RESEARCH PAPER

Combine Flake Like Magnesium Hydroxide and Cubic Like Aluminum Hydroxide Nanostructures in order to Improve Fire Retardant of PVC and PMMA

Ahmad Gholizadeh [1], Saeed Jame-Bozorgi [2], Mohammad Yousefi [3]* and Ali Niazi [1]

[1] *Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran*

[2] *Department of Chemistry, Hamedan Branch, Islamic Azad University, Hamedan, Iran*

[3] *Department of Chemistry, Yadegar-e- Imam Khomeini(RAH), Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran*

ARTICLE INFO

ABSTRACT

In this study, Flake-like magnesium hydroxide ($Mg(OH)_2$) and cubic-like aluminum hydroxide ($Al(OH)_3$) nanostructures were synthesized via a simple co-precipitation method at relatively low temperature. Chemical properties and surface morphology of the magnesium hydroxide and aluminum hydroxide were characterized by X-ray diffraction analysis (XRD), scanning electron microscopy image (SEM), transmission electron microscopy image (TEM), differential scanning calorimetery analysis (DSC) and thermo gravimetric analysis (TGA). Magnesium hydroxide and cubic-like aluminum hydroxide were then added to PVC, Graphite and PMMA polymers. The effect of cooperation between magnesium hydroxide and cubic-like aluminum hydroxide nanostructures on the fire retardant of the polymeric matrixes has been investigated. The results show that the thermal decomposition of the nanocomposites shifts towards higher temperature in the presence of the magnesium hydroxide and cubic-like aluminum hydroxide. As well as, the enhancement of fire retardant of nanocomposites is due to endothermically decomposition of these nanostructures and releases of water and dilutes combustible gases.

How to cite this article

INTRODUCTION

A fire retardant is a material that reduces flammability of polymer or delays their combustion. This includes chemical agents, but may also include substances that work by physical action, such as cooling the polymer, such as clay. There are several reports for improvement properties of composite materials by using nano-fillers which lead to the development of nanocomposites. Improvement the fire retardant behavior of polymers is still a major challenge for extending their use for most applications and various flame retardant additives like halogenated compounds are restricted with regard to the environmental demands. One of the most commonly used mineral flame retardants is magnesium hydroxide because when the temperature raises magnesium hydroxide decomposes endothermically (about 330◦C with an endothermic of 1.356 kJ/g) and absorbs energy [1-4]. Moreover, it provides water which dilutes combustible gases and provides heat insulation by reflecting heat when it accumulates on the surface. The main problem of using magnesium hydroxide is that for successful flame

* Corresponding Author Email: myousefi50@hotmail.com

retardancy tests, 35 to 65 wt% of metal hydroxide is required. Increasing the loading of inorganic metal hydroxides will result in a significant decrease in physical properties [5-9]. Nanostructures could solve this problem by providing high surface/volume rate. Recently, Baglioni et al. synthesized several metal hydroxide nanoparticles by various chemical reactions [10- 14]. These products were used as consolidants for wall paintings (frescoes), stone, paper, and wood. Many attempts have been put on the shape controlled fabrication of nanostructures [15-17].

Poly(vinyl chloride) (PVC) products are widely used in a large range of applications such as coatings, medical devices, paints, films, and food packaging and their thermal degradation has been the subject of some reviews [18,19]. Poly(methyl methacrylate), or PMMA, is an important thermoplastic for numerous uses and especially for optical applications due to excellent transparency in the visible region. Nevertheless, PMMA has limiting properties, particularly its low toughness and poor thermal stability.

MATERIALS AND METHODS

Sodium hydroxide, magnesium nitrate $(Mg(NO_3)_2$, aluminum nitrate $[Al(NO_3)_3]$, EDTA (ethylenediaminetatraacetic acid), PVC, PVD, PMMA, graphite, ethanol, cyclohexanol were purchase from Merck company. All of the chemicals were of analytical grade and used as received without further purification. Deionized water (DI) was used throughout the experiment.

Synthesis of aluminum hydroxide

66.4 g of aluminum nitrate was dissolved in water. Then 110 mL of NaOH solution (9 M) was added to the above solution and heated at 115 C for 30 min. Afterward, solution was cooled down to room temperature by adding distilled water. Finally, EDTA was added and stirred for 25 h. Final products were washed and dried.

