

MECHANICAL PROPERTIES AND FLAME RESISTANCE OF COMPOSITE BASED ON HIGH DENSITY POLYETHYLENE/ETHYLENE VINYL ACETATE BLEND AND NOVEL ORGANICALLY MODIFIED WASTE GYPSUM

Tran Huu Trung, Mai Duc Huynh, Do Van Cong, Nguyen Vu Giang*

Institute for Tropical Technology, VAST, 18 Hoang Quoc Viet, Cau Giay, Ha Noi

*Email: nvgiang@itt.vast.vn; yugiang.lit@gmail.com

Received: 30 July 2018; Accepted for publication: 9 September 2018

ABSTRACT

In this study, waste gypsum (WGS) was used as the filler in blend of high density polyethylene (HDPE) and ethylene vinyl acetate copolymer (EVA) in order to improve the flame resistance of this composite. After modification by ethylene bis stearamide (EBS), modified gypsum (EGS) at various contents was dispersed into HDPE/EVA (95/5 wt.%) blend by melt-mixing method to obtain EGS/HDPE/EVA composites. The IR analysis of the EGS showed the interaction between EBS and gypsum. The difference in morphology of HDPE/EVA/EGS and HDPE/EVA/OGS composites was also observed in SEM images. By adding EGS and amounts of flame retardant additives such as ammonia polyphosphate and zinc borate, the thermal stability and the flame resistance of HDPE/EVA/EGS composites have improved and classified at V2 grade of UL94 standard. Moreover, the second self extinguishing time (t_2) of EGS composite is shorter than that of unmodified gypsum (OGS) composite because of the quality char forming after the first burning and it plays a role as thermal barriers to protect material from heat of the second ignition. About mechanical properties, both tensile strength and elongation at break of the composite decreased with increasing the gypsum content and flame retardant additives because of filler aggregation.

Keywords: waste gypsum, HDPE, EVA, flame resistance, ethylene bis stearamide.

1. INTRODUCTION

Waste gypsum (WGS) has been known as a by-product of phosphate fertilizer production process. Normally, WGS is stored in landfills without treatments and becomes huge pollution sources [1]. To diminish this pollution, an amount of WGS has utilized as building materials such as bricks, cement, plasterboard or filler to amend the physico-chemical properties of soils [2, 3]. Besides, by owning many advantages such as small particle size, thermal stability, softness, light weight, low cost, etc. [4], WGS has attracted researchers to prepare composite with some kind of matrix materials such as thermoplastic, epoxy resin, etc. [5-8]. Yordan D. Denev et al. have introduced WGS into polyethylene at melting state at different concentration

ranging from 10 to 60 wt.% to obtain the composite owning high tensile strength and modulus strength [7]. Khuong V. H. also used sodium dodecyl sulfate modified WGS as the filler in HDPE/EVA blend to improve the flame resistance of the composite [8]. However, the compatibility between WGS and polymers is quite poor due to the difference in chemical nature such as polarity, surface activation energy etc. Hence, the organic modification of WGS is necessary to overcome this problem. Some surfactants, i.e stearic acid (SA) and sodium dodecyl sulfate (SDS) have been commonly used as organic modifiers for WGS [6, 8]. SA has been proved as one of the most popular organic substances for the modification of the additive fillers with low melting point around 70 °C. Meanwhile, SDS has the melting temperature much higher than that of polyolefins, thus it causes the inconvenience during material processing, such as polymer decomposition or low modification efficiency. EBS has melting point around 146 °C that near to the melt temperature of polyolefins. Thus, it expected to improve the interaction of EBS-modified WGS and polymer matrix in composite prepared by melt-mixing method. Nevertheless, using EBS as a surface modifier for WGS has been received little attention until now.

High density polyethylene (HDPE) is a widely used thermoplastic in industry and life because of its high mechanical properties, good corrosion resistance, excellent chemical resistance as well as easy processibility. By adding ethylene vinyl acetate copolymer (EVA) into HDPE, the obtained blend owns high stress crack resistance and good impact strength that can be applied in the interior decoration [9]. However, as nature of thermoplastic, both HDPE and EVA have low flame resistance that limits the application of these blends. In this work, the composites of EBS modified gypsum (EGS) and HDPE/EVA blend in the presence of ammonium polyphosphate (APP) and zinc borate (ZB) as flame retardant additives were prepared. The effects of the gypsum content with and without the modification by EBS on the morphology structure, thermal properties, flame resistance and mechanical properties of obtained composites were investigated.

