysis of

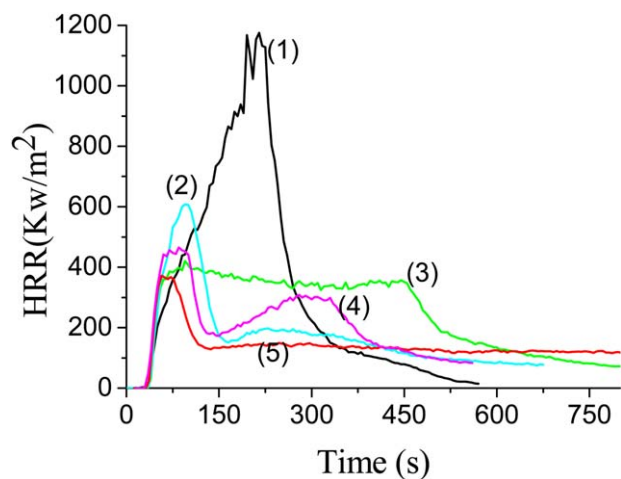


Figure 3. HRR plots for the PP/*x*% Ni–Mo–Mg/*y*% carbon black blends by cone calorimetry (50 kW/m²): (1) PP, (2) PP/5% Ni–Mo–Mg, (3) PP/5% carbon black, (4) PP/5% Ni–Mo–Mg/1% carbon black, and (5) PP/5% Ni–Mo–Mg/5% carbon black. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

carbonization as Ni–Mo–Mg catalysts do. As expected, PP showed the best flame retardancy with the combined addition of Ni–Mo–Mg catalysts and carbon black particles. The PP/5% Ni–Mo–Mg/5% carbon black blends possessed the lowest PHRR value of 360 kW/m². In addition, with the exclusion of a very short period of PHRR time, the HRR curve maintained a very low value of 128 kW/m². This implied that it took a very short time for the formation of this robust char barrier from the PP/5% Ni–Mo–Mg/5% carbon black blends. The results were consistent with SEM and TEM observations. As a comparison, we also measured the HRR of PP/5% Ni–Mo–Mg with the addition of 1 wt % carbon black. Certainly, it showed a relatively high PHRR value, whereas the major difference from the HRR curve of PP/5% Ni–Mo–Mg/5% carbon black was the presence of a second PHRR in the middle combustion stage. This indicated that the 1 wt % carbon black content was not sufficient to integrate the growing CNTs together to form a robust char layer. Overall, we confirmed that under middle-sized, forced-fire conditions, carbon black at an appropriate concentration effectively decreased the combustion rate and intensity of PP with the combination of Ni–Mo–Mg catalysts.

MLR, as another important flame-retardant factor of cone calorimetry, was also investigated. The MLR plots for PP and its blends shown in Figure 4 provide further certification for the role of carbon black in the flame retardancy of PP. Clearly, pure PP lost weight at the quickest rate. The PPs with both Ni–Mo–Mg catalysts and carbon black additives displayed relatively low MLRs. In contrast, the slowest MLR was achieved only for PP with the addition of 5 wt % Ni–Mo–Mg and 5 wt % carbon black. Additionally, this MLR curve had a changeless slope from 150 s to the final time; this meant that the PP lost its mass at a very low and fixed rate, and this fit with the HRR results. Thus, in association with the results of the char yields and structures, we demonstrated that the carbon black particles could combine the growing CNTs together with pyrolyzation or combustion at

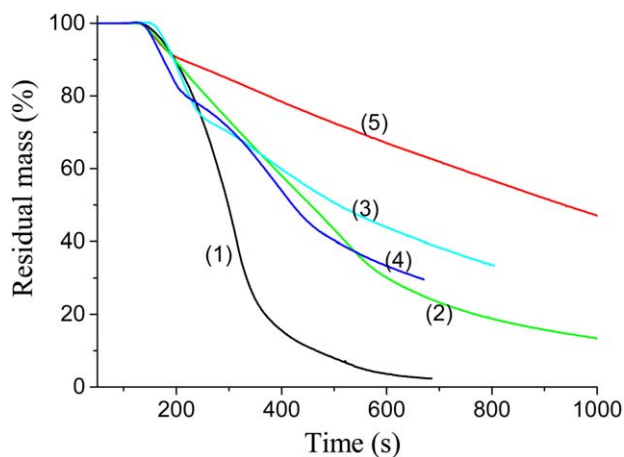


Figure 4. MLR plots for the PP/*x*% Ni–Mo–Mg/*y*% carbon black blends by cone calorimetry (50 kW/m²): (1) PP, (2) PP/5% Ni–Mo–Mg, (3) PP/5% carbon black, (4) PP/5% Ni–Mo–Mg/1% carbon black, and (5) PP/5% Ni–Mo–Mg/5% carbon black. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

750°C and then increase the char yield and significantly promote the flame retardancy of PP.