Synthesis of magnesium hydroxide

0.5 mol of magnesium nitrate was dissolved in water. Then 220 mL of NaOH solution (9 M) was added to the above solution and heated at 115 for 30 min. Afterward, solution was cooled down to room temperature by adding distilled water. Finally EDTA was added and stirred for 25 h. In the final step, the products were washed and dried.

Prepare nanocomposite
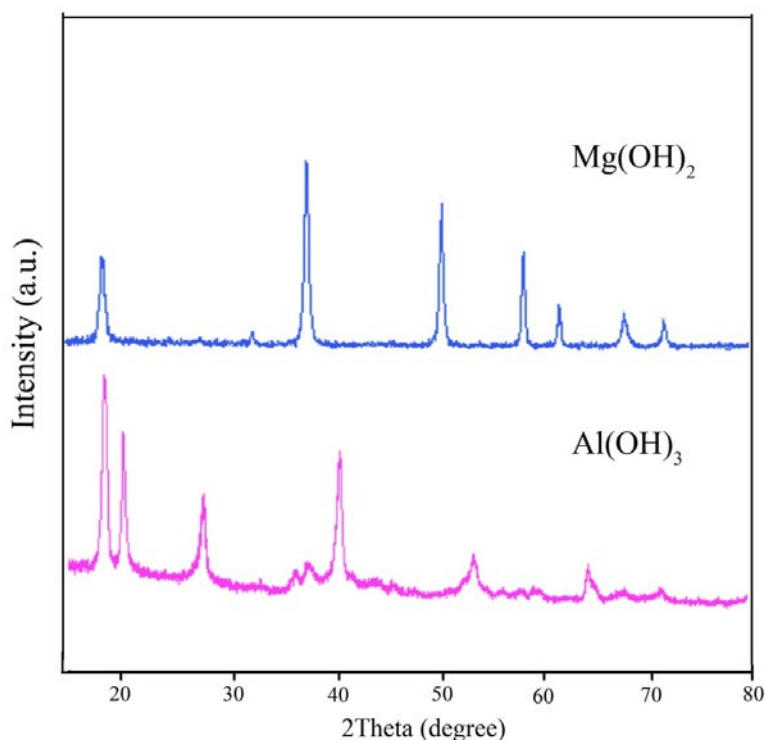
First, melted PVC, PMMA, and graphite were

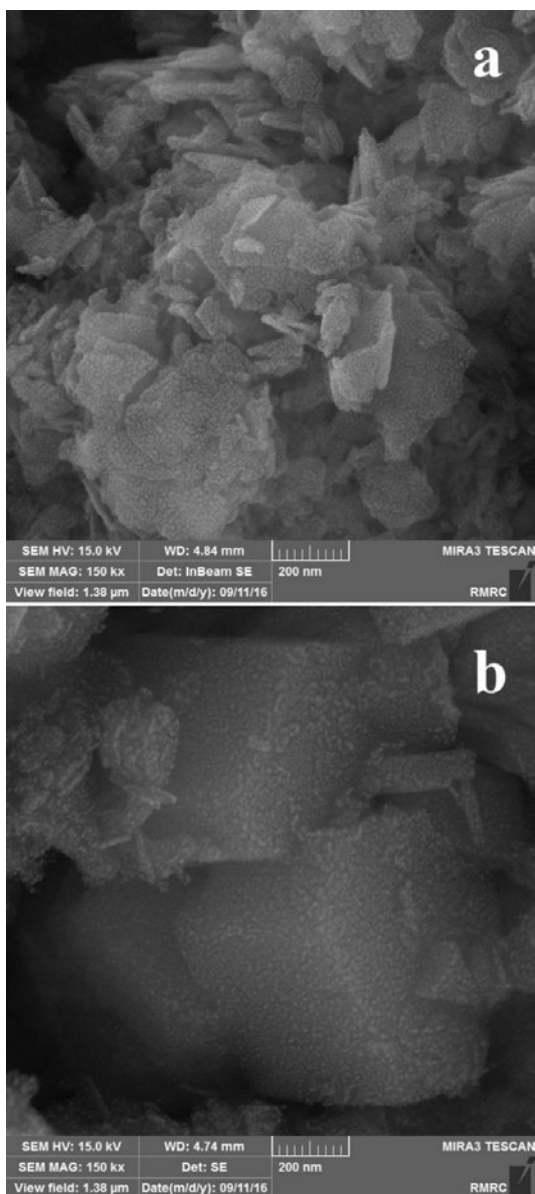Fig. 1. XRD pattern of as-prepared cubic like aluminum hydroxide and flake like magnesium hydroxide.