2. MATERIALS AND METHODS

2.1. Materials

Waste gypsum is a by-product of DAP-Vinachem Limited Company (Vietnam) with the particle size range in 20 – 30 µm. Ethylene bis stearamide (EBS), ammonium polyphosphate (APP) and zinc borate (ZB) are high purity commercial products provided by Guangdong Sci-Tech Co.ltd (China). High density polyethylene (HDPE), 20 g/10 min. of MFI (190 °C/2.16 kg) and 0.956 g/cm³ of density, was purchased from ExxonMobil Company (Saudi Arabia). Ethylene vinyl acetate copolymer (EVA) containing 18 wt.% of vinyl acetate, was purchased from Honam Petrochemical Corporation (South Korea).

2.2. Preparation of HDPE/EVA/EGS composite

WGS was neutralized to pH 7 by NaOH 5 wt.% solution and washed by water three times before drying at 110 °C for 3 hours and grinding to obtain unmodified WGS (OGS). The modification of gypsum was performed by melt-mixing OGS with EBS at 155 °C for 30 minutes by using low speed agitator. EBS contents for modifying WGS are 3, 4, and 5 wt.%.

In this study, HDPE and EVA was blended together at ratio 95/5 wt.%. HDPE/EVA/EGS composites containing 0, 2, 5, 7, 10, and 15 wt.% of EGS were prepared by melt mixing method

in a Haake internal mixer at 175 °C for 5 minutes. After that, the composites were hot-pressed in melting state at 175 °C to form the sheets with the thickness of 1.5 - 2.0 mm. The samples were maintained at room temperature for 24 hours before running property measurements.

In order to improve the flame resistance of HDPE/EVA/EGS composites, a mixture of flame retardant additives including APP and ZB was introduced into composites at melt-mixing state [10, 11]. By measuring the burning rate of composites consisting APP and ZB at various contents, the composites containing 5 wt.% APP and 3 wt.% ZB showed the best flame resistance and these optimum contents was kept for all works in this study.

2.3. Characterizations

The tensile strength and elongation at break results were obtained as average value by measuring each sample with five times at a crosshead speed of 50 mm.min⁻¹ in Zwick Tensiler 2.5 (Germany) according to ASTM D 638 standard. The Fourier transform infrared spectroscopy (FTIR, Nexus, USA) was carried out at conditions: resolution 16 cm⁻¹, each sample was scanned 32 times in wave number range from 4000 cm⁻¹ to 400 cm⁻¹. Before FTIR analysis, samples were extracted in ethanol solution by using soxhlet equipment for 2 hours to remove the excess EBS content. Field emission scanning electronic microscope (FESEM, model S-4500, Hitachi, Japan) was employed to examine the fracture surface of samples and also to investigate the dispersion of gypsum particles in polymer matrix. Burning experiments of the composites were carried out under UL94 standard in Institute for Tropical Technology in order to measure the burning time and burning rate of samples [12].

3. RESULTS AND DISCUSSION

3.1. Fourier transform infrared analysis

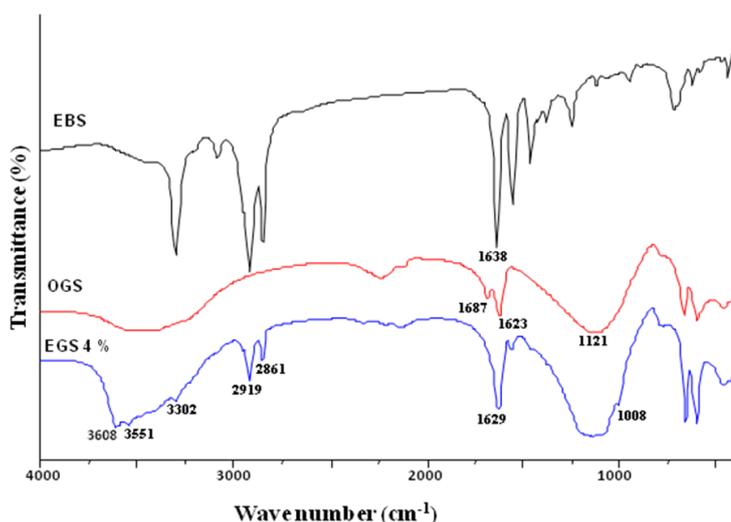


Figure 1. FT-IR spectra of gypsum before (OGS) and after EBS modification (EGS 4 %).

