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Short communication

Thermal degradation and flame retardancy of polypropylene/C_{60} nanocomposites

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ABSTRACT

Nanocomposites based on polypropylene (PP) and fullerene C_{60} (in the range of 0.5–2 wt%) were prepared by melt compounding. It was observed that C_{60} could not only significantly enhance the thermal stability in nitrogen but also considerably delay the oxidation decomposition in air of polypropylene. Unexpectedly, the incorporation of C_{60} greatly reduced the heat release rate of PP and resulted in a longer time to ignition. And the free radicals-trapping mechanism of C_{60} was proposed for explaining the enhanced thermal properties and improved flame retardancy of PP. Therefore, C_{60} will be an effective flame retardant like carbon nanotubes and clay for PP.

1. Introduction

After discovering that fullerene C_{60} could be produced in bulk quantities, widespread scientists are exploring its enticing chemistry [1]. One interesting aspect is its high reactivity to free radicals, and it was reported that one C_{60} molecule could trap from 1 to 34 free radicals [2].

Since the decomposition of polymers such as polypropylene and polyethylene is to experience free radical chain reaction [3], such process will be delayed if the free radicals created during the degradation of polymers could be trapped immediately. Consequently, the thermal stability and thermal oxidation of polymers will be dramatically improved. Thus, we herein study whether the addition of C_{60} could delay the decomposition process of polymers both in nitrogen and in air.

2. Experimental

2.1. Materials and measurements

Polypropylene (PP, S1003, MFR: 3.0 g/min) was purchased from Shanghai Petrochemicals Factory, and C_{60} (purity: >99%) was bought from Henan Puyang limited company.

Thermogravimetric analysis (TGA) was performed on a TA STD Q600 thermal analyzer at a heating rate of 20 °C/min, in nitrogen and air atmosphere, with a scan range from 50 to 600 °C. Cone calorimeter tests were performed using FTT, UK device according to ISO 5660 in triplicate at an incident flux of 35 kW/m^2, with a sample size of 100 mm × 100 mm × 3.0 mm. The data reported here were the average values of triplicate data.

Gel content was measured using Soxhlet extractor by refluxing PP and its composites in boiling xylene at 135 °C for 48 h, and subsequently dried in vacuum oven for 24 h. It should be pointed out that both PP and C_{60} can dissolve in xylene. The gel content was calculated through dividing the remained mass by the primary mass of the samples.

Rheological properties of PP and its nanocomposites were conducted on a controlled strain rate rheometer (ARES rheometer) in an air environment and the size of samples measured was 25 mm in diameter and with a gap of 1.1 mm. Time scanning and temperature scanning tests were performed at 260 °C for 20 min.

2.2. Preparation of PP/C_{60} nanocomposites

PP/C_{60} nanocomposites were prepared via melt compounding at 180 °C in Thermohaake rheomixer with a rotor speed of 60 rpm, and the mixing time was 10 min for each sample. Nanocomposites containing 0, 0.5, 1 and 2 wt% C_{60} content were designated as PP, PF1, PF2 and PF3, respectively.

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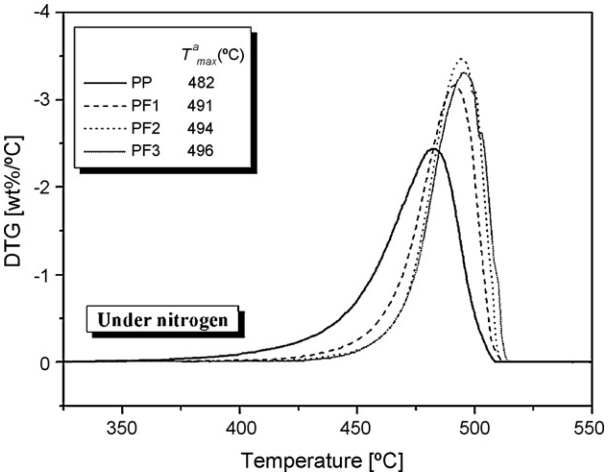

Fig. 1. Derivative weight (DTG) curves for PP and its nanocomposites under nitrogen. T^a_{max}: the maximum weight loss temperature.

3. Results and discussion

3.1. Thermal degradation behavior of PP nanocomposites

Figs. 1 and 2 present the derivative weight curves for PP and its nanocomposites in nitrogen and in air, respectively. In N_2, the initial decomposition temperature (T_{onset}) of PP was significantly enhanced with the addition of C_{60}, with T_{onset} 418 °C for PP and 455 °C for PF3 (2 wt% C_{60}), around 38 °C higher than pure PP. At the same time, the maximum weight loss temperature (T_{max}) of PP was also increased from 482 °C for PP and 496 °C for PP nanocomposite containing 2 wt% C_{60}. Similar results were reported for carbon nanotubes (CNTs) and clay. T_{max} of PP could be enhanced by 14 °C for PP/2 wt% CNTs [4] and 17 °C for PP/PP-g-MA/10 wt% clay [5].

