

Effect of dispersion of nano-magnesium hydroxide on the flammability of flame retardant ternary composites

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Abstract

A novel flame-retardant ternary composite of polymer/crosslinked rubber/nano-Magnesium hydroxide (MH), prepared by blending thermoplastic polymer with a special compound powder of crosslinked rubber/nano-MH, was introduced in this paper. The special compound powder of crosslinked rubber/nano-MH was prepared by co-spray drying the fluid mixture of nano-MH slurry and irradiated rubber latex. The cone testing results showed that the new flame-retardant ternary composite had better flame retardancy than the composite obtained by conventional process, such as longer “Time to ignition” and lower “mean heat release rate in initial time”. Thermogravimetry and transmission electron microscope were used to analyze the reason of different flame retardancy. It is found that more uniform dispersion of nano-MH in the new ternary composite than in conventional one maybe the main reason for better flame retardancy.

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Keywords: Co-spray drying; Dispersion; Flame retardancy; Nano-magnesium hydroxide; Ternary composite

1. Introduction

Recently, more and more environmental legislations have limited or prohibited the application of halogen-containing flame retardants on polymer materials. Hydrated fillers like aluminum trihydroxide (ATH) and magnesium hydroxide (MH) have been of increasing interest as flame retardants for polymers. As a halogen-free flame retardant, MH has attracted people’s attention because of its smoke suppression property, flame retardancy and good thermal stability which allows higher processing temperature than ATH [1–3]. However, hydrated fillers are relatively less effective. They require addition level of up to 60 wt% in order to achieve acceptable combustion resistance [3]. Such high addition will in turn lead to deteriorated toughness of plastics [3,4]. In order to minimize the negative effect of

MH, elastomer has been used as a third phase [4–6]. The elastomer can improve the toughness of the hydrated filler contained polymer, but can not effectively improve the dispersion of hydrated fillers. Therefore, surface treatment on hydrated fillers is necessary but usually resulted in worse thermal stability than untreated one [7].

In our previous work, we prepared several kinds of ultra-fine full-vulcanized powdered rubbers (UFPRs), or called elastomeric nanoparticles (ENPs) by spray-drying irradiated rubber lattices including styrene-butadiene, carboxyl styrene-butadiene, acrylonitrile butadiene (NB), carboxyl acrylonitrile butadiene (CNB), and butadiene styrene vinyl-pyridine latex, etc. Those UFPRs or ENPs were reported to have a tendency to disperse uniformly in related polymer matrix because of their special structure [8–17]. In this paper, UFPRs have been used as not only a toughener, but an additive to help hydrated fillers disperse in polymer matrix. With the help of UFPRs, nano-MH without surface treatment can disperse very well in

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polymer matrix. Meanwhile, nano-MH in return, also has the function of helping elastomer to disperse in the matrix. The novel polymer/UFPR/nano-MH ternary composites obtained by our new process have better flame retardancy than conventional ones.

2. Experimental part

2.1. Materials and preparation of ternary nanocomposites

The nano-MH particles, supplied by Yixing Reagent Chemical Factory, are of an average thickness of 20 nm and length of 90 nm. Rubber latices used in this study are acrylonitrile butadiene latex (Chemigum Latex 248, Elikem), with average micelle size of 200 nm; and carboxyl acrylonitrile butadiene latex (CNPC Lanzhou Chemical Group), with average micelle size of 90 nm. Polyamide 6 (PA 6, Ultramid B4, BASF) has number average molar mass (M_n) of 33,000, while poly (ethylene-co-vinyl acetate), (EVA, Levamelt 500, Bayer) has vinyl acetate content of 50%.

