Novel nanocomposite based on EVA/PHBV/Fullerene with improved thermal properties

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Abstract

A novel nanocomposite was prepared from ethylene-co-vinyl acetate copolymer (EVA) and poly-3-hydroxy butyrate-co-valerate (PHBV) in combination with small amounts of Fullerene (C_{60}). The thermal degradation as well as the incorporation effect of C_{60} on the thermo-oxidative decomposition of EVA/PHBV nanocomposites were investigated using thermogravimetric analysis (TGA). In order to assess the level of stabilization of nanocomposites, the oxidation induction time (OIT) test was also determined. The obtained results indicated that the dispersion of C_{60} even at low loading (0.3, 0.5 and 0.7 wt.%) exerts a significant increase on the thermal stability properties of nanocomposite. The oxidation induction time values of nanocomposites were remarkably increased with the increase of C_{60} amounts. Surprisingly, the oxidation induction time of EVA/PHBV/C_{60} (0.3 wt.%) is 1643 seconds higher than that of unfilled EVA/PHBV blend.

The flammability properties investigated in pyrolysis combustion flow calorimetry (PCFC) showed that the addition of C_{60} could prolong the time to peak of Heat Release Rate (pHRR) of around 30 °C compared to EVA/PHBV blend. It was demonstrated that C60 is inhibitor of the thermal and thermo-oxidative degradation of EVA/PHBV blend.

Keywords Poly-3-Hydroxy Butyrate-co-Valerate, Fullerene, Flammability, Oxidation Induction Time, Thermal stability.

1. Introduction

Like graphite and diamond, fullerenes are also in the family of carbon. They present a great variety of sizes and morphologies. Fullerene (C_{60}) is considered as the most stable and abundant molecule of this family [**1-2**] and has become an important object of scientific curiosity in many research areas. The presence of C_{60} induces numerous changes on the properties of the polymeric host. It can delay the thermal oxidation and increase the thermal stability of polymers [**3**]. For example, it can delay the thermal depolymerization of poly(methyl methacrylate) (PMMA) and the autocatalytic thermal dehydrochlorination of polyvinyl chloride (PVC) [**4**].

When incorporated into poly(alkyl methacrylate) and poly(n-butyl methacrylate), C_{60} was able to hinder prominently the thermal degradation of nanocomposites [**5**]. This effect has been associated to the ability of fullerenes to scavenge the macroradicals formed during polymer degradation.

Similar action has been also demonstrated in the case of PMMA containing C60 by Troitskii et al. [**6**]. Authors attributed the enhancement of the thermo-oxidative degradation of PMMA at elevated temperatures to the interaction of C60 with free radicals (R) and oxygen-containing radicals and consequently the formation of less reactive compounds.

Fernandes et al. [**7**] investigated the impacts of two different fullerenes (C_{60} and the derivative phenyl-C61-butyric acid ethyl ester derivative (PCBM)) on the thermal stability of polystyrene (PS). Results evidenced that under air, PCBM shows a higher thermal stabilization effect than C_{60} for identical fullerene content. The superior effect of PCBM in PS has been assigned to their improved dispersion state in the nanocomposite.

Liu et al. [**8**] have studied the flame-retardant effect of C_{60} in high-density polyethylene (HDPE)/ ethylene-co-vinyl acetate copolymer (EVA) blend. The incorporation of C_{60} induced a significant reduction of the peak of heat release rate (pHRR) and higher resistance to ignition during cone calorimeter test. The effect of the incorporation of C_{60} on the thermal stability and flammability (evaluated by Pyrolysis Combustion Flow Calorimeter (PCFC) test) of EVA containing C_{60} in combination with calcium hydroxide, obtained from chicken eggshell (Ceg-$Ca(OH)_2$), has been studied by Omri et al. [**9**]. The addition of low amounts of C_{60} to Ceg-$Ca(OH)_2$ induced significant enhancement of the composite thermal stability that was also evidenced by the increases of the temperature of pHRR. This positive effect was attributed to the interaction between Ceg-$Ca(OH)_2$ and C_{60} nanoparticles that promotes the formation of some C60-Calcium based derivatives.