Figure 1 shows FT-IR spectra of EBS, OGS and 4 % EBS modified waste gypsum (EGS 4 %). The peaks located at 3300-3600 cm⁻¹ were contributed to the vibration of water-OH in gypsum. Meanwhile, the peak at 1121 cm⁻¹ is characteristic of covalence bond of SO₄²⁻ of

gypsum. Besides, double peaks at 1687 cm^{-1} and 1623 cm^{-1} might contribute to stretching vibration of H-O in gypsum. After EBS modification, the appearance of new peaks at 2919 cm^{-1} and 2861 cm^{-1} are symmetric vibration of -CH- of hydrocarbon chain of EBS. Moreover, peak at 3608 cm^{-1} was contributed to N-H bond and peak at 1008 cm^{-1} characterized by -C-O linkage in EBS. These evidences show that EBS was successfully attached onto the surface of gypsum. Especially, there is a shift of stretching vibration of H-O groups from 1623 cm^{-1} to 1629 cm^{-1} , it might be due to the interaction between gypsum and EBS. This interaction is mainly hydrogen bonds between -OH groups in gypsum and amide groups of EBS (1638 cm^{-1}) attached on EGS surface.

3.2. Field emission scanning electronic microscope

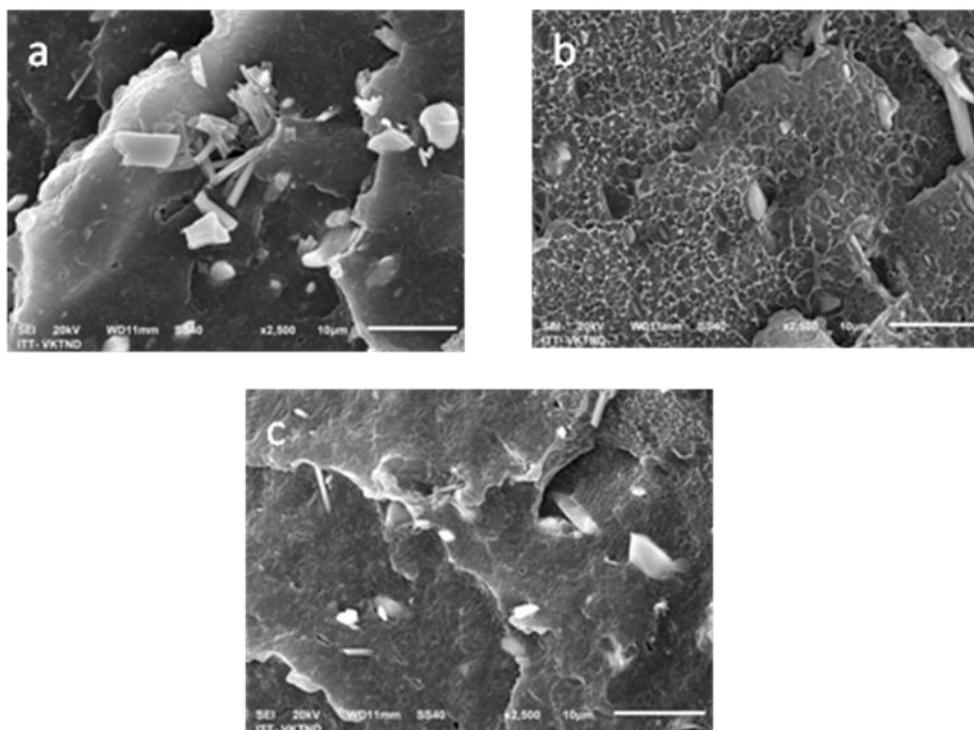


Figure 2. SEM images of (a)HDPE/EVA/OGS composite, (b) HDPE/EVA/EGS composite and (c) HDPE/EVA/EGS/APP-ZB at 7 wt.% EGS.

