Flame retardant polypropylene nanocomposites: Catalytic and synergistic effects between maleic anhydride grafted polypropylene and cobalt nanoparticles

Qingliang He[*], Suying Wei[**] and Zhanhu Guo[*]

[*]Integrated Composites Laboratory (ICL), Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, Texas 77710 USA, qhe@lamar.edu, zhanhu.guo@lamar.edu
[**]Department of Chemistry and Biochemistry, Lamar University, Beaumont, Texas 77710 USA, suying.wei@lamar.edu

ABSTRACT

Polypropylene-graft-maleic anhydride (PP-g-MA) has been demonstrated with an unusual function, *i.e.*, to reduce the heat release rate (HRR) of PP polymer nanocomposites (PNCs) reinforced with in-situ synthesized cobalt (Co)-cobalt oxide core-shell nanoparticles (NPs). PP-g-MAs with molecular weights of ~ 800 and 2500 g/mol have been chosen to demonstrate this function. Microscale combustion calorimetry (MCC) and thermal gravimetric analysis (TGA) were used for determining the combustion behaviors and thermal stability of the as-prepared PP/Co PNCs. MCC result showed that the peak HRR (PHRR) of PP were reduced by ~32% upon addition of 20.0 wt% Co NPs; more importantly, further reduction in PHRR more than 50% was observed by adding only 5.0 wt% non-flame retardant PP-g-MA into PP/20.0wt% Co PNCs. Through combining MCC with a fast TGA thermal degradation technique, it is believed that this flame retardancy was attributed to catalytical thermal decomposition mechanism and synergism between PP-g-MA and Co NPs.

Keywords: Cobalt nanoparticles, flame retardant, catalytic, synergism, polypropylene

INTRODUCTION

Cobalt (Co) NPs have been extensively studied due to their wealthy size dependent structural and catalytic properties.[1-4] The bottom up method by thermal decomposing organometallic precursors such as dicobalt octacarbonyl ($Co_2(CO)_8$) in organic solvents is one of the most commonly used approaches among the extensively reported chemical approaches for synthesizing Co NPs.[5, 6] In that case, it will facilitate using inert polymers such as polyolefin to serve as hosting matrix to these magnetic Co NPs for preparing polymer nanocomposites (PNCs).[2, 3, 7] The reason is that the intrinsic steric hindrance from the inert polyolefin backbones can stabilize the magnetic Co NPs through offsetting the strong attraction forces among magnetic NPs derived from their high surface energy, large specific surface area, strong magnetic dipole-dipole interactions and van der Waals forces.[7-9] Therefore, this bottom up method is ideal for using inert polyolefin as hosting matrix for magnetic NPs.

However, the increase of interfacial tension due to the lack of strong interaction at the polymer-nanofiller interface is a major drawback to hinder the the physicochemical property of the resulted PNCs such as thermal stability and flame retardancy. Besides, how and how much the thermal stability and flame retardancy will be improved through reducing the interfacial tension between polyolefin matrix and fillers like Co NPs are still obscure up to now. Since the proposed catalytic effect of the transition metal on the flame retardant PNCs during the 1990s,[10] the catalytic mechanism of Co is not well documented yet. PP-g-MA, an ole-fashioned polymer additive, has been widely used as compatibilizer /coupling agent to improve the dispersion of different nanofillers in polymer matrix by enhancing the interfacial adhesion between the polymer matrix and the nanofillers. In this work, we demonstrated the catalytic and syngeristic effect of PP-g-MA and Co NPs on improving the thermal stability and flame retardancy of the PP/Co PNCs. The PNCs were synthesized from an in-situ bottom up method, which is ideal to facilitate the PP-g-MA to coordinate and stabilize the in-situ formed Co NPs and to minimize the agglomeration of these magnetic NPs. PP is chosen to be the hosting polymer matrix due to its miscibility with the PP-g-MA attributed to their similarity in the backbone chemical structure. The synergistic and catalytic effect of PP-g-MA on the thermal stability and flame retardant of PP/Co were discussed.

MATERIALS

PP used here was supplied by Total Petrochemicals USA, Inc ($M_n \approx 40500$). The two PP-g-MA (provided by Baker Hughes Inc.) used here were: 1). PP-g-MA (S) ($M_n \approx 800$) is a gel-like propylene-hexene copolymer with one maleic anhydride (MA) group at one terminal and the other MA grafted on the main chain; 2). PP-g-MA (L) ($M_n \approx 2500$) is a solid homo-polypropylene with one terminal MA group. Dicobalt octacarbonyl ($Co_2(CO)_8$, stabilized with 1-5% hexane) was obtained from Strem Chemicals, Inc. Xylene (laboratory grade) was purchased from Fisher Scientific. All the chemicals were used as-received without any further treatment.

