



Short communication

Thermal degradation and flammability properties of HDPE/EVA/C₆₀ nanocomposites

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ABSTRACT

The thermal and flame retardancy properties of high-density polyethylene (HDPE)/ethylene vinyl-acetate copolymer (EVA)/fullerene (C₆₀) nanocomposites were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and cone calorimetry with C₆₀ loading varied from 0.5 to 2% by mass fraction. Dispersion of C₆₀ in HDPE/EVA blend was characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TGA and DSC results showed that the presence of C₆₀ could remarkably enhance the thermal stability, and cone calorimeter measurements indicated that incorporating C₆₀ could result in a significant reduction in the peak heat release rate and a much longer time to ignition of the HDPE/EVA blend. Furthermore, the larger the C₆₀ loading level, the better the flame retardancy of HDPE/EVA/C₆₀ nanocomposites.

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1. Introduction

Nowadays, in order to reduce the flammability and maintain the mechanical properties of the polymers simultaneously, new halogen-free flame retardant systems are focused on the nano-flame retardants, including clay and carbon nanotubes (CNTs) [1]. Cone calorimeter measurements showed that incorporating them would dramatically reduce the peak heat release rate (PHRR) of polymer nanocomposites at a low loading. The clay in the polymer matrix formed a thermally stable protecting barrier that could prohibit the feedback of heat and the permeation of oxygen [2], which is responsible for the improvement of flame retardancy. As for CNTs, the reduction is attributed to the formation of a network structure of CNTs in the polymer matrix during the combustion [3].

Our group recently reported that the presence of C₆₀ could delay the thermal oxidation degradation of the PP and reduce the PHRR of nanocomposites remarkably [4]. Due to the high reactivity towards free radicals of C₆₀ [5], a free radical-trapping mechanism [6] was proposed to explain the improved flame retardancy that the fullerene C₆₀ trapped the free radicals produced during the degradation process of the PP and subsequently *in situ* formed a crosslinking network.

The HDPE/EVA blend has attracted considerable attention for use as wire and cable insulated materials [7,8], and the flame

retardancy of the HDPE/EVA blend has become very important [9]. Since the combustion mechanism of the HDPE/EVA blend is also a free radical chain reaction, the presence of C₆₀ in the blend may also trap the free radicals created in the process of combustion of the composites. To our best knowledge, however, no efforts have been devoted to employing C₆₀ to flame retarding the HDPE/EVA blend since the discovery of C₆₀. In this present study, we focus on studying whether the presence of C₆₀ can improve the flame retardancy of the HDPE/EVA blend.

2. Experimental

2.1. Materials

High-density polyethylene (HDPE, 5502#, MFR = 0.35 g/10 min (230 °C × 2.16 kg), M_n = 17,300, M_w = 135,700, density = 0.955 g/cm³) was from Daelim, Korea. Ethylene vinyl-acetate copolymer (EVA, 8450#, VA = 15 wt%, MFR = 1.5 g/10 min (230 °C × 2.16 kg), M_n = 46,200, M_w = 224,000, density = 0.940 g/cm³) was from Nippon Unicar. Co. Ltd., Japan. Fullerene C₆₀ (purity >99.9%) was purchased from Henan Puyang Co., Ltd., China.

2.2. Preparation of HDPE/EVA/C₆₀ nanocomposites

HDPE, EVA (mass ratio: 50/50) and C₆₀ were mixed together via melt compounding at 180 °C in a Thermal Haake rheomixer with a rotor speed of 60 rpm and the mixing time was 10 min for