By heating PP in air, PP experienced an oxidative dehydrogenation accompanied by hydrogen abstraction [6]. As shown in Fig. 2, several samples suffered oxidation decomposition mainly in one step, and the T_{max} of PP nanocomposites was much higher than neat PP. For example, T_{max} for PF3 (2 wt% C_{60}) is 398 °C, around 60 °C higher than for PP (338 °C). All of said results demonstrated fullerene C_{60} could delay the oxidation decomposition process of PP. Kashiwagi et al. [4] have found that multi-wall CNTs could significantly improve oxidation degradation of PP, however, they observed PP/multi-wall CNTs underwent two-step degradation in air.

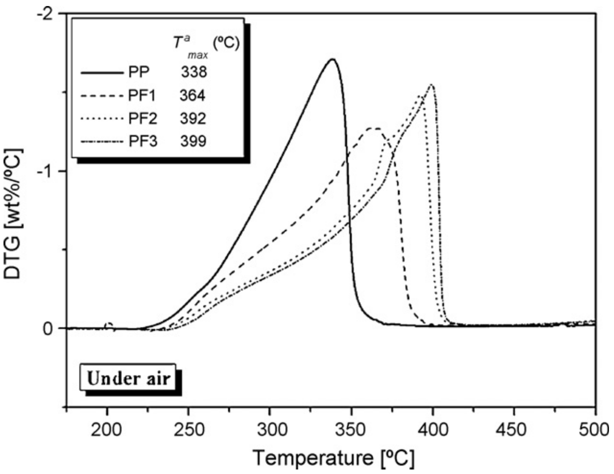

Fig. 2. Derivative weight (DTG) curves for PP and its nanocomposites under air. T^a_{max}: the maximum weight loss temperature.

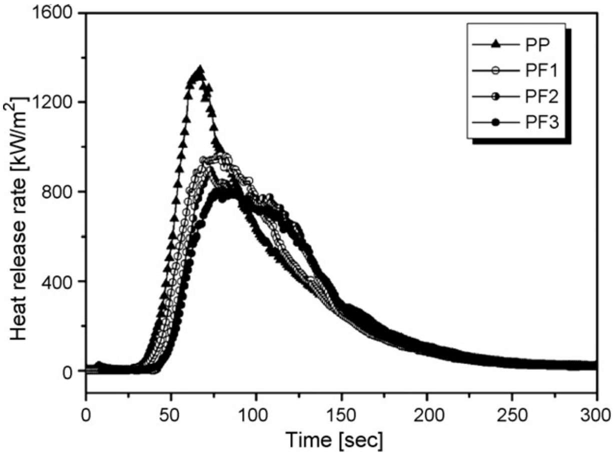

Fig. 3. Heat release rate for PP and its nanocomposites.

3.2. Flame retardancy of PP nanocomposites

Fig. 3 shows the heat release rate (HRR) curves for three nanocomposites with pure PP as a comparison. It was readily observed that the incorporation of C_{60} considerably reduced the heat release rate of PP, with a peak heat release rate (PHRR) of 1435 kW/m^2 for PP and 758 kW/m^2 for PF3, by 47% lower than that for PP. In comparison, CNTs and clay were reported to reduce the PHRR of PP by 70% for PP/1 wt% CNTs [4] and around 50–60% for PP/3 wt% clay [6]. On the other hand, incorporation CNTs and clay in polymers shortened the ignition time of samples, unlike them, the presence of C_{60} prolonged the time to ignition, which was an advantage over CNTs and clay for improving flammability of polymers. Although the flame retardancy capacity of C_{60} was not better than CNTs and clay in light of PHRR values, it at least provided a new strategy for reducing the flammability of polymers.

CNTs and clay were reported to reduce the flammability of polymers by forming network structure in polymer matrix, when polymers were exposed to high heat or flame, the network could cover the polymer substrates to prohibit outer heat or oxygen entering the underlying of polymers, thus protected the matrix and reduced the heat release rate of polymers [4,7,8]. Since C_{60}

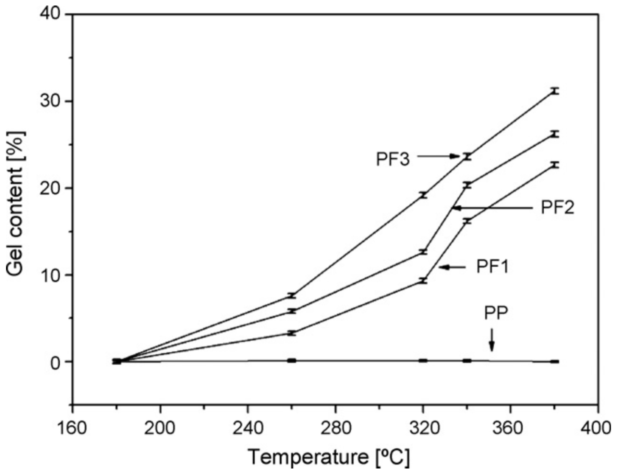

Fig. 4. Gel content for PP and its nanocomposites at various temperature.