Poly(3-hydroxybutyrate- co-3-hydroxyvalerate) (PHBV) is one of the commercially available polyhydroxyalkanoates (PHAs) [**10-11**], and have attracted much attention as biodegradable thermoplastic with potential application in different fields. However, PHBV is well known to be stiff and brittle with poor mechanical properties [**12**]. Several efforts have been described to improve the mechanical properties of PHBV, including the addition of plasticizers [**13, 14**] or with other polymers [**15, 16, 17**]. Blending PHBV with EVA was investigated as a good way for developing ductile materials [**18**].

In the light of above discussions and evidences, this work focus on the evaluation of the interest of combining PHBV and EVA in the presence of C60 in order to develop bio-based material presenting improved properties. The thermal properties of these blends were evaluated by different techniques, (i) oxidative induction time by differential scanning calorimetry (DSC), (ii) thermal stability by thermogravimetric analysis (TG, and (iii) flammability by using PCFC.

2. Experimental

2.1. Materials

Ethylene-co-vinyl acetate (EVA) copolymer (Escorene TM Ultra, MFI=0.25g/10min and vinyl acetate=14 wt.%) was purchased from ExonMobil. Poly-3-Hydroxy Butyrate-co-Valerate (PHBV) with 1.05 mol% 3-hydroxyvalerate (3HV) (M_n=1.16*10^4 g.mol^{-1}, PDI=2.30) was supplied by Tianan Biologic Material Co., Ltd. (Ningbo, China). [60]-Fullerene (>99.9% purity, M_w=720.64 g.mol^{-1}) was provided by Henan Puyang Co., China. Toluene and chloroform were purchased from Sigma Aldrich and were used as received.

2.2. Blends preparation

EVA/PHBV/C_{60} nanocomposites were prepared by solvent casting process. EVA/PHBV blends (mass ratio: 50/50 wt.%/ wt.%) and Fullerene (C_{60}) nanoparticles (0.3%, 0.5% and 0.7 wt.%) were added to toluene under mechanical stirring and heated at 120 °C under reflux for 60 minutes. Then, toluene was evaporated under a hood and the obtained materials were dried in an oven at 60 °C overnight. The information of sample compositions are summarized in Table 1.

Table 1 : Name and composition of the samples prepared in this study.

Sample code	EVA (wt.%)	PHBV (wt.%)	C_{60} (wt.%)
EVA/PHBV	50	50	-
EVA/PHBV/C_{60} (0.3 wt.%)	49.85	49.85	0.3
EVA/PHBV/C_{60} (0.5 wt.%)	49.75	49.75	0.5
EVA/PHBV/C_{60} (0.7 wt.%)	49.65	49.65	0.7

2.3. Measurements

Thermogravimetric analysis (TGA) was used to evaluate the thermal stability of EVA/PHBH blends as well as the effect of the incorporation of C_{60} nanoparticles. Analyses were carried out using TGA apparatus from Metler Toledo. Approximately 5 mg of the sample was submitted to a temperature ramp from 100 °C to 700 °C at a heating rate of 20 °C/min under a flow gas of 60 ml/min nitrogen (alumina pan).

Oxidation Induction Time (OIT) measurements were performed on a DSC 131 from Setaram according to the ISO 11357-6:2013. Samples of approximatively 5 mg were heated from 30 °C to 200 °C at 20 °C/min and kept at that temperature for 3 minutes under nitrogen (50 ml/min). After that, the nitrogen atmosphere was replaced by air (50 mL/min) and maintained at this temperature for a maximum duration of 2 h. The OIT corresponds to the time between the passage under oxidizing atmosphere and the onset of the exothermic peak (Fig. 1). Each sample was analyzed at least three times.