EXPERIMENTAL SECTION

Typical synthesis of PP/Co PNCs was described as below: First, 7.5 g PP pellets, 0.5 g PP-g-MA (type S, or L) and 100 mL xylene were added into a 500 mL three-neck round bottom flask. Then, the mixed solution was heated to reflux (~140 °C) under mechanic stirring at 200 rpm, and kept refluxing for 2 hours to fully dissolve PP and PP-g-MA into a homogeneous transparent solution. After that, the solution was cooled down to ~110 °C; meanwhile, 5.8 g $Co_2(CO)_8$ was dissolved in 120~130 mL xylene in nitrogen protected glove box. The freshly prepared $Co_2(CO)_8$/xylene solution was injected into the flask to obtain a 20.0 wt% Co loading in PP/PP-g-MA system (Calculation was based on the pure elemental weight fraction). While maintaining stirring speed at 200 rpm and heating temperature at 140 °C, the solution was immediately turned from transparent to brown and then gradually black during an additional 3-hour refluxing. Finally, the solution was cooled down to room temperature in the flask and then poured into a large glass container to evaporate the solvent in the fume hood overnight. The black powders were collected and dried in a vacuum oven at room temperature overnight. The PP/20.0 wt% Co PNCs were also synthesized for comparison (8.0 g PP and 5.8 g $Co_2(CO)_8$ without any PP-g-MA). Pure PP was also prepared as reference using the same procedures without adding $Co_2(CO)_8$. The PP-g-MA concentration was 5.0 wt% for all the samples except pure PP and PP/20.0 wt% Co PNCs. The experimental Co loading in this study was controlled constantly at 20.0 wt%.

CHARACTERIZATION

The thermal stability of the pristine PP and its PNCs was investigated using thermogravimetric analysis (TGA, TA Instruments Q-500). For simulating the pyrolysis condition of Microscale combustion calorimetry (MCC), the fast degradation of all the samples was performed at a heating rate of 60 °C/min (1 °C/sec) in nitrogen. The flow rate was 60 mL/min.

MCC was utilized to measure the heat release related parameters. Specifically, heat release capacity (HRC), heat release rate (HRR), peak heat release rate (PHRR), temperature at PHRR (T_{PHRR}), and total heat release (THR) can be obtained. Here, the data was recorded using a "MCC-2" calorimeter manufactured by Govmark Inc. according to the standard method ASTM D7309-2007 (Method A). In a typical measurement, about 5 mg sample was heated up from 80 to 650 °C using a heating rate of 1 °C/sec in a continuous stream of nitrogen flowing at 80 mL/min. The thermal decomposition products (also called as "fuel gases") were mixed with a 20 mL/min stream of oxygen before entering a 900 °C combustion furnace to complete the non-flaming combustion.

For the PP/Co PNCs without/with PP-g-MA, the char residues collected after the MCC test were further studied by X-ray photoelectron spectroscopy (XPS) on a Kratos

AXIS 165 system. The scan of each specimen was carried out with a monochromatic Al X-ray source at the anode of 10 kV and beams current of 15 mA.

RESULTS AND DISCUSSION

Flame Retardancy

MCC was utilized to assess the fire hazards of the PP and its PNCs. Fig. 1 depicts the HRR curves. HRR is the single most important parameter to assess the fire hazard of one flammable material.[11] The higher PHRR one material behaves under a specific heat flux, the more dangerous it will act under a fire accident. Pure PP is a highly flammable material as the observed PHRR of 1513.0 w/g. Adding 5% PP-g-MA(L/S) only slightly decreased the flammability as indicated by the small amounts of reduction in HRC, PHRR, and THR; which was apparently due to the less gas fuels generated from the oxygen-containing PP-g-MA(L/S) than pure hydrocarbon PP. Moreover, the initial thermal decomposition and T_{PHRR} were barely changed.
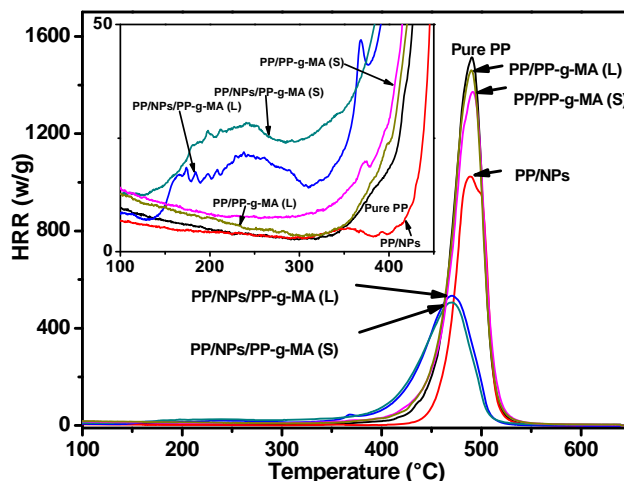

Fig. 1 HRR curves of pure PP and its PNCs. Insert is enlarged zone between 100-400°C.