“The new process” of preparing ternary composites comprises two steps (Fig. 1): the preparation of compound powder (CP) by co-spray drying method and melt blending process to make ternary composites. The methodology of preparing CP was similar to that of making UFPRs or ENPs [12]. Firstly, a certain amount of crosslinking sensitive (3% for NB latex and 5% for CNB latex) was added into the UFPR latex and stirred for 1 h, then kept for more than 10 h under room temperature. The latex was then irradiated by gamma rays from a ^{60}Co source for a certain absorbed dose (10kGy for CNB latex and 15kGy for NB latex). Secondly, nano-MH was dispersed into water by an emulsifier for an hour to obtain a MH slurry. The

nano-MH slurry was then mixed with the crosslinked rubber latex and stirred for half an hour, an even mixture of UFPR and nano-MH in water was obtained. Finally, the above fluid mixture was Spray-dried under inlet temperature of around 180 °C and outlet temperature of around 70 °C to get the CP of UFPR and nano-MH. In this article, two kinds of CP (CP_A and CP_B) were prepared for fabricating polyamide 6 composites and EVA composites respectively. CP_A refers to the compound powder of carboxyl acrylonitrile butadiene-UFPR (CNB-UFPR)/nano-MH and CP_B refers to the compound powder of acrylonitrile butadiene-UFPR (NB-UFPR)/nano-MH.

The materials used for making polyamide 6 composites were dried at 100 °C (polyamide 6, nano-MH) or 60 °C (CNB-UFPR, CP_A) for 5 hours. Melt compounding procedure was carried out in a Haake Rheomix inner-mixer. The mixer was set at 230 °C for preparing polyamide 6 composites or at 160 °C for EVA composites. Polyamide 6 or EVA was added into the mixer while the rotors were spinning at 20 rpm. After the matrix melted, CPs was then fed into the mixer. Increase the rotor speed to 60 rpm and keep on mixing for 10 minutes, ternary composites of PA/ CP_A or EVA/ CP_B were finally obtained. In order to make comparison, we also prepared PA/CNB-UFPR/nano-MH composite and EVA/NB-UFPR/nano-MH composite at the same conditions and the same formulations by just simply putting three components into the mixer, which was called “conventional process”.

Table 1 listed the compositions of three polyamide 6 composites for this paper. PA 6/ CP_A nanocomposites was fabricated by our new process (A1) and PA 6/CNB-UFPR/nano-MH composites by conventional process (A2) with the same formulation (PA6/NB-UFPR/nano-MH = 90/40/60). A1 and A2 have the same formulation

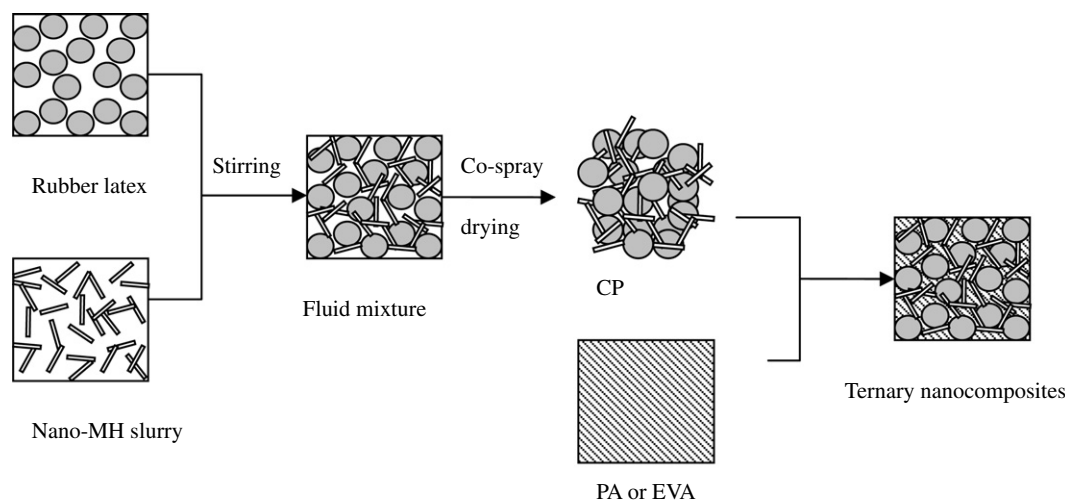


Fig. 1. Schematic illustration for the preparation of polyamide 6/ CP_A and EVA/ CP_B nanocomposites: CP_A , CNB-UFPR/nano-MH = 40/60, wt, CP_B , NB-UFPR/nano-MH = 40/60, wt.