Figure 2 presents FE-SEM fracture surface images of HDPE/EVA/OGS composite (a) and HDPE/EVA/EGS composites with (c) and without (b) flame retardant additives. Without modifying by EBS, gypsum particles dispersed unevenly in HDPE/EVA blend matrix and aggregated to clusters with about $2\text{--}6\text{ }\mu\text{m}$ in size that separated with polymer matrix at the interface (Fig. 2a). This illustrates that the unmodified gypsum particles are not compatible with the polymer matrix and the poor adhesion between them. After modifying by EBS, gypsum particles dispersed finely and more homogeneous in the blend matrix, the agglomeration of these particles is less to occur (Fig. 2b). In addition, a very thin film seemingly appeared surrounding the gypsum particles and blend matrix connecting these two phases together and the phase separation is not existed. It is clear that the modification by EBS improved the dispersion and adhesion of filler particles in polymer matrix. When the flame retardant additives APP and ZB

were introduced into the composites, the gypsum particles and additive particles poorly dispersed widely in the blend matrix, but tend to aggregate together to form some clusters due to the great affinity between them. It is interesting that the quite good adhesion between these dispersed particles and polymer matrix is still observed (Fig. 2c). This confirms again that the surface modification by EBS has improved significantly on the adhesion between the components in the composites.

3.3. Thermal gravimetric analysis

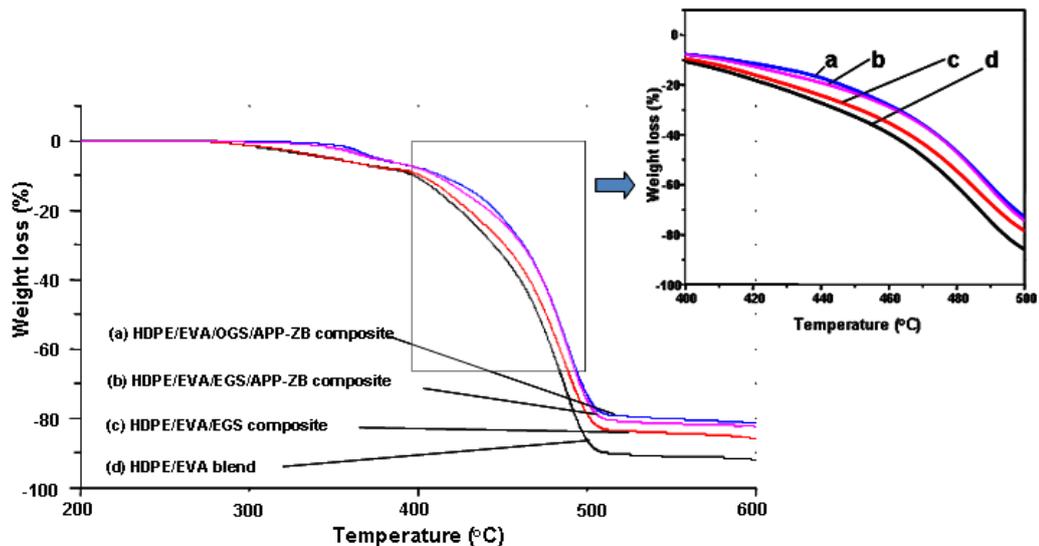


Figure 3. Thermal gravimetric curves of composite samples at 7 wt.% gypsum.

To determine the effect of gypsum and flame retardant additives on the thermal property of composites, these samples were analyzed by TGA from room temperature to 600 °C in nitrogen environment as shown in Fig. 3.

There is a slight weight loss (10 wt.%) at the temperature up to 400 °C which is ascribed to the evaporation of absorbed water in gypsum and partly decomposition HDPE/EVA blend and HDPE/EVA/EGS composites. The decomposition process of HDPE and EVA chains mainly occurred from 400 to 500 °C. Thus, the samples with higher EVA and HDPE ratios resulted in high weight loss. The total weight losses at 500 °C were recorded about 91.05 wt.% and 84.26 wt.% for HDPE/EVA blend and HDPE/EVA/EGS composites, respectively. Whereas, the HDPE/EVA/EGS/APP-ZB and HDPE/EVA/OGS/APP-ZB samples were lower at about 81.52% lower and 80.23 wt.%, respectively. In presence of flame retardant additives, the composites have higher thermal stability by showing the smaller weight loss than materials without APP and ZB. This different weight loss was observed clearly in temperature range from 440 to 480 °C. Finally, the complete degradation of HDPE and EVA chains was recognized at the last stage between 500 °C and 600 °C, while gypsum was not affected by heat and remained at the end of analysis.