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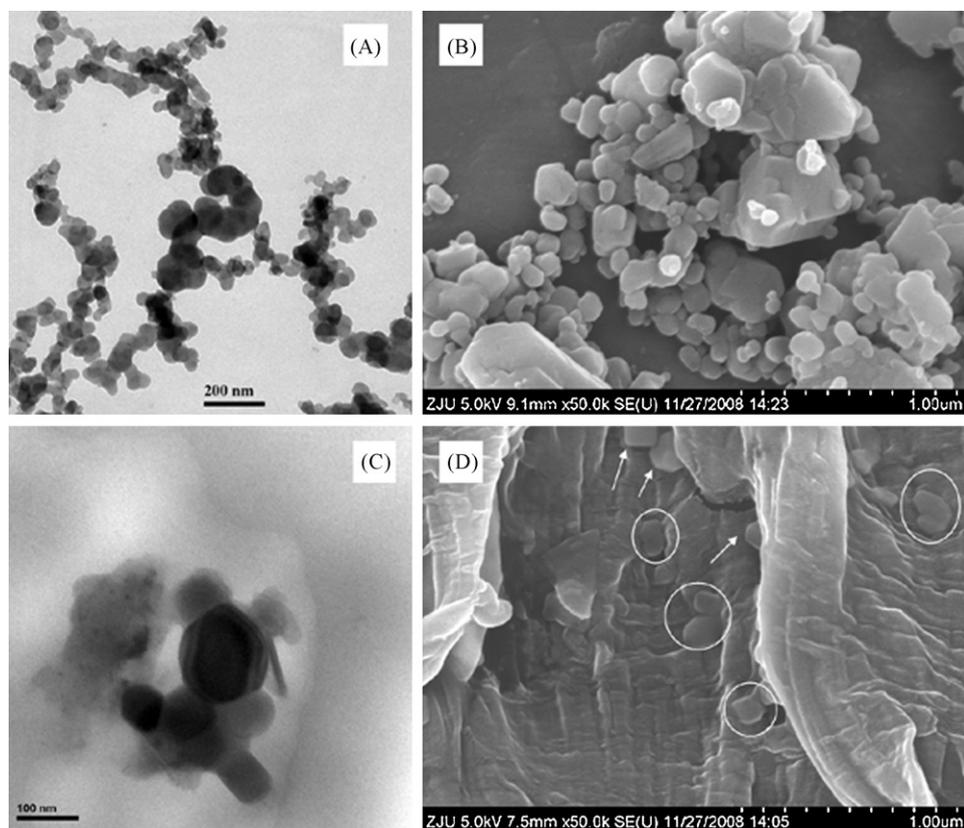


Fig. 1. TEM (A) and SEM (B) images of C_{60} ; TEM (C) and SEM (D) images of C_{60} -1%.

each sample. Nanocomposites containing 0 wt%, 0.5 wt%, 1 wt% and 2 wt% C_{60} were designated as C_{60} -0%, C_{60} -0.5%, C_{60} -1% and C_{60} -2%, respectively.

2.3. Measurements and characterization

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA STD Q600 thermal analyzer at a heating rate of $10^{\circ}\text{C min}^{-1}$ in the air and nitrogen atmosphere in a scanning range from 50°C to 600°C , and each specimen was examined in triplicate. The fluid flow was 120 ml/min air or nitrogen atmosphere, and the type of pan is alumina. Cone calorimeter tests were performed using an FTT, UK device according to ISO 5660 at an incident flux of 35 kW m^{-2} , with a specimen size of $100\text{ mm} \times 100\text{ mm} \times 1.0\text{ mm}$, and each sample was tested three times. The microstructures of C_{60} and the dispersion of C_{60} in the HDPE/EVA blend were observed by transmission electron microscopy (TEM, JEM-1200EX) and scanning electron microscopy (SEM, JSM-5510, JEOL).

3. Results and discussion

3.1. Dispersion of C_{60} in HDPE/EVA blend

The diameter of the spherical C_{60} molecule is 0.71 nm, and its crystal size differs with methods of fabrication. Fig. 1 shows the TEM and SEM images of pure C_{60} and C_{60} -1%. The sizes of C_{60} crystals in Fig. 1(A) and (B) were from 50 nm to 150 nm. From Fig. 1(C), in HDPE/EVA blend, C_{60} crystalline aggregated and did not disperse well through melt blending. In Fig. 1(D), C_{60} in the blend has been circled to show the dispersion.

3.2. Thermal degradation behavior of HDPE/EVA/ C_{60} nanocomposites

Since polymer materials are usually used in air environment, from a practical application view, it is much more important to evaluate the thermal properties of materials in air than in nitrogen. Figs. 2 and 3 present the TGA curves of HDPE/EVA/ C_{60} nanocomposites in air and in nitrogen atmosphere, respectively, with detailed data listed in Table 1. To better estimate the effect of C_{60} on the thermal stability of the nanocomposites, TGA curves of pristine C_{60} was also presented. In air atmosphere, the HDPE/EVA blend experienced a rapid thermal oxidation decomposition accompanied by hydrogen abstraction [10], an initial decomposition temperature (T_{onset}) about 306°C , and a sharp maximum mass loss peak (T_{max}) about 406°C was observed (see Table 1). Obviously, the presence of C_{60} delayed the oxidation degradation of polymer blend, and