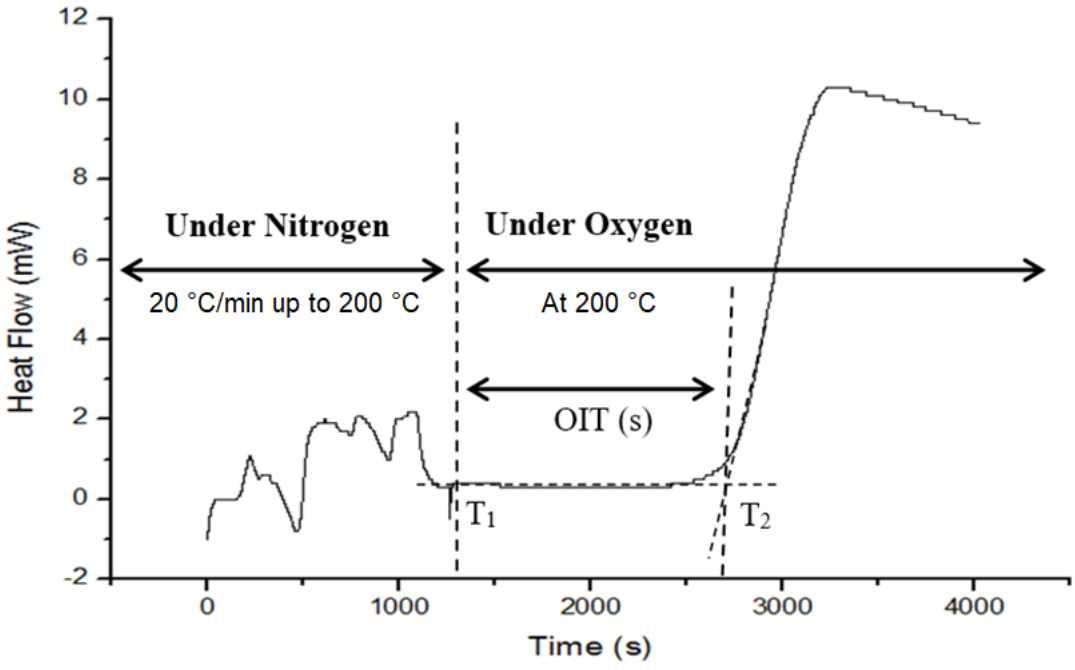

Fig. 1: Schematic diagram for the determination of OIT as the time period between T_1 and T_2.

The flammability of the different compositions was studied using a Pyrolysis Combustion Flow Calorimeter (PCFC) from Fire Testing Technology (FTT). 2-3 mg samples were heated to 750 °C at a heating rate of 1 K/sec in a stream of nitrogen. The combustor temperature was fixed at 900 °C, and the oxygen/nitrogen ratio was 20/80.

3. Results and discussion

3.1. Oxidation Induction Time

Polymer thermal oxidation is a well-known phenomenon that can induce dramatic changes of material chemical structure when exposed to heat and oxygen over time. These changes induce a dramatic effect on the material properties and their service life.

C_{60} nanoparticles were incorporated into EVA/PHBV blends in order to take advantage of their ability to delay polymers thermal oxidation and increase their thermal stability [**3**].

The Oxidation Induction Time (OIT) measurement by DSC analysis is a well-known method allowing an estimation of the oxidative stability of material. The procedure used for OIT measurements is schematically sketched in Fig. 1. OIT is defined as the time between the passage under oxidizing atmosphere and the onset of the exothermic peak,

As the OIT value increases, the the oxidative stability of material increases. Figure 2 shows the curves obtained from OIT test of unfilled EVA/PHBV and EVA/PHBV/C_{60} nanocomposites. Results are summarized in table 2 and evidenced the higher resistance to oxidation of nanocomposites in respect to unfilled blends. OIT increase from 1430 s for EVA/PHBV blend up to 4075 s for EVA/PHBV/0.7 wt.% nanocomposite. It is worth to mention that increasing the amount of C_{60} enables increasing OIT value. From these results, it is clearly shown that the incorporation of very small amount of C_{60} delay the thermo-oxidative degradation of EVA/PHBV blends.

The significant effect of C_{60} on the oxidative stability of EVA/PHBV blends is due to its specific structure and electronic properties which gives them the ability to act as effective free radicals scavenger [19-21]. The inhibiting effect of C_{60} could be thus explained by their interaction with oxygen containing radicals leading to the formation of more stable derivatives. C_{60} nanoparticles can also react with the free radicals formed during the oxidation and therefore protect the nanocomposites from decomposition and degradation.