Fig. 2. SEM image of a) magnesium and b) aluminum hydroxide nanostructure.

Fig. 3. TEM images of (a) magnesium hydroxide and (b)) aluminum hydroxide nanostructure.

added into beaker and stirred under 80 rpm. Then, aluminum hydroxide nanoparticles and cyclohexanol were added to the above solution. The obtained solution was transferred to the watch glass. In addition, composite with different ratio of PVC/Mg(OH)$_2$/Al(OH)$_3$ was prepared.

RESULT AND DISCUSSIONS

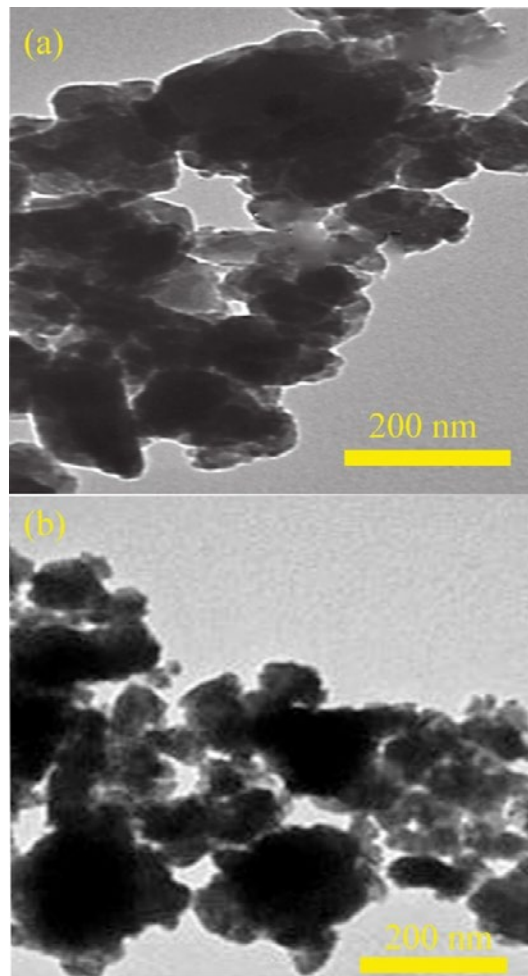The samples were characterized by X-ray diffraction (XRD) patterns were recorded by an X'pert pro diffractometer using Ni-FILTERED Cu Kα radiation (l= 1.54° A). the morphology and structure of nanoparticles were characterized using a scanning electron microscopy (SEM) images using an LEO instrument model 1455VP (Prior to taking an image, to obtaining a better contrast and to make the sample surface conducting and prevent charge reposition the sample was coated with a very thin layer of Au) and energy dispersive spectrometry analysis (EDS) was investigated by XL30, Philips microscope. Thermogravimetric–differential thermal analysis (TG–DTA) was carried out using an instrument (Shimadzu TGA-50H) with a flow rate of 20.0 mL min^{-1} and a heating rate of 10 C min-1 under nitrogen atmosphere.

The XRD pattern of flake like magnesium and aluminum hydroxide is illustrated in Fig. 1. The XRD pattern of as-prepared magnesium hydroxide shows a good agreement with literature values (JCPDS No. 33-0018) with pure cubic phase while aluminum hydroxide shows pure monoclinic phase.

The SEM image of magnesium and aluminum hydroxide nanostructure is shown in Fig. 2 and Fig. 3. As seen from Fig. 2, 3, flake like magnesium hydroxide was formed. In this work, flake like magnesium hydroxide and aluminum hydroxide were used as flame retardants to improve thermal stability of PVC, PMMA. Firstly, the effect of magnesium hydroxide on fire retardant of PVC was investigated. The TGA, DTG and DSC results are shown in Fig. 4 a-c. Base of these results, two possible reactions were introduced during burning composite. Reaction 1 (eq. 1) refer to the reaction of PVC with oxygen which lead to produce CO_2, HCL and H_2O. Base of DTG and DSC curve in Fig. 4, this reaction is exothermic and release 4.7kcal/gr energy. The second reaction (eq. 2) is related to the burning of magnesium hydroxide and produced magnesium oxide. Reaction 2 is an endothermic reaction and need 1.356 kJ/g.