In the case of the PP/20.0 wt% Co PNCs, PHRR was decreased from 1513.0 to 1024.0 W/g (~32.3 % reduction), THR was decreased from 40.6 to 27.7 W/g (~31.8% reduction); and the initial decomposition temperature was enhanced upon adding the Co NPs (Fig. 1). Apparently, with excluding the dilution of combustible PP through the 20.0wt % non-combustible Co loading, an additional 12.3% decrease in HRR and 11.8% decrease in THR indicated a flame retardancy effect of these in-situ synthesized Co NPs. A barrier effect from these Co NPs is believed to be responsible for this flame retardancy. Heat and mass transfers between gas- and condense- phases were slowed down by forming an insulating layer when these PNCs were exposed under heat, thus fast decomposition of the PP matrix was suppressed.[12] Therefore, the HRR reduction suggests a slower speed of combustible volatiles generated

from the random chain scission of PP backbones in the presence of Co NPs.

Synergistic effect in reducing HRR was observed when adding 5.0% PP-g-MA(L/S) in the PP-20.0 wt% Co system (Fig. 1). HRC and PHRR were observed to decrease sharply, i.e., PHRR was further decreased ~50% (from 1024.0 to 532.4 W/g in the case of PP- PP-g-MA (L) -Co PNCs, or to 500.8 W/g in the case of PP- PP-g-MA (S) -Co PNCs). Meanwhile, THR was further slightly decreased from 27.7 to 25.6 KJ/g with the addition of 5.0% PP-g-MA (L); or to 25.1 KJ/g with the addition of 5.0 % PP-g-MA (S) into PP-20.0% Co PNCs. This remarkable decrease in the flammability of PP by a non-flame retardant additive – PP-g-MA has never been reported. Although conventional synergistic effect (such as nitrogen-phosphorus,[13-15] phosphorus-silicon,[16, 17]) on flame retardant PNCs has been extensively studied, the synergistic effect between PP-MA and Co NPs have rarely been reported. In addition, when PP-g-MA(L/S) was added in the PP-20.0% Co system, a small HRR peak was observed during the initial decomposition stage (around 100-300 °C) and T_{PHRR} was decreased to 471.0 °C (shown in the insert of Fig. 1).

XPS analysis and flame retardancy mechanism

XPS analysis was further carried out to identify the atomic composition of solid char residues of the PP/Co PNCs after the MCC test and to determine flame retardancy mechanism. Upon the analysis, it was found that the carbon species mass percentage increased sharply from 61.80% for the PP/20.0 wt% Co PNCs to 71.08% for PP-PP-g-MA (L)-20.0 wt% Co PNCs, and to 80.92% for PP-PP-g-MA (S)-20.0 wt% Co PNCs; corresponding to 83.16%, 89.43%, and 90.89% atomic percentage of carbon, respectively. This further indicates that the combination of Co NPs and PP-g-MA in the PP matrix can facilitate the char formation at high temperature combustion through their synergistic and catalytic effect, which effectively decreased the heat release rates of PP.

In order to elucidate the synergism between PP-g-MA and Co NPs in dramatically reducing the flammability of PP matrix, a fast thermal degradation test was performed by TGA via using the same condition as MCC measurements- a heating rate of 60 °C/min (1 °C/s) under nitrogen (TGA and derivative weight loss, DTG curves shown in Fig. 2). MCC measurements here were performed through using an inert sample thermal degradation procedure to pyrolyze the sample into combustible gas volatiles followed by a non-flaming oxidation of these volatiles. The fast thermal degradation by TGA can illustrate the dynamic sample weight loss under temperature ramping at a constant high heating rate (1 °C/s); meanwhile, the DTG (%/°C) from the insert of Fig. 2 can reproduce the thermal degradation stage of MCC clearly. Therefore, the degradation and weight loss processes can be demonstrated simultaneously. It is noticed from Fig. 2 that the addition of 5.0% PP-g-MA(L/S) barely decreased the initial thermal degradation temperature of PP;