Table 1
Compositions of polyamide 6 composites

Sample code	Formulations (wt)	CP ratio (wt)	Process
A0	PA6/CNBR = 90/40	–	–
A1	PA6/CP _A = 90/100	CNBR/nano-MH = 40/60	Our new process
A2	PA6/CNBR/nano-MH = 90/40/60	–	Conventional process

of three components: polyamide 6, CNB-UFPR and nano-MH. The only difference is that A1 was obtained by our new process while A2 by conventional one.

2.2. Cone calorimeter testing

The Cone Calorimeter (Fire Test Technology) was used to test the materials' fire performance under an external heat flux of 35 kW/m² according to ISO5660. The composites under testing were compression molded into plates of 100 × 100 × 4 mm³ for the test. Heat release rate (HRR), time to ignition (TTI), and other parameters were recorded simultaneously. TTI is the period required for the entire surface of the sample to burn with a sustained luminous flame. As for HRR, just using the peak value may mislead us for evaluating the flame retardancy of a material. Therefore, we use mean HRRs here, the average values of the heat release rate for the different periods from ignition to 300 s. The mean HRRs are usually thought to much more correlate with the heat release in a room burn condition where not all material are ignited at the same time [18,19].

2.3. Thermogravimetric analysis (TGA)

TGA was carried out at a heating rate of 10 °C/min under nitrogen flow of 50 ml/min by a thermogravimetric analyzer TGA 7 (Perkin Elmer, US).

2.4. Morphology observation

Direct observation on the dispersion of magnesium hydroxide filler was undertaken using a transmission electron microscope (TEM, Philips Tecnai 20, Netherland) on ultra-thin slices of about 50–100 nm thick. The slices were microtomed at –50 °C and then stained with osmium tetroxide (OsO₄).

3. Result and discussion

3.1. Flame retardancy

TTI data of the above samples from cone calorimetry test were shown in Fig. 2. The none-filled samples A0 needed 108 s to ignite and both filled sample markedly postponed the ignition time. The result was in accordance with others [2–4,20] regarding the MH function of prolonging the materials' ignition time. However, the two nano-MH filled samples were different; A1 requires much longer ignition time than A2 (22 s longer).

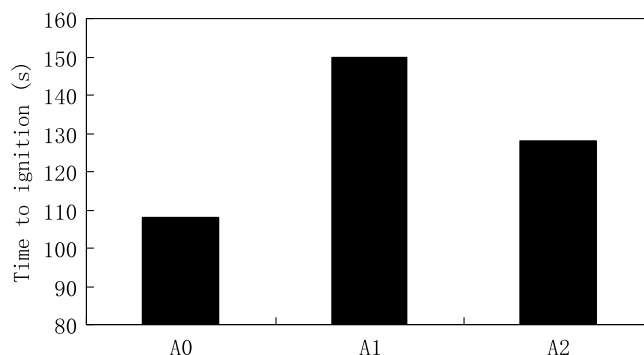


Fig. 2. TTI(s) of polyamide 6 composites under heat flux of 35 kW/m²: A0 (PA/CNB-UFPR, 90/40, wt), A1 [PA/CP_A, 90/100, wt, (CP_A, CNB-UFPR/nano-MH, 40/60, wt)], A2 (PA/CNB-UFPR/nano-MH, 90/40/60, wt).

Mean HRRs (within 5 min after ignition) of the three samples were given in Fig. 3. It is obvious that mean HRRs of A1 and A2 after ignition were far lower than those of A0 in the beginning 300 s. Furthermore, the mean HRR of A1 was 28 kW/m² lower than that of A2 for the starting 60 s, and 19 kW/m² lower for the starting 120 s after ignition. Although the mean HRRs for longer periods after ignition were similar for the two ternary composites, it is a common understanding that the decreasing of average HRRs at the beginning several minutes are much more important than those afterwards. Therefore, A1 exhibits better flame retardancy than A2 in terms of mean HRRs in the initial period. It is important for us to know why the two ternary composites with the same formulation perform differently on flame retardancy.