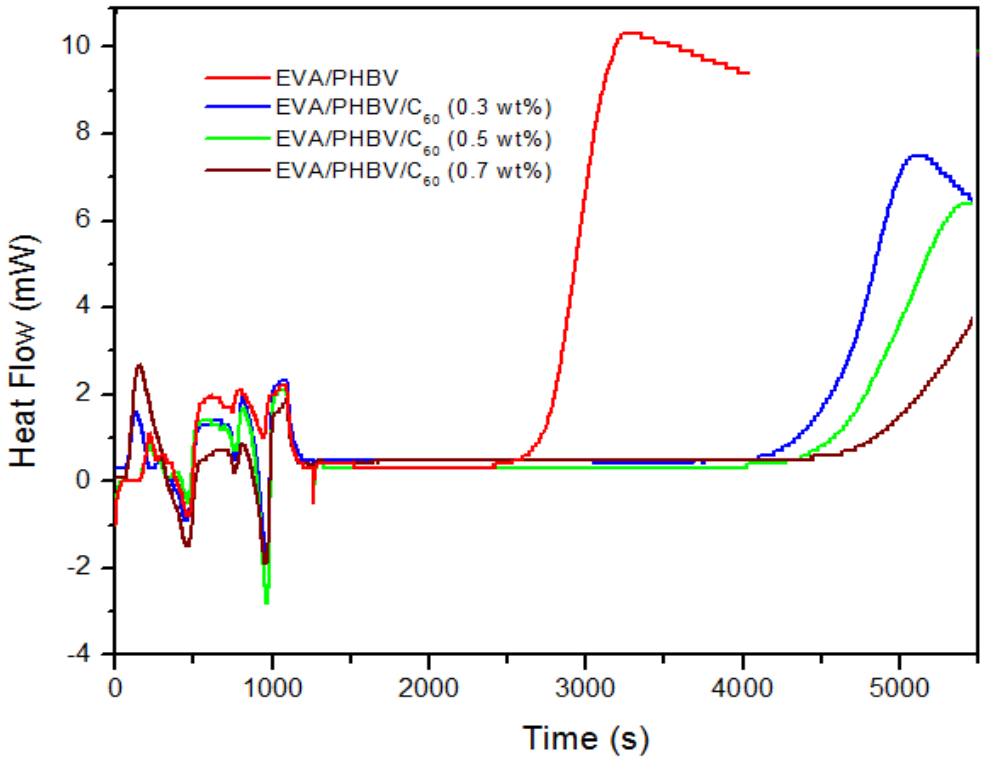

Fig. 2. Time-dependent heat flux curves obtained from OIT tests performed on the different EVA/PHBV blends.

Samples	T_2 (s)	OIT* (s)
EVA/PHBV	2714	1428
EVA/PHBV/C_{60} (0.3 wt.%)	4357	3070
EVA/PHBV/C_{60} (0.5 wt.%)	4643	3357
EVA/PHBV/C_{60} (0.7 wt.%)	5360	4075

Table 2: Results of the oxidation induction time, performed for EVA/PHBV and EVA/PHBV/C_{60} nanocomposites with different C_{60} amounts (*OIT (s)=T_2-T_1)

3.2. Thermal degradation

Thermal degradation and stability of all samples were evaluated using TGA analysis under nitrogen. First, the thermal stability of unfilled blend was evaluated in comparison with the pristine polymers (EVA and PHBV). Figure 3 indicates that PHBV and EVA present different thermal degradation trend. PHBV degrades in one step while EVA undergoes a two steps thermal degradation. The first step corresponds to EVA deacetylation and to the formation of C=C double bonds. This step is followed by a plateau and by the second decomposition step that corresponds to the scission of the polymeric chain. Moreover, Figure 3 shows that EVA demonstrated higher thermal stability than PHBV since its thermal degradation starts at higher

temperatures. Temperature of 10% weight loss ($T_{-10\%}$) of EVA is about 385°C while it is only 287 °C for PHBV. It could be thus expected that the incorporation of EVA within PHBV induces some improvement of the blend thermal stability or at least to the formation of a blend presenting similar thermal stability than PHBV. However, TGA curves evidence unexpected behavior since the thermal stability of the blend is lower to that of pristine polymers, i.e. (T-10% = 255 °C for EVA/PHBV blend in comparison with 287 °C and 385 °C obtained for PHBV and EVA, respectively). The presence of EVA induces a premature thermal degradation of PHBV. This effect could be attributed to acetic acid groups that are known to be generated during the first step of EVA thermal decomposition and that are able to induce PHBV degradation by transesterification.