Influence of the Addition of Carbon Black to PP/5% Ni–Mo–Mg on the Char Yield and Char Structures in a Range of Temperatures

The temperature for char formation also belongs to an important factor in determining the flame retardancy of a polymer. Generally, for char formation from a polymer, the lower the temperature is, the more nonflammable the polymer is. Then, the influence of the addition of carbon black into PP/5% Ni–Mo–Mg on the char yield was investigated for a range of temperatures. Apparently, the catalytic ability of the Ni–Mo–Mg catalyst was observed to decline with decreasing temperature; this was reflected by the reduction of the char yield of the PP/5% Ni–Mo–Mg blends at relatively lower temperatures (Figure 5). However, we found that the addition of carbon black always had a positive influence on the char yield of PP/5% Ni–Mo–

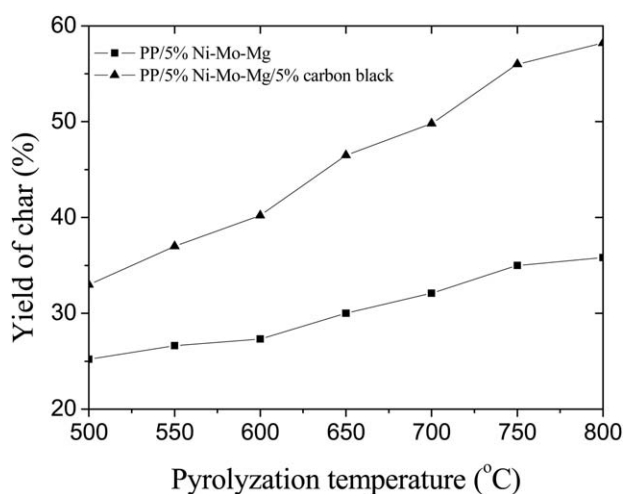


Figure 5. Effects of the carbon black on the char yield of PP/5% Ni–Mo–Mg for a range of temperatures.

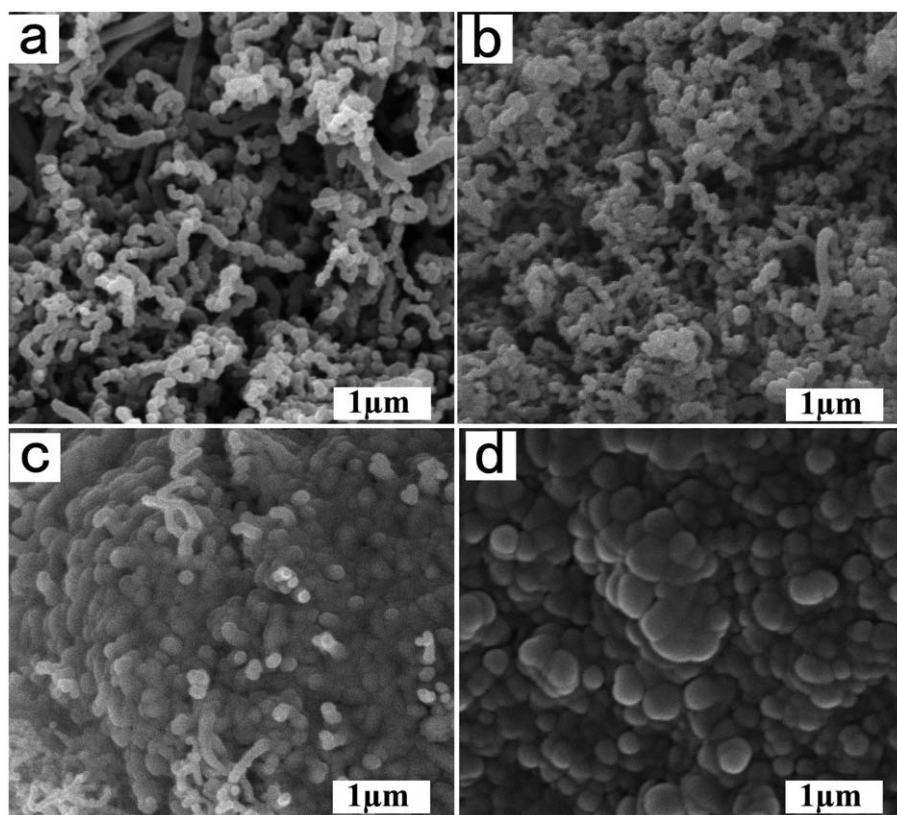


Figure 6. Typical SEM images of the residual chars from the PP/ $x\%$ Ni–Mo–Mg/ $y\%$ carbon black composites by pyrolyzation at 550°C.

Mg, whereas the increased amplitude became smaller with a reduction in the temperature. At 550°C, the char yield increased from 26.6 to 37.1%, when 5 wt % carbon black was added to the PP/5% Ni–Mo–Mg blends.