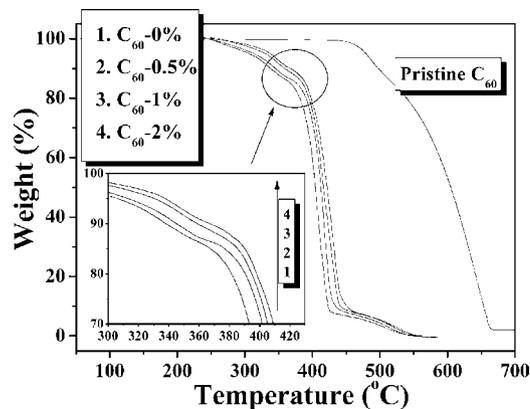


Fig. 2. TGA curves for the pristine C_{60} and HDPE/EVA/ C_{60} nanocomposites in air.

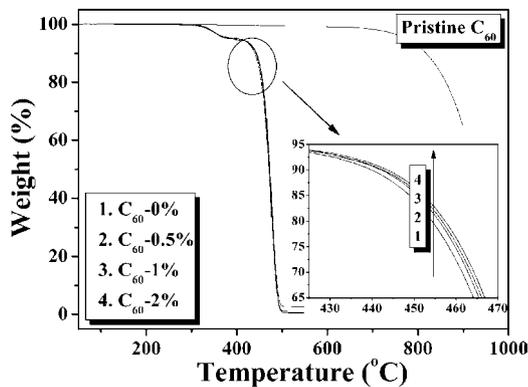


Fig. 3. TGA curves for the pristine C_{60} and HDPE/EVA/ C_{60} nanocomposites in nitrogen.

Table 1

Detailed data obtained from TGA curves in Figs. 2 and 3.

Sample ID	In air		In nitrogen	
	T_{onset} (°C)	T_{max} (°C)	T_{onset} (°C)	T_{max} (°C)
C_{60} -0%	306	406	388	474.9
C_{60} -0.5%	313	416	390	476.7
C_{60} -1%	330	422	401	477.1
C_{60} -2%	337	432	406	477.6

T_{onset} , the temperature where 5 wt% weight loss occurred; T_{max} , the temperature where maximum weight loss rate occurred.

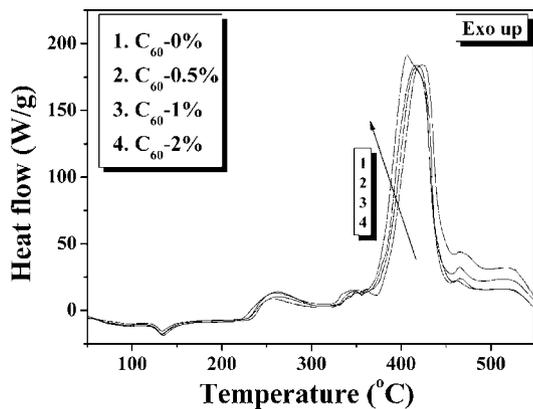


Fig. 4. DSC curves for HDPE/EVA/ C_{60} nanocomposites in air.

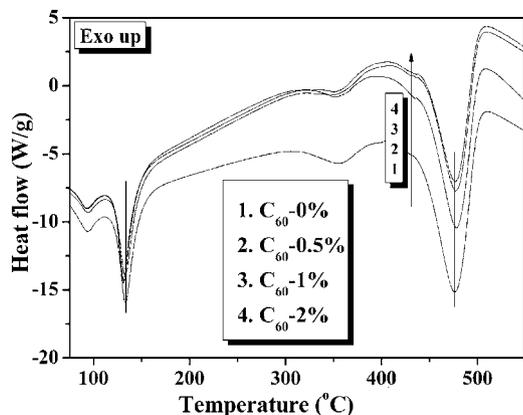


Fig. 5. DSC curves for HDPE/EVA/ C_{60} nanocomposites in nitrogen.

Table 2

Detailed data of high temperature obtained from DSC curves in Figs. 4 and 5.