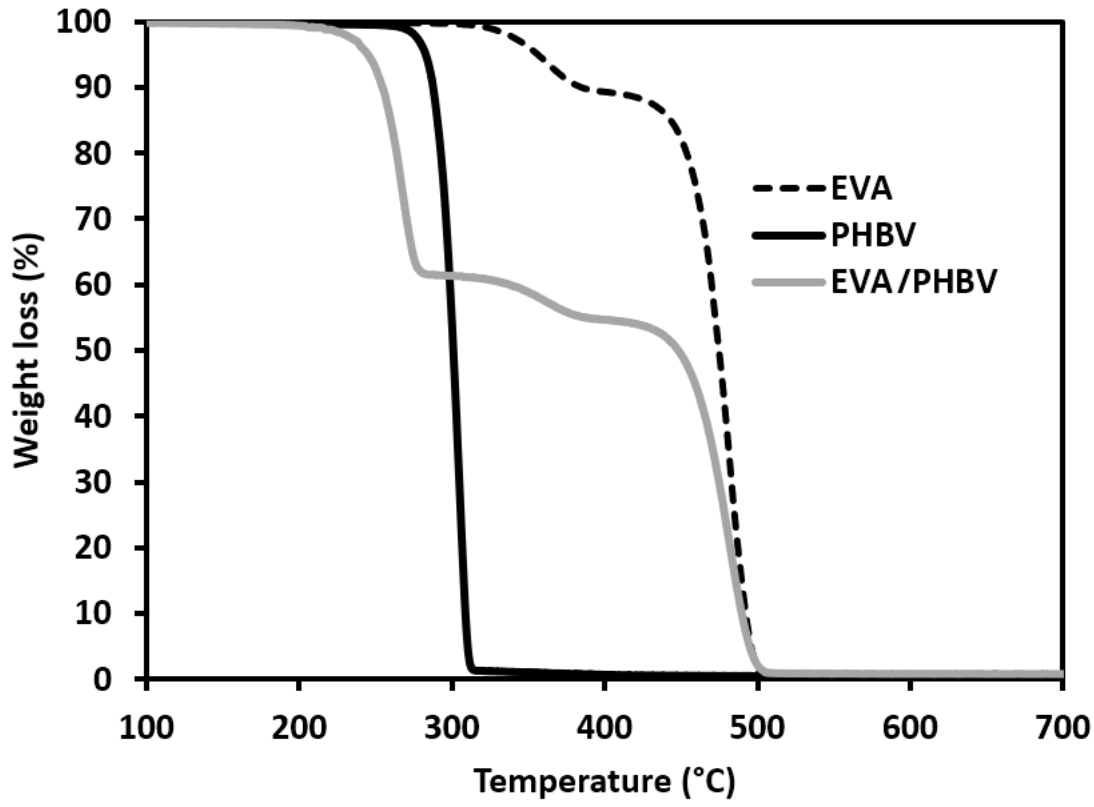

Figure 3: TGA curves of EVA, PHBV and EVA/PHBV under nitrogen (20 °C/min).

Table 2: Thermal decomposition data for EVA, PHBV, EVA/PHBV blends and nanocomposites under nitrogen atmosphere (20 °C/min).

	$T_{-10\%}$	T_{max}	
EVA	385	480	
PHBV	287	300	
EVA/PHBV	255	265	480
EVA/PHBV/C_{60} (0.3% wt.%)	280	290	484
EVA/PHBV/C_{60} (0.5% wt.%)	280	290	484
EVA/PHBV/C_{60} (0.7% wt.%)	290	296	486

The incorporation of C_{60} nanoparticles induces an interesting behavior on EVA/PHBV blends thermal stability. TGA curves of EVA/PHBV and EVA/PHBV/C_{60} nanocomposites (0.3, 0.5 and 0.7 wt.%) (Figure 4) evidence that the presence of C_{60} nanoparticles enables for stopping the premature thermal degradation of PHBV. TGA curves of EVA/PHBV blends containing C_{60} nanoparticles, whatever their content, start to degrade at the same temperature than pristine PHBV. This result demonstrates the ability of C_{60} nanoparticles to scavenge free acetic acid groups and avoid thus their reaction with PHBV. Increasing C_{60} content induces an increase of the amount of the material generated after the first decomposition step. This result suggests that a part of acetic acid and PHBV remains in the material without complete degradation.

The protective effect of C_{60} nanoparticles is not active only against oxidation but is effective also at higher temperature by preventing PHBV thermal degradation induced by free acetic acid groups.