3.4. Flame resistance and self-extinguishing time

In order to evaluate the flame resistance of HDPE/EVA/WGS composites, the samples were burned vertically to measure the burning time according to UL-94 standard. Figure 4 presents the burning time of the composites at various OGS and EGS contents. When the content of gypsum varied from 0 to 15 wt.%, the burning time of composite samples increased. It can be explained by the role of gypsum particles as thermal absorption sites in the composites. The more gypsum particles in composite, the more thermal absorption sites which improves thermal barriers and slow down the burning process [6]. However, without EBS modification, OGS could not dispersed well in HDPE/EVA matrix resulting the defects in composite. Those defects might contain oxygen in air that promote the burning process. That explained the burning time of OGS composites is shorter than EGS composites at same gypsum content.

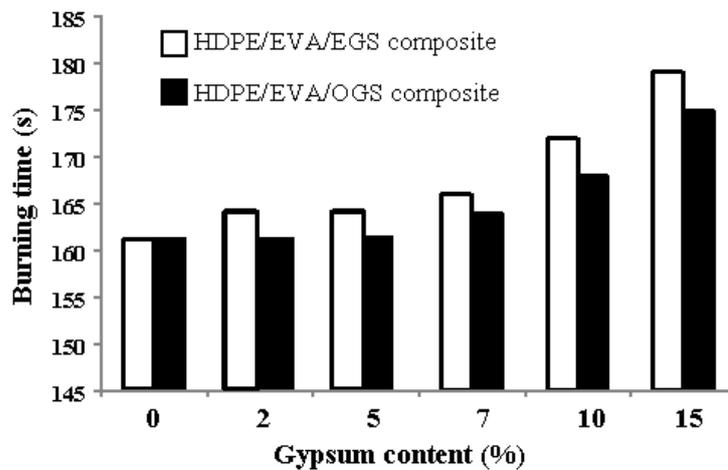


Figure 4. Effect of gypsum content on burning time of HDPE/EVA/EGS/APP-ZB and HDPE/EVA/OGS/APP-ZB composites.

To improve the flame resistance ability, APP and ZB were added in melting composite in preparation process. By adding a mixture of 5 wt.% APP and 3wt. % ZB, the composite became self-extinguished. To measure the self-extinguishing time of the material, the samples were burned horizontally according to UL-94 standard. During burning process, APP will be degraded to form phosphorus acid derivatives which suspend the burning process of polymer [10, 11]. On the other hand, ZB is known as a flame retardant and smoke suppressant. The combination of ZB with APP could enhance both char formation and char quality that improving of flame retardancy of material [10].

Self-extinguishing time (t) of material is the time that material extinguished itself after removal of flame source, the short t means the materials is good resistance to flame. As defined by UL-94 standard, t is the sum of t_1 and t_2 of five pieces of sample, in which t_1 and t_2 are respective to the self-extinguishing time of the first and second ignition. By adding APP and ZB, composites using OGS and EGS became self-extinguished and achieved V2 grade of UL-94 standard. In Figure 5, t_1 of OGS composites are not different from that of EGS composites at the same gypsum contents. However, at the second burning, t_2 of EGS composite is shorter than that of OGS composite. This phenomenon can be explained that the char formation of EGS composite might be more quality than that of OGS composite, thus, it works as thermal barriers to protect material from heating of flame source.