Sample ID	In air		In nitrogen	
	T_p (°C)	ΔH_d (J/g)	T_p (°C)	ΔH_d (J/g)
C_{60} -0%	416	4224	473.4	202
C_{60} -0.5%	418	3923	476.5	212
C_{60} -1%	420	3673	477.0	223
C_{60} -2%	426	3440	478.1	229

T_p , the temperature where maximum heat flow occurred; ΔH_d , enthalpy during the degradation process of samples.

the T_{onset} and T_{max} of the HDPE/EVA/ C_{60} nanocomposites were noticeably increased with the increase of the C_{60} content (see Table 1). As for C_{60} -2% (containing 2 wt% C_{60}), its T_{onset} and T_{max} were about 337°C and 432°C, respectively, 31°C and 26°C higher than those of the HDPE/EVA blend, which indicated that the presence of C_{60} could slow down the thermal oxidation decomposition of HDPE/EVA remarkably. Troitskii et al. [11] also found that C_{60} and C_{70} were effective inhibitors for thermal oxidative destruction of PMMA and polystyrene. In comparison, Song et al. [6] found that C_{60} were effective inhibitors for thermal oxidative destruction of PP, and 2 wt% C_{60} could increase T_{max} of PP by 62°C. Kashiwagi et al. [12,13] observed that 2 wt% carbon nanotubes (CNTs) could increase T_{max} (second step) of PP by 78°C.

In nitrogen atmosphere, the T_{onset} and T_{max} of C_{60} -2% were about 406°C and 477°C (see Table 1), respectively, 18°C and 3°C higher than those of HDPE/EVA blend. The difference in thermal behavior between the atmospheres indicated that the presence of oxygen could speed up the thermal oxidation decomposition of HDPE/EVA/ C_{60} nanocomposites remarkably. On the other hand, the oxygen and C_{60} in nanocomposites during the thermal decomposition was competitive.

Unlike TGA, DSC measurements could provide the temperature and the heat enthalpy of thermal degradation during the decomposition process of materials. Figs. 4 and 5 present the DSC curves of HDPE/EVA/ C_{60} nanocomposites in air and in nitrogen atmosphere, respectively. Detailed data of the high temperature from DSC curves are listed in Table 2. In air atmosphere, HDPE/EVA/ C_{60} nanocomposites experienced rapid exothermic oxidation decomposition at high temperature. As for C_{60} -2% (containing 2 wt% C_{60}), its maximum heat flow temperature (T_p) is 426°C, and 10°C higher than that of the HDPE/EVA blend. The enthalpy was an important parameter since it could quantify the heat evolution produced in the process of oxidation decomposition (ΔH_d). The enthalpies of the nanocomposites were greatly reduced from 4224 J/g to 3440 J/g, indicating that nanocomposites with the same mass released much less heat in the process of oxidation dehydrogenation, and this

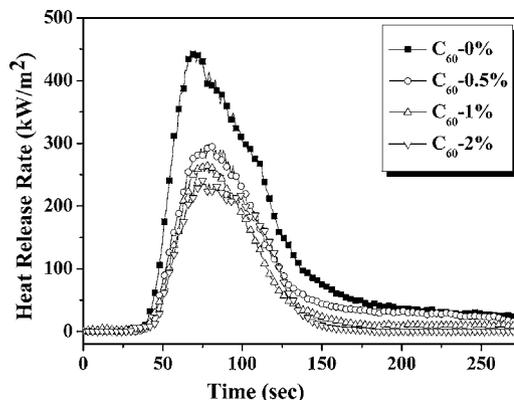


Fig. 6. Effects of C_{60} concentration on heat rate of HDPE/EVA/ C_{60} nanocomposites at an incident heat flux of 35 kW m^{-2} .

Table 3Cone calorimeter data for HDPE/EVA/C₆₀ nanocomposites at an incident heat flux of 35 kW m⁻².

Samples ID	t_{ign} (s)	t_{PHRR} (s)	PHRR (kW m ⁻²)	PHRR reduction	AHRR (kW m ⁻²)	AMLR (g s ⁻¹)	THR (MJ m ⁻²)	AEHC (MJ kg ⁻¹)
C ₆₀ -0%	26 ± 1	69 ± 1	442 ± 30	–	123 ± 5	0.032 ± 0.001	27.9 ± 1.0	60 ± 3
C ₆₀ -0.5%	28 ± 1	80 ± 3	298 ± 20	33%	81 ± 3	0.019 ± 0.002	22.0 ± 0.5	38 ± 2
C ₆₀ -1%	30 ± 1	78 ± 3	263 ± 15	41%	61 ± 2	0.015 ± 0.001	21.1 ± 0.4	35 ± 1
C ₆₀ -2%	40 ± 2	76 ± 2	242 ± 10	45%	54 ± 2	0.013 ± 0.001	14.5 ± 0.3	27 ± 1

t_{ign} , time to ignition; PHRR, peak heat release rate; AHRR, average heat release rate; t_{PHRR} , time to PHRR; AMLR, average mass loss rate; THR, total heat release; AEHC, average effective heat of combustion.