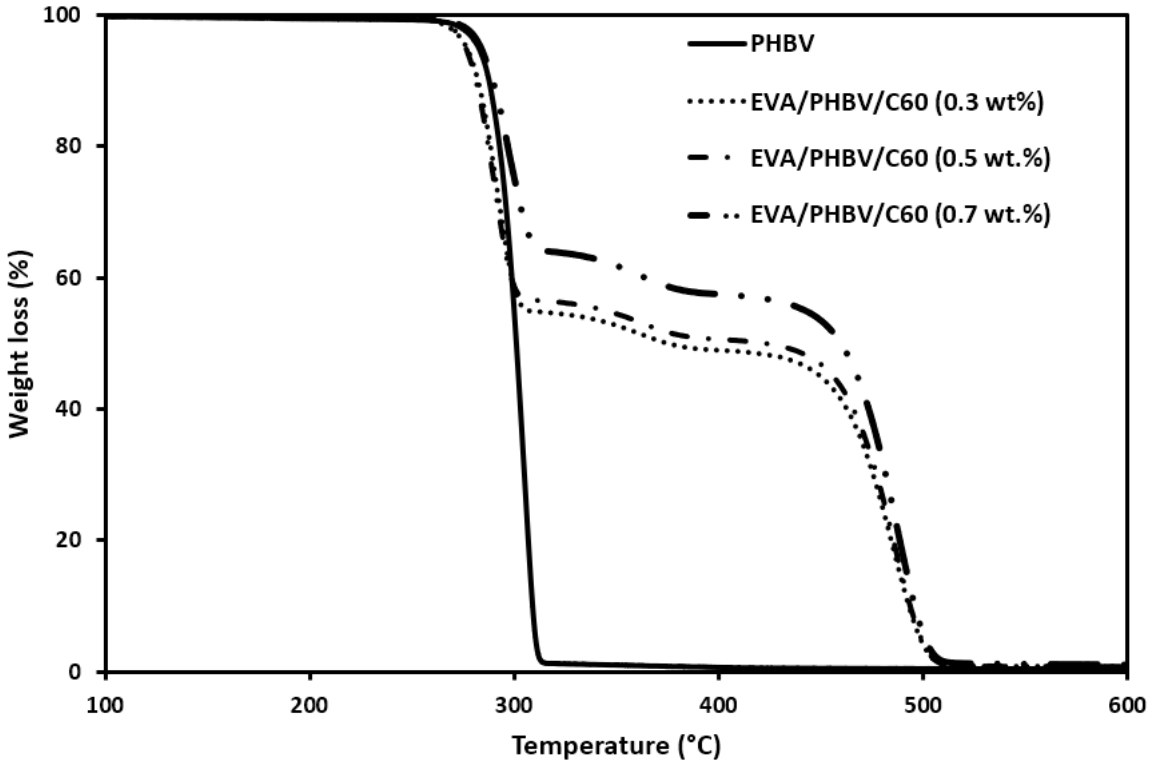

Figure 4: Effect of the incorporation of C_{60} nanoparticles on the thermal stability of EVA / PHBV (50/50 wt./wt.) during TGA analysis under nitrogen (20 °C/min).

3.3. Flammability

Pyrolysis combustion flow calorimeter analysis (PCFC) is a well-known apparatus for measurement of some important flammability parameters of polymers through non-flaming combustion [19]. Small sample (3 milligrams) is pyrolyzed following a heating ramp of 1 K/s up to 750°C under nitrogen. The gases released during this first step are evacuated into an oven at 900°C in the presence of an 80/20 N_2/O_2 mixture. These conditions allow a complete combustion of these gases and very good reproducibility of the data (generally less than 5% of deviation between two analyses for pHRR is obtained).

Figure 5 presents HRR curves of EVA, PHBV and their blend. Detailed data are summarized in table 5. These results show that both PHBV and EVA present single HRR peak but at different temperatures. The peak corresponding to the inflammation of the pyrolysis products of the PHBV occurs at 312°C while the one related to EVA takes place at 475 °C. It is important to mention that the first decomposition step, evidenced by TGA experiment and corresponding to the release of acetic acid present a very week peak at about 350 °C. Moreover, we can also observe that the total heat release during the combustion of gases released during PHBV pyrolysis (24 kJ/g) is lower to that obtained with EVA (39 kJ/g).

Blending PHBV and EVA induce significant reduction of the HRR peak corresponding to the flammability of products generated during PHBV degradation. In fact, time of PHRR decreases from 312 °C when PHBV is tested alone to 280 °C when blended with EVA. These results are in good agreement with those obtained during TGA analysis.

However, this degradant effect of PHBV induced by EVA affects only the temperature of pHRR but not the nature of degradation product since the total heat release of the blend is equal to the theoretical one (THR_{PHBV} +THR_{EVA})/2).