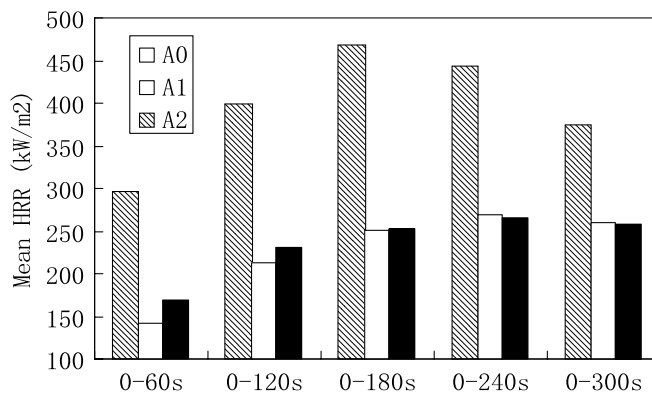
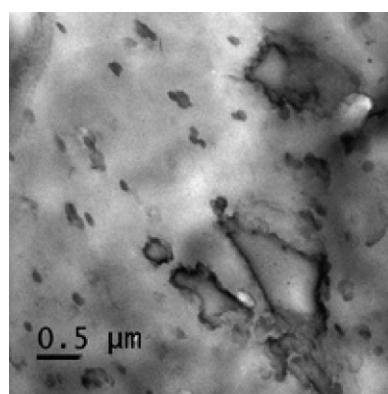


Fig. 3. Mean HRRs in different periods after ignition of polyamide 6 composites: A0 (PA/CNB-UFPR, 90/40, wt), A1 [PA/CP_A, 90/100, wt, (CP_A, CNB-UFPR/nano-MH, 40/60, wt)], A2 (PA/CNB-UFPR/nano-MH, 90/40/60, wt).

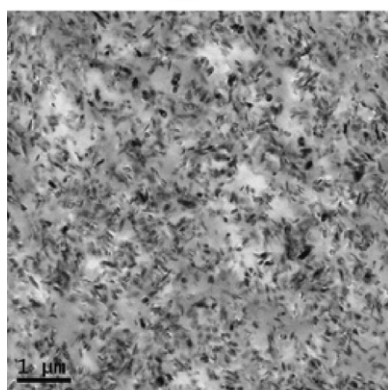
3.2. Morphology observation

In order to find out the reason that A1 (PA/CP_A) and A2 (PA/CNB-UFPR/nano-MH) performed differently on flame retardancy, TEM was used to observe the dispersion of nano-sized MH particles in the above two ternary composites.

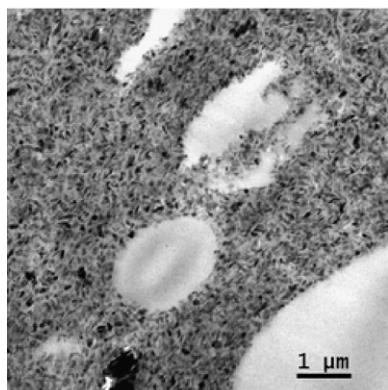
Fig. 4 showed the TEM images of binary composite A0 and ternary composites A1 and A2. Nano-MH particles can be observed as small dark platelet and UFPR particles



A0



A1



A2

Fig. 4. TEM image of polyamide 6 binary composite A0 and ternary composites A1 and A2: A0 (PA/CNB-UFPR, 90/40, wt), A1 [PA/CP_A, 90/100, wt, (CP_A, CNB-UFPR/nano-MH, 40/60, wt)], A2 (PA/CNB-UFPR/nano-MH, 90/40/60, wt).

are gray spheres. From Fig. 4, the binary composite of polyamide and CNB-UFPRs did not get a satisfying dispersion, nor did the ternary composites by conventional process. The rubber domains in A2 have a wide distribution in size, with diameters of 0.5–10 μm, while the UFPR particles were dispersed at a much smaller size and narrower distribution in A1. Besides, well-dispersed nano-MH fillers can be observed both in and outside the rubber domains of A1. On the contrary, serious agglomerations were found for both nano-MH particles and UFPRs in A2, and no nano-MH particles were observed inside the rubber domains of A2. It is obvious that nano-MH and CNB-UFPR particles were dispersed more evenly in A1 than in A2. As matter of fact, UFPRs and nano-MH were dispersed well in the fluid mixture of rubber latex and nano-MH slurry. The complex powder can maintain the structure after co-spry drying as shown in Fig. 1. During the process of melt blending, the separated nano-MH platelets are hard to aggregate due to the separating effect of UFPR particles; in the meantime, the separated UFPR particles are also difficult to coalescent due to the barrier effect of MH platelets. Therefore, the nano-MH fillers and UFPR particles can help each other to better disperse in polyamide 6 matrix by the new process.