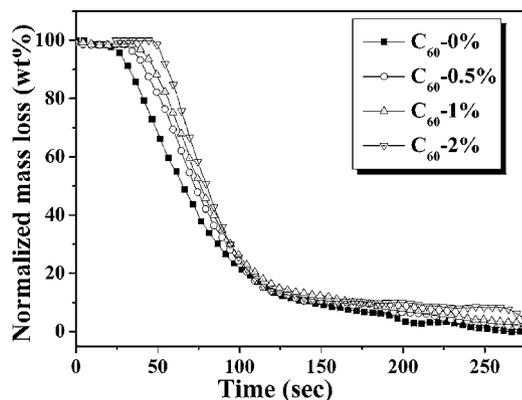


Fig. 7. Effects of C₆₀ concentration on normalized mass loss of HDPE/EVA/C₆₀ nanocomposites at an incident heat flux of 35 kW m⁻².

phenomenon was favorable to flame retarded polymer materials. In nitrogen atmosphere, HDPE/EVA/C₆₀ nanocomposites experienced an endothermal degradation process at high temperature. As for C₆₀-2%, T_p increased from 473 °C to 478 °C, and ΔH_d increased from 202 J/g to 229 J/g. The enthalpies of the nanocomposites in air atmosphere were much higher than those in nitrogen due to the existence of oxygen.

3.3. Flammability of HDPE/EVA/C₆₀ nanocomposites

The heat release rate (HRR) curves of HDPE/EVA/C₆₀ nanocomposites are shown in Fig. 6, and detailed data are listed in Table 3. The results showed that the presence of C₆₀ not only prolonged the ignition time (t_{ign}) and time to peak heat release rate (t_{PHRR}) of the HDPE/EVA blend, but considerably reduced the peak heat release rate (PHRR). C₆₀-2% (2 wt% C₆₀) sample gave a t_{ign} of 40 s and t_{PHRR} of 76 s, both of which were much longer than those of the HDPE/EVA blend, which implied that C₆₀ could delay the initialization of the combustion process. Furthermore, the PHRR values of HDPE/EVA/C₆₀ nanocomposites were reduced about 41% for C₆₀-1% and 45% for C₆₀-2% of that of the HDPE/EVA blend, which demonstrated the addition of C₆₀ improved the flame retardancy of HDPE/EVA blend. In comparison, C₆₀, CNTs and clay have been reported to significantly reduce the PHRR of PP by 45% for PP/C₆₀ (2 wt%), by 70% for PP/CNTs (1 wt%) [6,12,13], and about 20–50% for PP/clay nanocomposites [14]. However, incorporating CNTs and clay would lead to a shorter time to ignition of nanocomposites, which suggested that nanocomposites containing CNTs and clay were easier to be ignited than PP itself. Although the capacity of C₆₀ was not as good as CNTs and clay in terms of reducing the PHRR values, it at least conferred a longer time to ignition, namely, enabled the HDPE/EVA blend more difficult to burn. Although C₆₀ is chemically close to CNTs, the flame retardation mechanism is quite different. As for C₆₀, it is a free radical-trapping mechanism. The

fullerene C₆₀ trapped the free radicals produced during the degradation process of the HDPE or PP. But for CNTs, the flame retardation is attributed to the formation of a network structure of CNTs in the polymer matrix during the combustion. In corporation of C₆₀, the total heat release (THR) and the average effective heat of combustion (AEHC) of HDPE/EVA/C₆₀ nanocomposites were greatly reduced, which could be explained that C₆₀ had a free radical effect and caused additional char formation.

As is shown in Fig. 7, the curves of normalized mass loss demonstrated that the presence of C₆₀ slowed down the combustion process of HDPE/EVA/C₆₀ nanocomposites because the residual mass of nanocomposites was always higher than that of the HDPE/EVA blend in the whole burning process, which was well consist with the data of AMLR listed in Table 3.

4. Conclusion

The presence of C₆₀ could significantly improve the thermal stability properties in air. Incorporating C₆₀ into the HDPE/EVA blend could remarkably prolong the time to ignition and the time to PHRR, and reduce the PHRR, THR and AEHC of polymer materials and slow down the combustion process. The above results suggest that people will have more time to escape from a fire and open up a new strategy for reducing the flammability of polymers.

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