$$(CH_2CHCl)_n + O_2 \xrightarrow{\Delta H = -4700cal/gr} CO_2 + HCl + H_2O$$

$$Mg(OH)_2 \rightarrow MgO + 2H_2O \qquad (2)$$
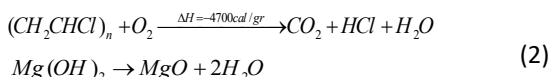
Thermal decomposition of the PVC nanocomposite shift towards higher temperature in the presence of flake like $Mg(OH)_2$ nanostructures. Magnesium hydroxide has barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. So the initial degradation temperature (Tonset) increases. In addition, we studied the effect of cooperation between magnesium hydroxide and aluminum hydroxide on thermal stability of PVC. Fig. 5 a-c show the TGA, DTG, and DSC of $Al(OH)_3/Mg(OH)_2/PVC$ Nano-composite, respectively. As seen from the results, cooperated nanostructures show better results. Exfoliated aluminum hydroxide has a barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymers. Adsorption of polymer chains onto the surface of aluminum hydroxide nanoparticles leads to restriction of the segmental mobility and suppress chain-transfer reactions [20, 21]. The TGA graph indicate that adding of aluminum hydroxide to the PVC leads to a little reduction of the Tonset but enhances the residue at the temperatures
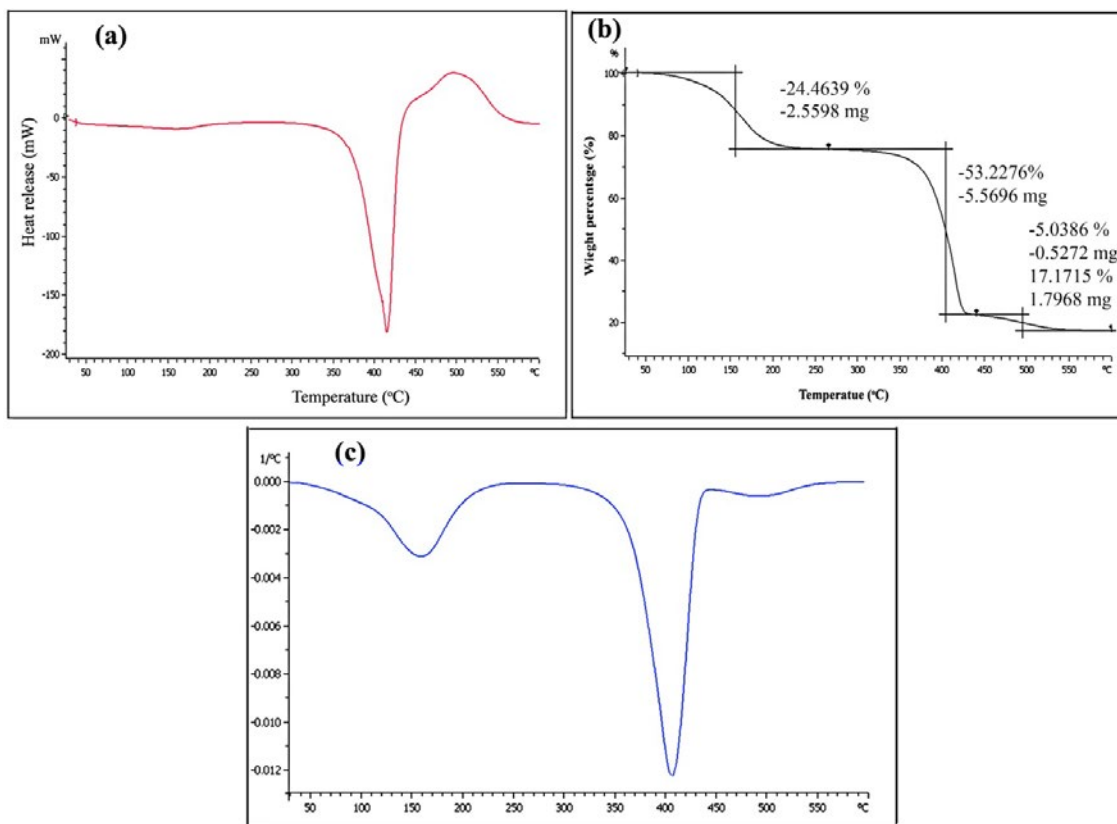