SEM was also used to examine the morphologies of char formed from PP/5% Ni–Mo–Mg/5% carbon black blends at 550°C (Figure 6). The same occurred with pyrolyzation at 750°C; the PP/5% Ni–Mo–Mg blends also presented CNTs with porous structures [Figure 6(a)]. However, as shown in Figure 6(b), relatively more CNT morphologies were observed in the char residue of the PP/5% Ni–Mo–Mg/1% carbon black blends. This was comparable to those formed at 750°C. With further improvements in the content of carbon black to 3 and 5 wt %, an integrated char structure occurred, as shown in Figure 6(c,d). The results demonstrate that the carbon black particles were also effective in combining the growing CNTs at relatively low temperatures.

LOI and UL-94 Rating Measurements

The LOI and UL-94 rating, as two traditional techniques, are commonly used to determine the flame retardancy of polymers without external heating. The LOI results for PP and its blends are listed in Table II. The LOI value of 17% for pure PP implied its rapid combustion properties in air. When 5 wt % Ni–Mo–Mg catalysts were incorporated into PP, the LOI value increased very slightly, despite a char yield of 26.6% at 550°C. However, the LOI value increased quickly with the addition of carbon black into PP/5% Ni–Mo–Mg blends. With the presence of 3 wt % carbon black, the LOI value increased to 22.8%. The highest

LOI value of 26.1% was successfully achieved for the PP/5% Ni–Mo–Mg/5% carbon black blends. Unfortunately, all of the samples had no rating in the UL-94 test because of the presence of melt dripping. With respect to this problem, one explanation is that the char took too long to form an effective protection char layer before dripping; another explanation was that the PP samples in this work still had a relatively low LOI value, which was comparable to that flame-retarded by traditional flame retardants.

To further clarify the function of carbon black in the enhancement of LOI value, the following combustion experiments were designed. Three types of materials (pure PP, PP/10% Ni–Mo–Mg, and PP/5% Ni–Mo–Mg/5% carbon black blends) were ignited simultaneously in the air. When the PP/5% Ni–Mo–Mg/5% carbon black was extinguished by itself, two other burning

Table II. PP Compositions, LOI Values, and Corresponding Char Yields by Pyrolyzation at 550°C

Sample	PP (wt %)	Ni–Mo–Mg (wt %)	Carbon black (wt %)	Char yield (%)	LOI
1	100	0	0	0	17
2	95	5	0	26.6	17.8
3	92	5	3	33.5	22.8
4	90	5	5	37.1	26.1
5	88	5	7	26.7	23.9

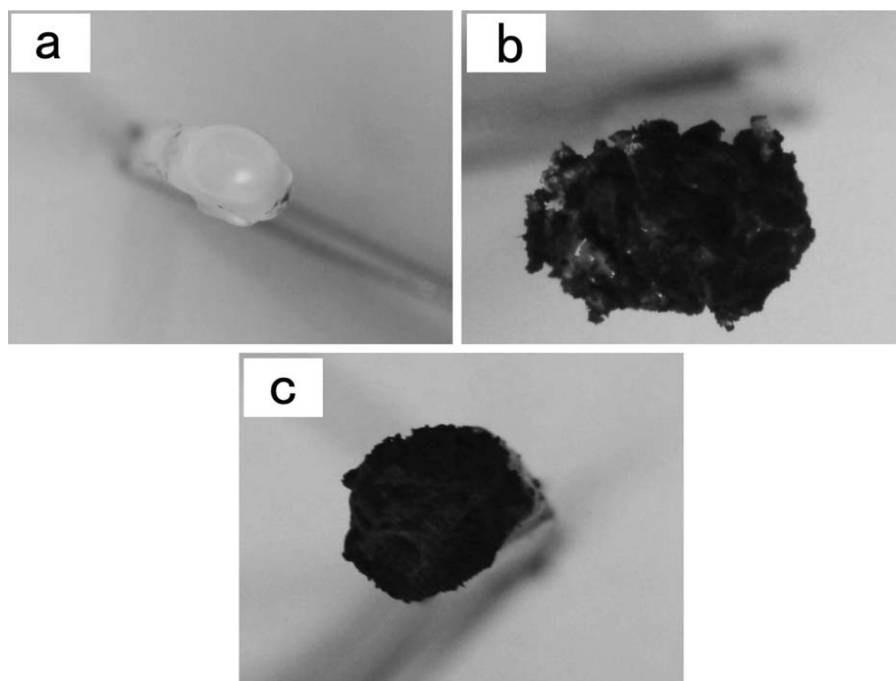


Figure 7. Typical photographs of the generated char over the course of LOI measurements for (a) PP, (b) PP/10% Ni–Mo–Mg, and (c) PP/5% Ni–Mo–Mg/5% carbon black.