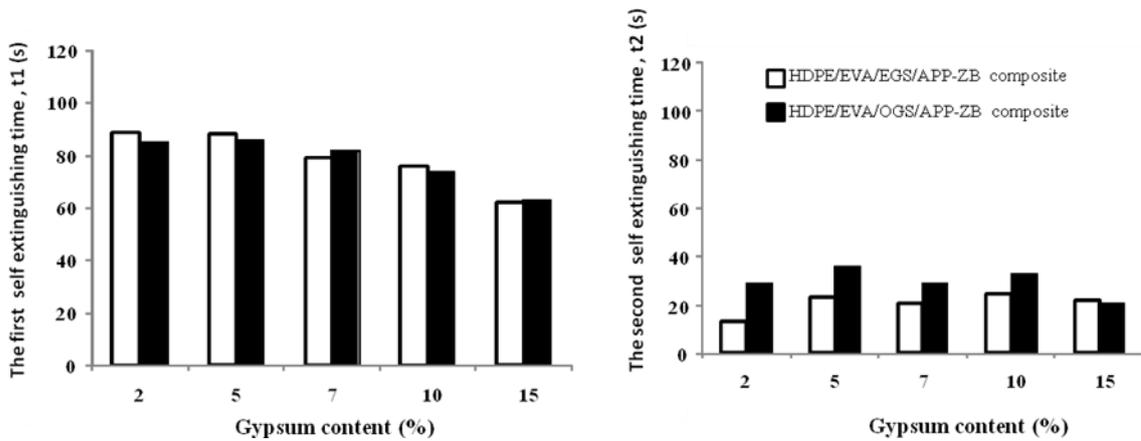


Figure 5. Self-extinguishing time t_1 and t_2 of composites with various EGS and OGS contents.

3.5, Mechanical properties

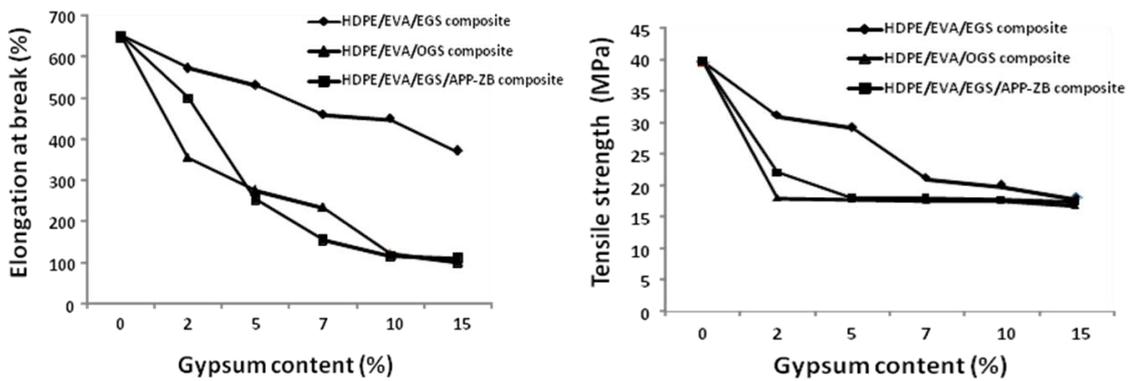


Figure 6. Influence gypsum contents and flame retardant additives on elongation at break and tensile strength of composites.

Figure 6 presents the influence of gypsum contents and flame retardant additives on tensile strength and elongation at break of HDPE/EVA/WGS composites. It is seen that both tensile strength and elongation at break of all composites decreased with the raise of gypsum content. The graphs showing the dependence of tensile strength and elongation at break of HDPE/EVA/EGS composites on the gypsum content lied above in comparison to those of two other composites. It means that at the same gypsum content, tensile strength and elongation at break of HDPE/EVA/EGS composites are the highest among three composites. When adding 2 and 5 wt.% gypsum, tensile strength and elongation at break of HDPE/EVA/EGS composites decreased gradually whereas their reduction in the other composites happened intensively. The incorporation of 5 wt.% EGS only reduced 26.5 % tensile strength (from 39.2 MPa down to 28.8 MPa) and 17 % elongation (from 650 % down to 540 %) of HDPE/EVA blend. While these declines reached to 54 % and 57 % respective to tensile strength and elongation at break for HDPE/EVA/OGS composites with the same gypsum content. Obviously that the modification of WGS by EBS improved the interaction and adhesion of gypsum particles with HDPE/EVA blend matrix, therefore enhanced the mechanical properties of the obtained composites. The

addition of the flame retardants as APP and ZB resulted good resistance to flame for both HDPE/EVA/EGS and HDPE/EVA/OGS composites as mentioned in the above section. Unexpectedly, the presence of APP and ZB caused the decrease in mechanical properties of the composites. Tensile strength and elongation at break of HDPE/EVA/EGS composites declined relative quickly with the introduction of APP and ZB. However, these parameter values are still higher than those of HDPE/EVA/OGS composites with the same filler content. In other words, the modification of gypsum by EBS helps to lower the reduction in mechanical properties of the HDPE/EVA/EGS/APP-ZB composites. The improvement of the adhesion between the additive filler particles (including gypsum and flame retardant filler particles) with HDPE/EVA blend matrix after the modification with EBS but the aggregation caused by their great affinity is the reason explain for this phenomenon. The aggregation of gypsum and APP, ZB particles as observed in Fig.2 leads to the void formation and interrupts the continuity of the matrix phase, hence caused the decrease in tensile strength and elongation at break of the composites.