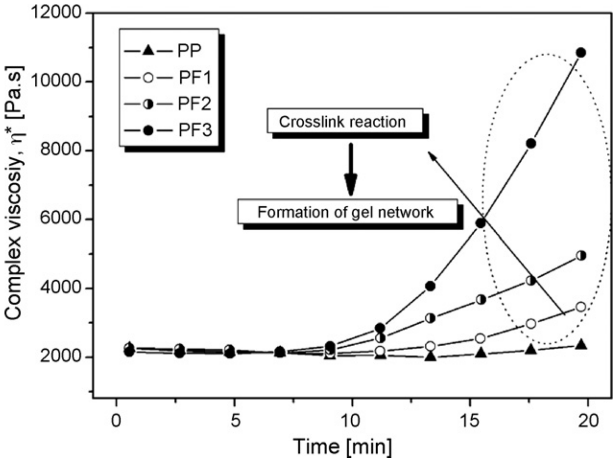

Fig. 5. Dependence of complex viscosity on time for PP and its nanocomposites at 260 °C.

is a spherical molecule, not like CNT with an extended structure and clay with two-dimension structure, thus cannot form a network in PP matrix, why C_{60} could considerably improve thermal property and flame retardancy of polymers? In Section 1, we mentioned that the decomposition of polymers is to experience free radical chain reaction and C_{60} can trap easily a number of free radicals. Considering these, it was reasonable to draw a conclusion that free radicals-trapping effect of C_{60} could be responsible for the enhanced thermal properties and improved flame retardancy of PP nanocomposites. Since one C_{60} molecule theoretically can at most trap 60 free radicals, thus at very low concentration, the C_{60} can trap the macromolecular radicals created from the degradation of polymers at a given temperature, and consequently form a 3D gelation network. And the gel content will increase with increasing concentration of C_{60}.

In order to confirm the above hypothesis, we designed a strategy that gel content of the nanocomposites should be much higher than that for pure PP if above explanation was correct. Fig. 4 presents the gel content of PP and its nanocomposites heat-treated at different temperature in air. Clearly, the gel content of PP was very low, below 0.3% at 320 °C, while those for PF1, PF2 and PF3 were 9.32%, 12.62% and 19.21%, respectively, much higher than that of PP, indicating that the presence of C_{60} could increase the gel content at elevated temperature. The gel content of nanocomposites dramatically increased after 260 °C, in that PP has started to degrade by 4.36%, while at and after 260 °C, C_{60} simultaneously trapped the PP macromolecular free radicals and other small free radicals like $H^\bullet$ and $^\bullet OH$ to form cross-link gel networks. On the other hand, the radical-trapping effect of C_{60} made partial macromolecular radicals have more time to combination, which also contributed to the formation of gel network. Furthermore, at elevated temperature above 260 °C, the degradation of polymers will produce the macromolecular radicals, and one macromolecular radical may have several active sites. These active sites were easily attacked by the C_{60} particles and subsequently form branching-like or 3D gel network structure. All of the factors may be responsible for the formation of gel network and improved flame retardancy.

Expectedly, we also observed the complex viscosity of PP nanocomposites dramatically increased at 260 °C in rheological measurements at a time-sweeping mode (see Fig. 5). Since the formation of 3D gel network occurred at elevated temperature, the viscosity of nanocomposites would increase with increasing scanning time and increasing concentration of C_{60} in the composites. And the increasing melt viscosity in turn confirmed the above hypothesis proposed. It should be pointed out that oxidation cross-linking reaction of PP did not basically occur or took place to a very small extent at that temperature, for the viscosity of PP almost kept the same value. As for the detailed action mechanism, we will report them in future.

4. Conclusions

C_{60} could not only remarkably enhance the thermal stability and improve thermal oxidation but also reduce the flammability of polypropylene, with a remarkable reduction in heat release rate and much longer time to ignition, through trapping free radicals produced on decomposition of materials. The free radicals-trapping mechanism of C_{60} was proposed for explaining the enhanced thermal properties and improved flame retardancy of PP. As a promising flame retardant, although C_{60} does not reduce the heat release rate like carbon nanotubes and clay, it at least provide scientists another new strategy for improving thermal and flame retardancy of polymers.

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