Fig. 4. DSC graph of PVC- $Mg(OH)_2$ nanocomposite (a), TGA graph of PVC- $Mg(OH)_2$ nanocomposite (b) and DTG graph of PVC- $Mg(OH)_2$ nanocomposite (c).
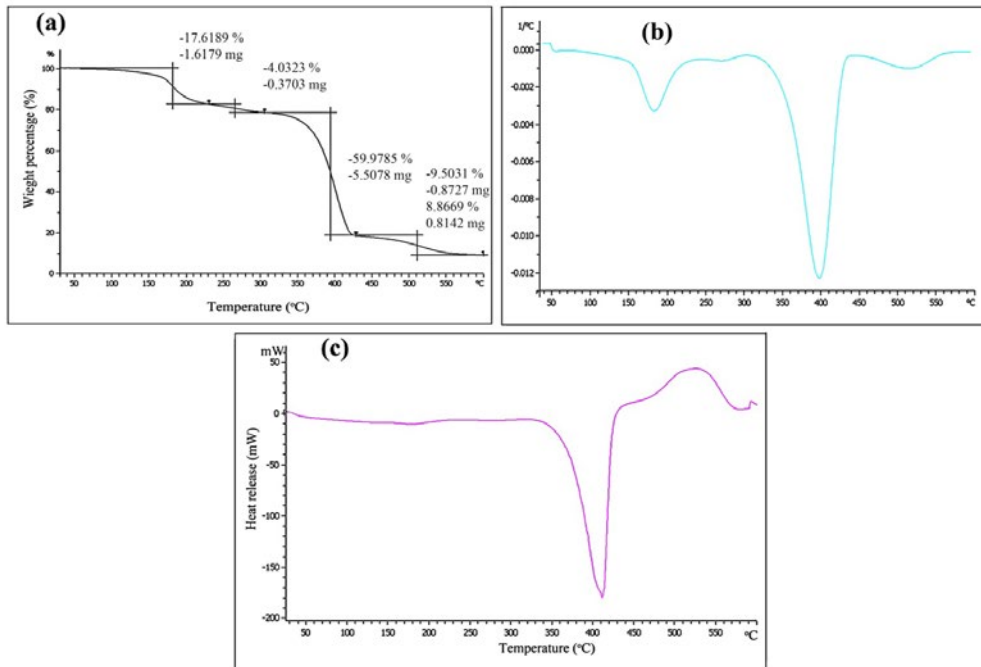
Fig. 5. TGA graph of Al(OH)$_3$/Mg(OH)$_2$/PVC Nano-composite (a), DTG graph of Al(OH)$_3$/Mg(OH)$_2$/PVC Nano-composite (b) and DSC graph of Al(OH)$_3$/Mg(OH)$_2$/PVC Nano-composite (c).
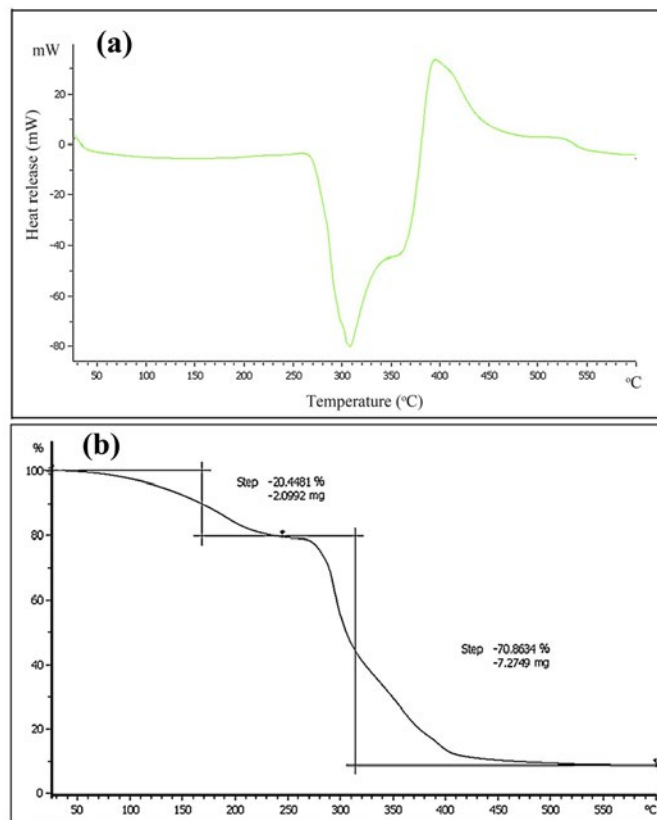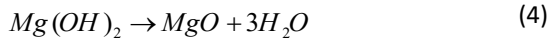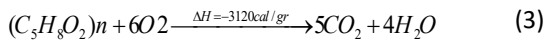