The incorporation of small amounts of C_{60} induced a significant variation on the pHRR temperature of the nanocomposites (Figure 6 and table 5). Thus, the first peak of HRR, that was registered at 272 °C for EVA/PHBV sample, was shifted to higher temperature (300 °C) when very small amount of C_{60} is incorporated. This result confirms the trend highlighted by TGA analysis and confirm the stabilizing effect of C_{60} that stop the degradant effect of acetic acid groups. However, the incorporation of C_{60} (0.3, 0.5 and 0.7 wt.%) did not reduce the peak of heat release rate (pHRR) of EVA/PHBV nanocomposites compared to that of EVA/PHBV sample. In fact, both first and second pHRR peaks of nanocomposite containing 0.7 wt.% (289 and 538 W/g) are very similar to those obtained with unfilled EVA/PHBV blend (283 and 552 W/g). THR values were thus approximately remained unchanged around 31 kJ/g whatever the composition of the EVA/PHBV blend.

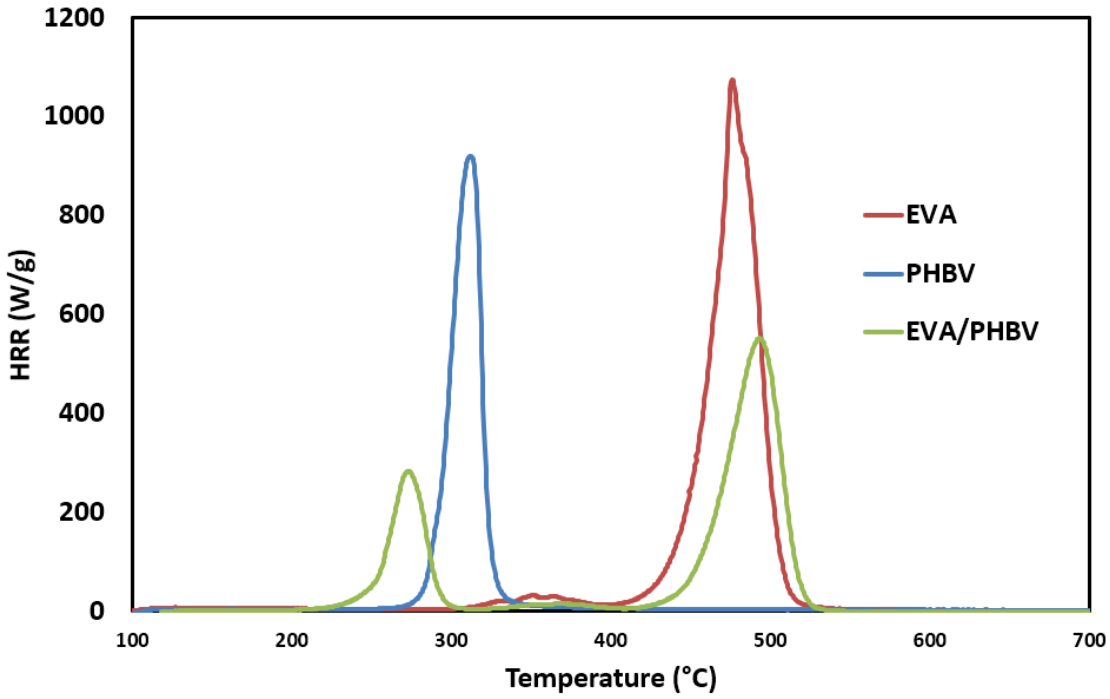

Figure 5: Heat Release Rate curves of EVA, BHBV and EVA/PHBV blend obtained in PCFC test.