It is believed that better dispersion of nano-MH in A1 is the main reason that A1 exhibit better flame retardancy than A2. The combustion of polymers arises from their thermal degradation at a certain temperature and the release of highly flammable decomposition products [21]. The function of MH as a flame retardant filler is that its endothermic decomposition cools the condensed phase and the released water also cools and dilutes the flammable products in the vapour phase. The residue of Magnesium oxide crust after combustion can also protect the underlying polymer from the outside heat [1]. The nano-MH particles in the ternary composites of A1 (PA/CP_A) dispersed very well; therefore, the decomposition of nano-MH undergo evenly on the surface of the sample and the sample was also cooled evenly without locally overheated by the external heat flux. As to sample A2 (PA/CNB-UFPR/nano-MH), there exist some larger rubber domains, and no nano-MH platelets were dispersed in the domains. The temperatures should be higher near such domains than other zones. As a result, earlier ignition of A2 than A1 occurred at the same conditions. Besides, better dispersion of nano-MH platelets in the ternary composites ensured a more compact heat insulate layer on the sample's surface, which also prevented the released combustible gases or low molecular organic compounds from passing through. Even after the decomposition of MH, the inorganic residue of magnesium oxide (MgO) remained on the surface still maintained the compact structure which might also has the function of a thermal insulating barrier between the underlying polymer substrate and the external heat source. The residue pictures of the two samples after cone calorimetry test confirmed the above explanation (Fig. 5).

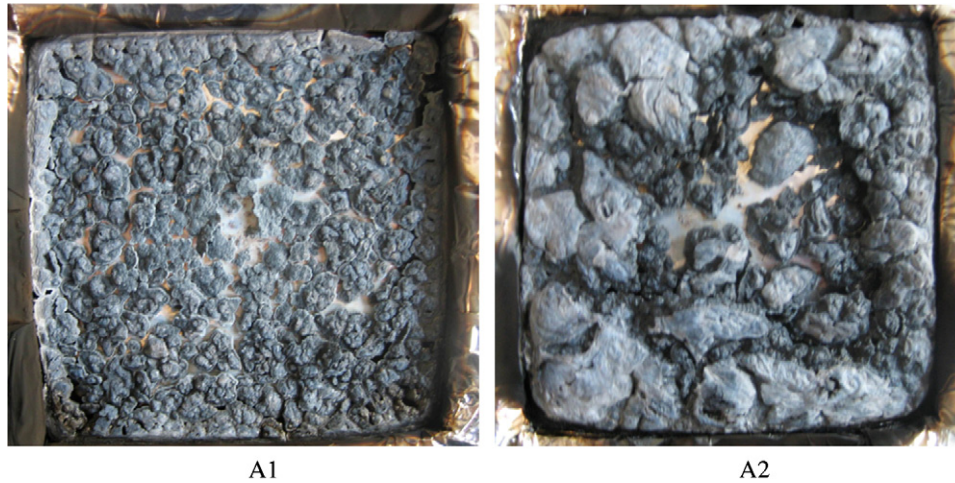


Fig. 5. The residues' picture of A1 and A2 after burning for cone calorimetry test: A1 [PA/CP_A, 90/100, wt, (CP_A, CNB-UFPR/nano-MH, 40/60, wt)], A2 (PA/CNB-UFPR/nano-MH, 90/40/60, wt).

3.3. Thermal stability

In order to further confirm the above explanation, we analyzed the thermal degradation performance of the two ternary composites. TGA curves and the mass changing rate curves of the above two ternary composites, A1 and A2 were shown in Fig. 6.

It can be found from the TGA results that the onset temperature of thermal degradation of A1 was about 10 °C higher than A2, from 362 °C of A2 to 371 °C of A1. The temperature of 20% mass lost of A1 is 10 °C higher than that A2, from 400 °C to 410 °C. From the curves of mass change rate versus temperature, it can be found that A2 reached the highest mass loss rate at 424 °C, while A1 at 453 °C, almost 30 °C higher. It is obvious that under the same external heat, the thermal degradation of ternary composite A1 obtained by the new process

was much later and slower than that of the conventional ternary composite A2. A1 had better resistance to ignition than A2 because less combustible gases were released from A1 than A2.