while 20.0% Co NPs increased the initial degradation of PP as evidenced by the higher thermal degradation temperature than that of pure PP (no detectable HRR increase before 400 °C, shown in the insert of Fig. 1). However, the degradation of PP–5.0% PP-g-MA (L/S)– 20.0 % Co PNCs was definitely altered by the evidence of: broad HRR peaks appeared in the range of 130-310 °C (insert of Fig. 1), and ~18.0% weight loss within the thermal degradation temperature of 100-310 °C (dash square in Fig. 2)
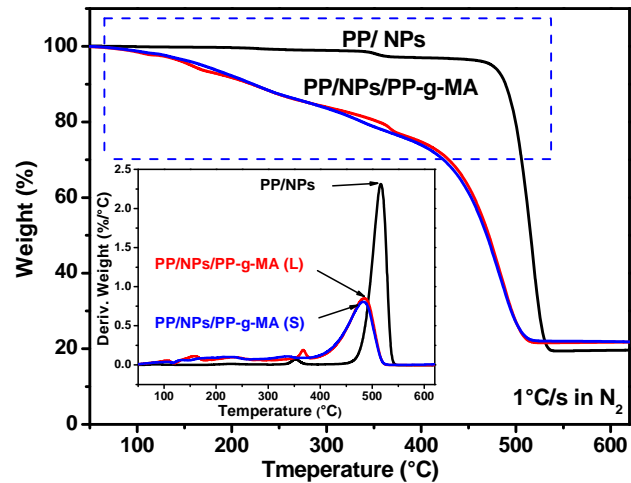

Fig. 2 TGA and DTG curves of PP PNCs under a heating rate of 1°C/s (60 °C/min).

When exposed to heat flux at elevated temperature from 80 to 650 °C, the inert thermal degradation of PP was initiated mainly by chain scission and chain transfer; then reductions in molecular weight were first observed at 227 to 247 °C and gas volatiles became significant above 302 °C. Finally, ignition of PP was observed at a surface temperature of 337 °C,[18] which is consistent with the initial HRR jump at ~ 330 °C observed from MCC. Meanwhile, the addition of 5.0% PP-g-MA (L/S) has limited influence on initiating the degradation of the PP matrix. With adding 20.0% Co NPs, only shielding effect was responsible for reducing the HRR through slowing the release of gas volatiles.[12] When adding PP-g-MA with Co NPs in the PP, the catalytic effect was responsible for lowering the initial thermal degradation temperature of the resulted PNCs (from 330 °C for pure PP to ~100-130 °C for the PNCs), and leaded to a smaller HRR in the range of 100-310 °C due to a small amount of gas volatiles released from bulk material. Probable mechanism includes random chain scission of C-C bond of PP backbone to generate hydrocarbon radicals during initial decomposition, the formation of lower hydrocarbons such as propylene from further degradation of these hydrocarbon radicals, the β-scission and abstraction of H radicals from other hydrocarbons to produce a new hydrocarbon radicals during propagation stage, and finally the disproportionate or re-combination of two radicals as termination reaction.[19] Meanwhile, slightly similar to a "smoldering" fire, a substantial fraction of the total mass of PP/5.0% PP-g-MA

(L/S)/Co PNCs (~18.0 %) was consumed during 100-310 °C subjected to a slow heat release process, effectively decreased the total available gas fuels which would generate large quantity of heat if placed under higher temperatures. One can be also observed that the peak width of the PP/PP-g-MA/Co PNCs was much wider than those of pure PP, PP/PP-g-MA and PP/Co PNCs (Fig. 1), further indicating a longer combustion period upon introducing the PP-g-MA and Co NPs in the PP matrix. This is another sign of low fire hazard for the PP/PP-g-MA/Co PNCs. Although the catalytic effect has been long proposed to be responsible for enhancing the flame retardancy for the PNCs filled with flame retardants with transitional metals, this synergistic catalytic effect from combining Co NPs with non- flame retardant PP-g-MA has rarely been reported.

CONCLUSION

The catalytic and synergistic effect on significantly surpressing the combustion behaviors of PP has been demonstrated by adding small amount (5.0 wt%) non-flame retardant additive – PP-g-MA in the PP PNCs reinforced with the in-situ prepared Co NPs. Combining Co NPs with PP-g-MA has changed the thermal decomposition pathway of PP by accelerating the low temperature weight loss rate (observed from MCC); and facilitating the high temperature char formation (confirmed by XPS). Those changes further result in ~50.0% reduction in PHRR compared with PP/Co PNCs without PP-g-MA. This high efficiency in reducing the flammability of polyolefin will give rise to further insight to the design of novel catalytic flame retardant composition for practical applications.

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