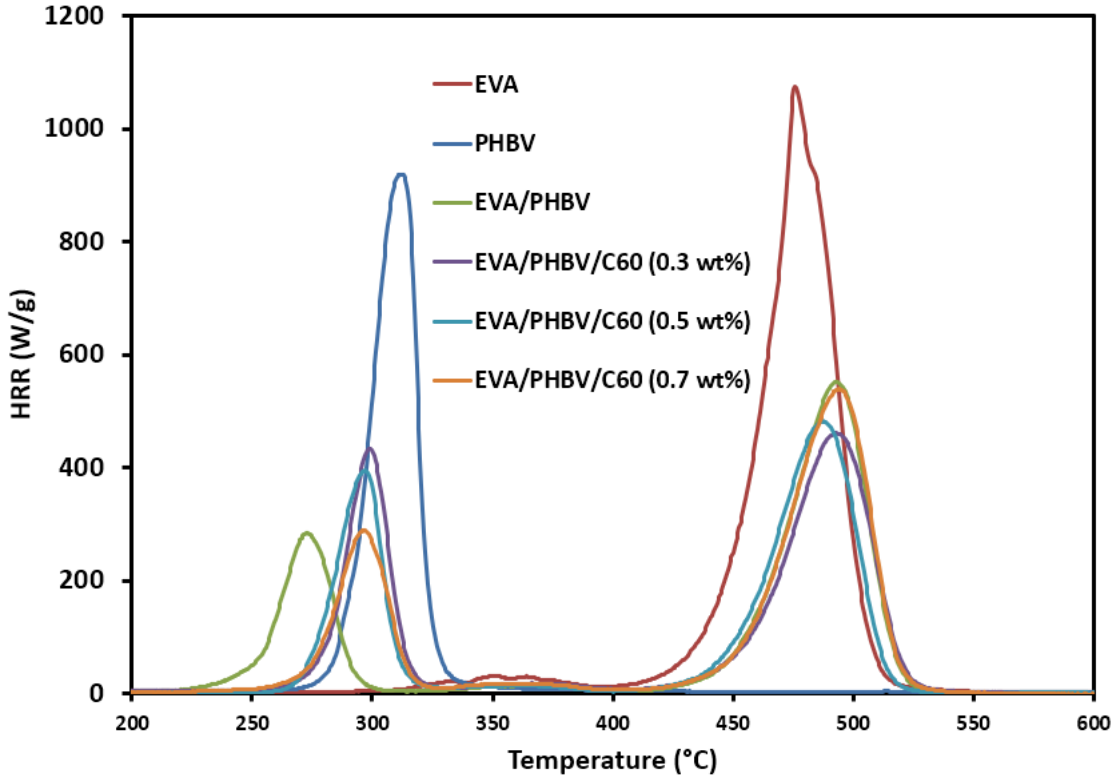

Figure 6: Heat Release Rate curves of EVA, BHBV, EVA/PHBV, and EVA/PHBV/C_{60} nanocomposites, obtained in PCFC test.

Table 5: PCFC data of EVA, BHBV, EVA/PHBV, and EVA/PHBV/C_{60} nanocomposites.

Sample code	$pHRR_1$ (W/g)	$*T_{pHRR1}$ (°C)	$pHRR_2$ (W/g)	$**T_{pHRR2}$ (°C)	THR (kJ/g)
EVA	-	-	1074-	475	39
PHBV	914	312	-	-	24
EVA/PHBV	283	272	552	493	31
EVA/PHBV/C_{60} (0.3 wt.%)	435	299	461	492	30
EVA/PHBV/C_{60} (0.5 wt.%)	395	297	482	488	31
EVA/PHBV/C_{60} (0.7 wt.%)	289	296	538	493	32

* TpHRR1: Temperature of 1st peak of heat release rate
** TpHRR1: Temperature of 2nd peak of heat release rate

4. Conclusion

In the present study, the effect of the incorporation of small amounts of C_{60} nanoparticles on thermal oxidation, thermogravimetric stability and flammability of EVA/PHBV blend was investigated. Then addition of small amount of C_{60} nanoparticles (0.3, 0.5 and 0.7 wt.%) to the blend enable

Results of the Oxidation Induction Time (OIT) measurement performed by DSC analysis highlighted the improvement of the resistance to oxidation of nanocomposites in respect to

unfilled blends. The presence of C_{60} nanoparticles enables an important increase of OIT from 1430 s for EVA/PHBV blend up to 4075 s for EVA/PHBV blend containing only 0.7 wt.% C_{60} nanoparticles.

This stabilizing effect of C_{60} nanoparticles has been also evidenced during TGA analysis. In fact, the incorporation of C60 nanoparticles enables stopping the premature thermal degradation of PHBV that occurs in the presence of EVA. This effect was also evidenced during PCFC analysis. C_{60} nanoparticles have thus demonstrated their effectiveness for improving EVA/PHBV resistance to oxidation, limiting PHBV premature degradation during TGA and PCFC analysis owing to their specific structure and electronic properties which give them the ability to act as effective free radicals scavenger and the formation of more stable derivatives.

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Conflict of interest statement

Authors declare that this work has not been published previously and there are no conflicts of interest.

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