3.4. EVA/UFPR/nano-MH composites

In order to confirm the above conclusion that nano-MH's dispersion has influence on the flame retardancy of polymer composites, we also fabricated two ternary EVA composites: EVA/CP_B nanocomposites by our new process (B1) and EVA/NB-UFPR/nano-MH composites by conventional process (B2) with the same formulation (EVA/NB-UFPR/nano-MH = 60/40/60). TEM images of the two composites also indicated that both UFPRs and nano-MH particles were dispersed more uniformly in B1 than in B2 (Fig. 7).

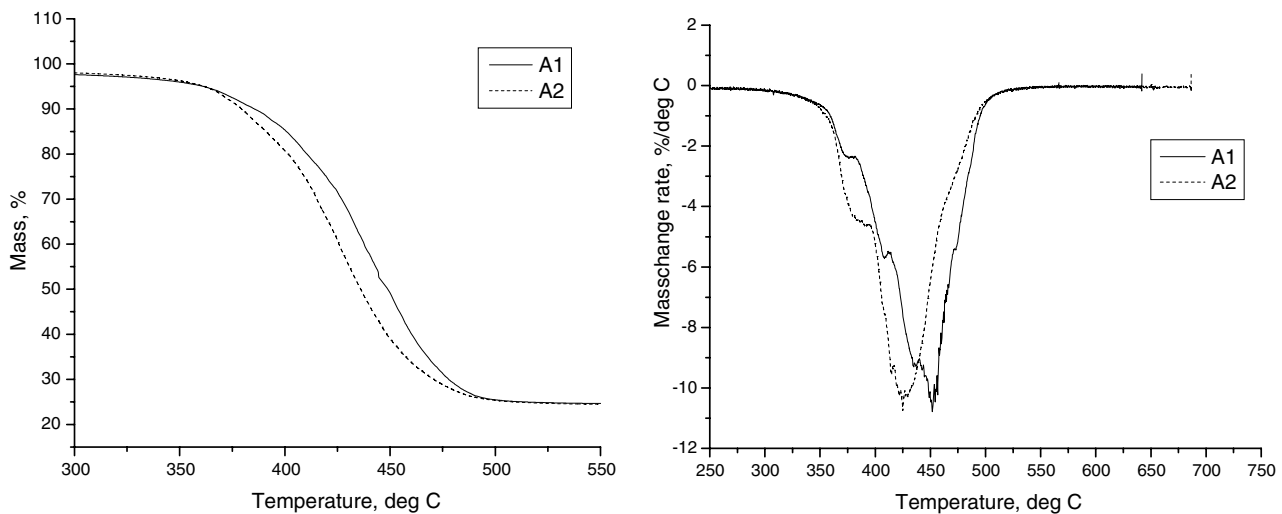


Fig. 6. TGA results of polyamide 6 composites A1 and A2: A1 [PA/CP_A, 90/100, wt, (CP_A, CNB-UFPR/nano-MH, 40/60, wt)], A2 (PA/CNB-UFPR/nano-MH, 90/40/60, wt).