Fig. 6. The DSC results of PMMA-Mg(OH)$_2$ nanocomposite (a) and the TGA results of PMMA-Mg(OH)$_2$ nanocomposite (b)

above 400 C. In addition, we studied the effect of different ratio of PVC/MgOH)$_2$/Al(OH)$_3$ on fire retardant of PVC. As seen from results, best result was obtain for 1:1:1 of PVC:Mg(OH)$_2$/Al(OH)$_3$.

The DSC results of PMMA-Mg(OH)$_2$ nanocomposite is shown in Fig. 6a. As seen, by increasing temperature, two main reactions are occurred. First, reaction of PMMA with oxygen (burning of PMMA) which produces CO$_2$ (g) and H$_2$O (g) and releases were about 3120 Cal/gr energy (eq. 3). Second reaction is related to the combine magnesium hydroxide with oxygen and produce magnesium oxide and water (eq. 4).

$$(C_5H_8O_2)n + 6O2 \xrightarrow{\Delta H = -3120cal/gr} 5CO_2 + 4H_2O \qquad (3)$$

$$Mg(OH)_2 \rightarrow MgO + 3H_2O \qquad (4)$$

According to the above equations and DSC results, peak in 280- 300 is an exothermic and refer to burning PMMA and release CO$_2$ and H$_2$O.

The TGA results of PMMA-Mg(OH)$_2$ nanocomposite is illustrated in Fig. 6b. As seen from figure, the thermal stability of PMMA is improved by the addition of flake like magnesium hydroxide. In the system containing pre-dispersed flake like magnesium hydroxide, mass loss

starts very subtly near 100. The Comparing the decomposition of these alumina-filled composites with neat PMMA, the thermal stabilities of main chain decompositions in composites are shifted toward higher temperatures.

Beside this, we studied the effect of cooperation between magnesium hydroxide and aluminum hydroxide on thermal stability of PMMA. TGA, DTG, and DSC of Al(OH)$_3$/Mg(OH)$_2$/PVC Nano-composite illustrated in Fig. 7a-c. Cooperate magnesium hydroxide and aluminum hydroxide show similar result on improve stability of PMMA.

In the case of graphene-PVC- magnesium hydroxide nanocomposite, three possible reactions are proposed (Fig. 8a). First two reactions are related to the combine oxygen with PVC and magnesium hydroxide (eq1 and 2). Third reaction is related to the burning of graphene in the nanocomposite (eq. 5).

$$C + O_2 \xrightarrow{\Delta H = 2600cal/gr} CO \qquad (5)$$

As previously mentioned, the exothermic peaks in 320-400 are related to the burning PVC which released H$_2$O (g), HCL (g) and CO$_2$. The main difference between DSC of PVC- Mg(OH)$_2$ nanocomposite and graphite- PVC- Mg(OH)$_2$ nanocomposite is the intensity of peak at 410
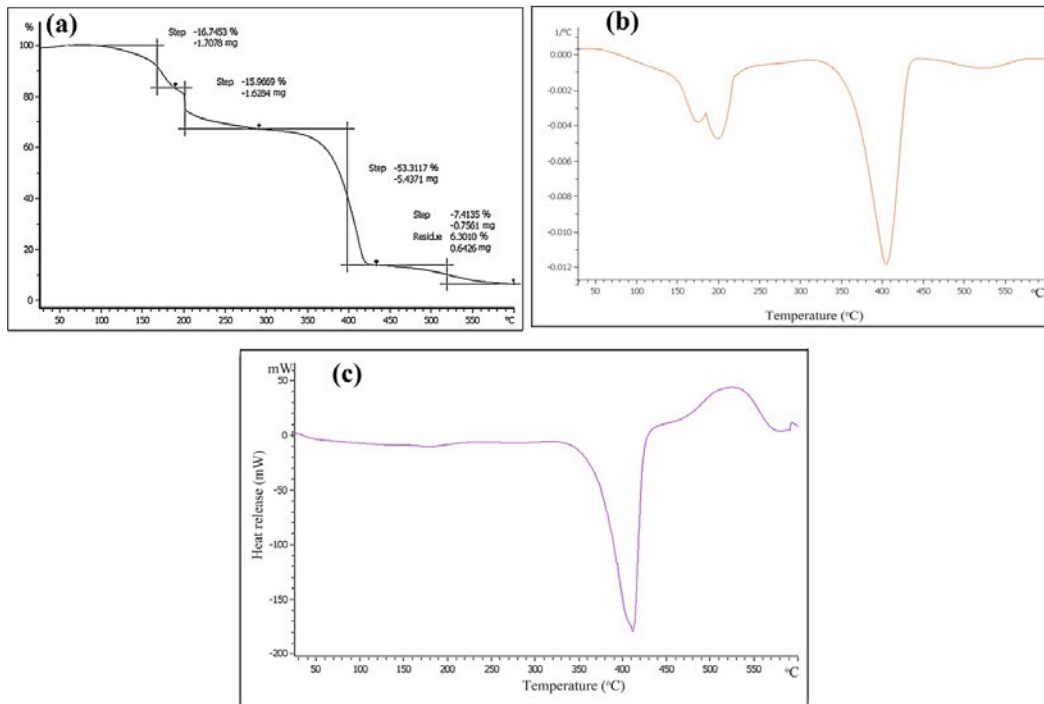