samples were quenched as well. The optical images of the samples are compared in Figure 7. Almost no carbonaceous materials were formed on the pure PP after combustion. In the case of the PP/10% Ni–Mo–Mg blends, a large number of char materials was observed on the surface of the sample. However, these char materials presented in a scattered state, among which some melts of PP were found. This illustrated that a high yield of char materials formed from PP/10% Ni–Mo–Mg and suppressed the burning intensity to some extent, but the barrier performance was too weak to extinguish the flame. As for the PP/5% Ni–Mo–Mg/5% carbon black blends, however, we observed a more integrated and compact char layer on the top of the sample [Figure 7(c)]; this directly certified the integrated actions of the carbon black particles as the CNTs formed from PP.

Proposed Mechanism for the Combination of Carbon Black with Growing CNTs

In this study, we demonstrated that carbon black with an appropriate concentration in PP/Ni–Mo–Mg was capable of combining the growing CNTs to form char with an integrated and compact structure under high-temperature conditions. Importantly, this integration resulted in a significant improvement of the flame retardancy of the PP blends. To clearly elucidate the action of carbon black in the formation of integrated char structure, a proposed mechanism is sketched in Figure 8. When PP was exposed to high temperature, the long molecular chain broke to form many organic molecular radicals. As for the PP/Ni–Mo–Mg composites, some of these radicals were catalyzed to generate CNT structures [Figure 8(a)]. In another case, when only carbon black was incorporated into PP, some carbon black particles trapped organic molecular radicals to form carbon black/organic species radicals [Figure 8(b)]. In this study, we found that these solid radicals resulted in the

formation of some island amorphous structures. For the third case of PP/Ni–Mo–Mg/carbon black, an integrated and continuous CNT/carbon black char structure was fabricated by the combination of carbon black [Figure 8(c)]. We attributed this to three aspects:

1. The first was the large number of topological defects located on the carbon black surface. These provided lots of connected points for CNTs.

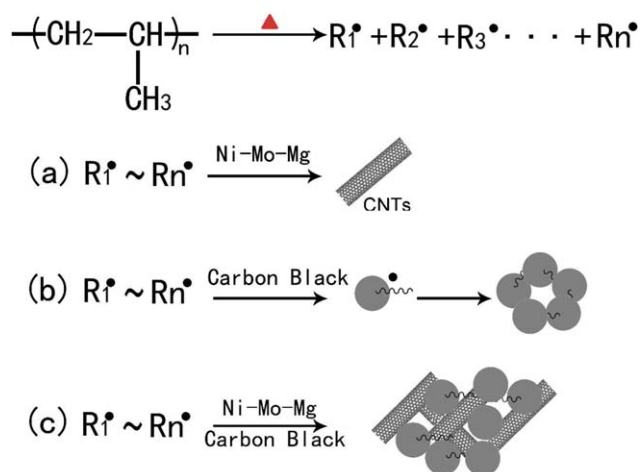


Figure 8. Proposed reaction mechanism of PP with the addition of Ni–Mo–Mg and carbon black particles during pyrolyzation: (a) PP/Ni–Mo–Mg, (b) PP/carbon black, and (c) PP/Ni–Mo–Mg/carbon black. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- The second was the trapped radicals, which also belonged to the carbon source of CNTs. Thus, when the CNTs were growing extensively, some of the carbon black particles took part in the CNT growing and acted as ideal binders to connect the growing CNTs under proper situations.
- The third was the proper situation. It was realized by the one-step pyrolyzation of the PP/Ni–Mo–Mg/carbon black blends.

CONCLUSIONS

In summary, the effects of carbon black addition on the carbonization and flame retardancy of PP in combination with Ni–Mo–Mg catalysts follow. First, carbon black had a positive effect on the char yield of PP/5% Ni–Mo–Mg blends for a series of temperatures, and this effect was more obvious at higher temperatures. Second, the presence of carbon black in the PP/Ni–Mo–Mg blends combined the growing CNTs to generate char with integrated and compact structures, as verified by SEM and TEM measurements and directly demonstrated by the designed experiments. Third, the results of cone calorimetry and LOI show that the addition of carbon black led to a significant improvement in the flame retardancy of the PP/Ni–Mo–Mg blends, although no UL-94 rating was reached because of dripping. The catalytic carbonization of degradation fragments of polyolefin are a promising route to flame retardants for the polyolefin matrix, in which finding a technique to promote the barrier properties of char is a practical direction for further improving the flame retardancy of polyolefin. Further attempts and explorations along this route are underway in our laboratory.

ACKNOWLEDGMENTS

This work was subsidized by the Fundamental Research Funds for the Central Universities (contract grant number DL12DB02) and the Natural Science Foundation of Heilongjiang Province of China (contract grant number B201401).

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