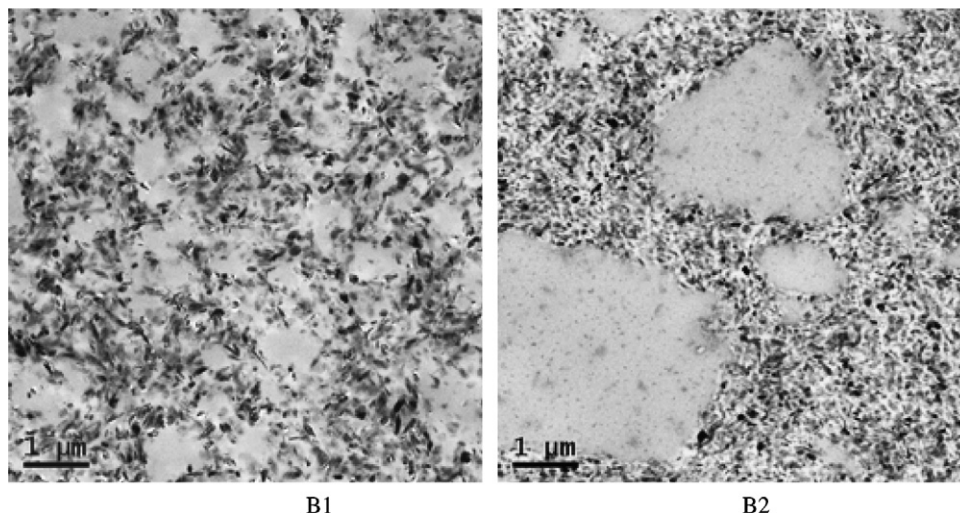


Fig. 7. TEM image of EVA ternary composites B1 and B2: B1 [EVA/CP_B, 60/100, wt, (CP_B, NB-UFPR/nano-MH, 40/60, wt)], B2 (EVA/NB-UFPR/nano-MH, 60/40/60, wt).

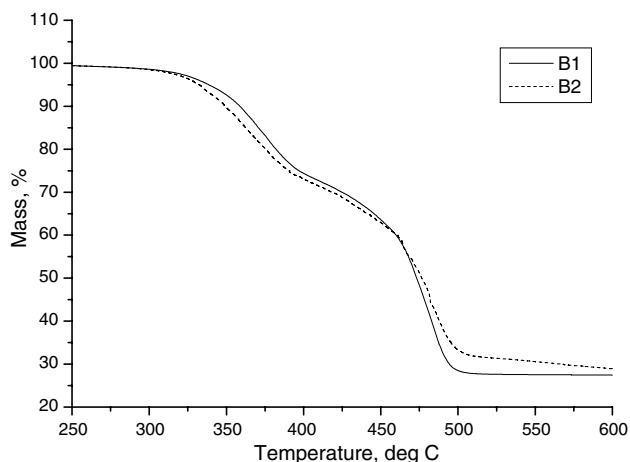


Fig. 8. TGA result of EVA composites B1 and B2: B1 [EVA/CP_B, 60/100, wt, (CP_B, NB-UFPR/nano-MH, 40/60, wt)], B2 (EVA/NB-UFPR/nano-MH, 60/40/60, wt).

The thermal degradation of EVA in nitrogen usually shows two distinct regions, which have been assigned to the loss of acetic acid and the degradation of the resulting unsaturated material, poly (ethylene-co-acetylene), respectively [22,23]. TGA results on the two ternary composites showed that the first stage of thermal degradation of B1 took place at a higher temperature than that of B2 (Fig. 8). The onset temperature of sample B1 (EVA/CP_B) was 329 °C while that of B2 (EVA/NB-UFPR/nano-MH) was 321 °C.

Cone calorimetry test also found a 33 s delay on ignition time for B1 (95 s) than B2 (62 s) under the external heat flux of 35 kW/m², prolonging for about 53%. The HRRs of composites EVA/CP_B are lower than that of composites EVA/NB-UFPR/nano-MH within the first 3 min after ignition (Table 2).

Obviously, the above results of EVA composites also indicated that better dispersion of nano-MH contribute to increasing the materials' thermal stability and flame retardancy.

Table 2
Mean HRRs in different periods after ignition of EVA composites

EVA composites	Average HRR, kW/m ²					
	0–60 s	0–120 s	0–180 s	0–240 s	0–300 s	0–360 s
B1	116	210	248	264	245	216
B2	136	221	261	277	250	217

B1: EVA/CP_B = 60/100, wt, (CP_B: NB-UFPR/nano-MH = 40/60, wt),
B2: EVA/NB-UFPR/nano-MH = 60/40/60, wt.

4. Conclusion

A novel flame retardant ternary nanocomposite of polymer/crosslinked rubber/nano-magnesium hydroxide can be fabricated by melt blending thermoplastic polymer with a compounding powder of UFPR/nano-MH that was prepared by co-spray drying the mixture of nano-MH slurry and irradiated rubber latex. The new ternary composite has better flame retardancy and thermal stability than the conventional one because nano-MH can disperse much more homogeneous in the new ternary composite than in the conventional one.

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