Fig. 7. TGA of Al(OH)$_3$/Mg(OH)$_2$/PMMA Nano-composite (a), DTG of Al(OH)$_3$/Mg(OH)$_2$/PMMA Nano-composite (b) and DSC of Al(OH)$_3$/Mg(OH)$_2$/PMMA Nano-composite.
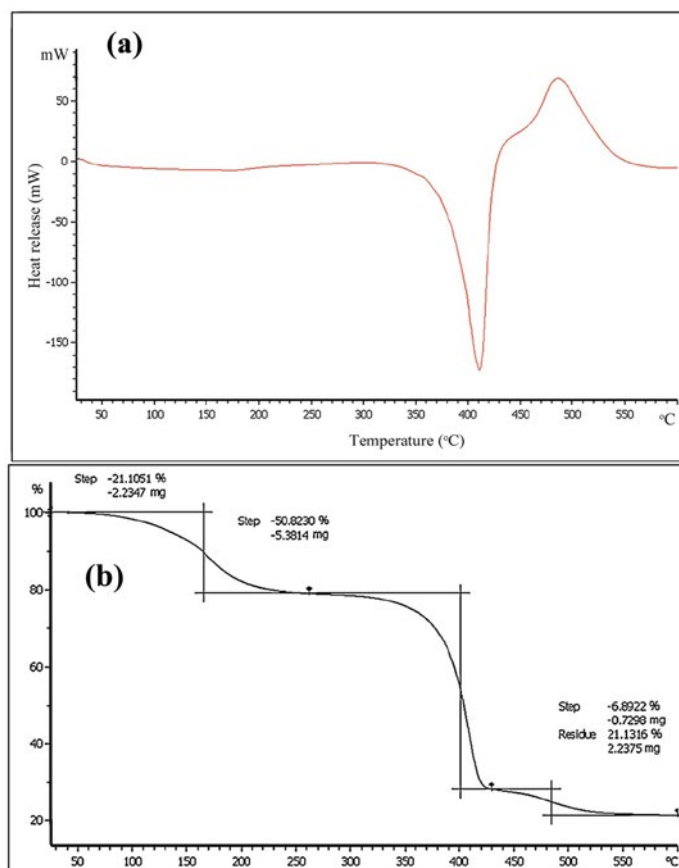
Fig. 8. DSC graph of as-prepared Graphite-PVC- Mg(OH)$_2$ nanocomposite (a) and
TGA result of as-prepared graphite-PVC-Mg(OH)$_2$ nanocomposite (b).

. In the case of PVC- Mg(OH)$_2$ nanocomposite, intensity is higher than graphite- PVC-Mg(OH)$_2$ nanocomposite. This happens because energy released by combine oxygen and graphite is absorbed by magnesium hydroxide.

TGA result of graphite-PVC nanocomposite and graphite-PVC-Mg(OH)$_2$ nanocomposite are shown in Fig. 8b. In below 400 C, both curve for graphite-PVC nanocomposite and graphite-PVC-Mg(OH)$_2$ nanocomposite are same. In above 400 C, weight losing percentage for graphite-PVC-Mg(OH)$_2$ nanocomposite is lower than graphite-PVC nanocomposite.