4. CONCLUSIONS

Gypsum filler was successfully modified by EBS using melt-mixing method at 155 °C for 30 minutes. Stretching vibration of H-O-H shifted from 1,623 cm⁻¹ to 1,629 cm⁻¹ could be assigned to the hydrogen bonds between –OH groups of gypsum and amide groups of EBS. By adding 5 wt.% APP and 3 wt% ZB into HDPE/EVA/Gyp composite, the material reached V2 grade of flame resistance according to UL- 94 standard. While **t1** of both EGS composite and OGS composite are same, **t2** of EGS composite is shorter than that of OGS. The tensile strength and elongation at break of composite containing EGS are higher than that of composite containing OGS proved the EBS modification effect on the gypsum.

REFERENCES

1. Tayibi H., Choura M., Lopez F. A., Alquacil F. J. - Environmental impact and management of phosphogypsum, *Journal of Environmental Management* **90** (2009) 2377-2386.
2. Suarez S., Roca X., Gasso S. - Product-specific life cycle assessment of recycled gypsum as a replacement for natural gypsum in ordinary Portland cement, *J. Clean. Prod.* **117** (2016) 150-159.
3. Nisti M. B., Saueia C. R., Malheiro L. H., Groppo G. H., Mazzilli B. P. - Lixiviation of natural radionuclides and heavy metals in tropical soils amended with phosphogypsum. *Journal of Environmental Radioactivity* **144** (2015) 120-126.
4. Rodrigo H. G., Sayonara M. P., Jefferson S. S. - Gypsum plaster waste recycling: A potential environmental and industrial solution, *Journal of Cleaner Production* **164** (2017) 288-300.
5. Myung Y. K., Dong S. H., Yeong S. K., Jin K. H., Nguyen V. G. - Mechanical Properties of PVC Complex Using Waste-Gypsum Fillers, *Journal of KASBIR*, **4** (2003) 92-97.
6. Thai H., Do Q. T., Nguyen V. G.. - Preparation and study on properties, structure of composite based on polyethylene and organic modified phosphogypsum, *Vietnam Journal of Chemistry* **49** (3) (2011) 291-295 (in Vietnamese).
7. Yordan G. D., Georgi D. D., Anton N. P. - Surface modification of phosphogypsum used as reinforcing material in polyethylene composites, *Journal of elastomers and plastics* **41** (2009) 119-132.

8. Khuong V. H., Le H. D., Nguyen T. M., Tran T. M., Tran H. T., Mai D. H., Thai H., Nguyen V. G. - Study on properties and morphology of polyethylene /ethylene vinyl acetate copolymer/sodium dodecyl sulphate modified gypsum **54** (1A) (2016) 72-79.
9. Yang C., Huawei Z., Mei L., Ya C. - Melting and crystallization behavior of partially miscible high density polyethylene/ethylene vinyl acetate copolymer (HDPE/EVA) blends, *Thermo Chimica Acta* 586 (2014) 1-8.
10. Tugba O., Ali N. H., Jale H., Cevdet K. - Thermal degradation mechanisms of aluminium phosphinate, melamine polyphosphate and zincborate in poly(methyl methacrylate), *Polymer Degradation and Stability* 96 (10) (2011)1780–1787.
11. Pan L.L., Li G. Y., Su Y. C., Lian J. S. - Fire retardant mechanism analysis between ammonium phosphate and triphenyl phosphate in unsaturated polyester resin, *Polymer degradation and stability* **97** (2012) 1801-1806.
12. Test for Flammability of Plastic Materials for Parts and Devices and Appliances, North brook, IL: Underwriters Laboratories Inc. United States Patent, 1997.