CONCLUSION

Herein, flake like magnesium hydroxide and cubic like aluminum hydroxide were synthesized via a simple surfactant-free precipitation reaction at room temperature. The effect of prepared nanostructures and their cooperation on fire retardant of PVC, PMMA, and graphite- PVC were investigated. The results show that cooperated nano-filler show significant effect on improve thermal stability and flame retardancy of the PVC and graphite- PVC because of endothermic decomposition that release water simultaneously. Nanoparticles were characterized using XRD and SEM techniques.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Kashiwagi T, Inaba A, Brown JE, Hatada K, Kitayama T, Masuda E. Effects of weak linkages on the thermal and oxidative degradation of poly(methyl methacrylates). Macromolecules. 1986;19(8):2160-8.
2. Manring LE, Sogah DY, Cohen GM. Thermal degradation of poly(methyl methacrylate). 3. Polymer with head-to-head linkages. Macromolecules. 1989;22(12):4652-4.
3. Manring LE. Thermal degradation of poly(methyl methacrylate). 2. Vinyl-terminated polymer. Macromolecules. 1989;22(6):2673-7.
4. AB. Morgan, CA. Wilkie, John Wiley & Sons; New Jersey 2007.

5. Guo X, Zhao L, Zhang L, Li J. Surface modification of magnesium aluminum hydroxide nanoparticles with poly(methyl methacrylate) via one-pot in situ polymerization. Applied Surface Science. 2012;258(7):2404-9.

6. Liu S, Ying J, Zhou X, Xie X. Core-shell magnesium hydroxide/polystyrene hybrid nanoparticles prepared by ultrasonic wave-assisted in-situ copolymerization. Materials Letters. 2009;63(11):911-3.

7. Jamshidi P, Salavati-Niasari M, Ghanbari D, Shams HR. Synthesis, Characterization, Photoluminescence and Photocatalytic Properties of CeO2 Nanoparticles by the Sonochemical Method. Journal of Cluster Science. 2013;24(4):1151-62.

8. Shabanian M, Ghanbari D. Synthesis of magnesium hydroxide nanofiller and its use for improving thermal properties of new poly(ether-amide). Journal of Applied Polymer Science. 2012;127(3):2004-9.

9. Giorgi R, Bozzi C, Dei L, Gabbiani C, Ninham BW, Baglioni P. Nanoparticles of Mg(OH)2: Synthesis and Application to Paper Conservation. Langmuir. 2005;21(18):8495-501.

10. Giorgi R, Chelazzi D, Fratini E, Langer S, Niklasson A, Rådemar M, et al. Nanoparticles of calcium hydroxide for wood deacidification: Decreasing the emissions of organic acid vapors in church organ environments. Journal of Cultural Heritage. 2009;10(2):206-13.

11. Baglioni P, Giorgi R, Dei L. Soft condensed matter for the conservation of cultural heritage. Comptes Rendus Chimie. 2009;12(1-2):61-9.

12. Ciliberto E, Condorelli GG, La Delfa S, Viscuso E. Nanoparticles of Sr(OH)2: synthesis in homogeneous phase at low temperature and application for cultural heritage artefacts. Applied Physics A. 2008;92(1):137-41.

13. Giorgi R, Chelazzi D, Baglioni P. Nanoparticles of Calcium Hydroxide for Wood Conservation. The Deacidification of the Vasa Warship. Langmuir. 2005;21(23):10743-8.

14. Gomez-Villalba LS, López-Arce P, Alvarez de Buergo M, Fort R. Structural stability of a colloidal solution of Ca(OH)2 nanocrystals exposed to high relative humidity conditions. Applied Physics A. 2011;104(4):1249-54.

15. Zinatloo-Ajabshir S, Mortazavi-Derazkola S, Salavati-Niasari M. Sonochemical synthesis, characterization and photodegradation of organic pollutant over Nd2O3 nanostructures prepared via a new simple route. Separation and Purification Technology. 2017;178:138-46.

16. Mortazavi-Derazkola S, Zinatloo-Ajabshir S, Salavati-Niasari M. Facile hydrothermal and novel preparation of nanostructured Ho2O3 for photodegradation of eriochrome black T dye as water pollutant. Advanced Powder Technology. 2017;28(3):747-54.

17. Mortazavi-Derazkola S, Salavati-Niasari M, Amiri O, Abbasi A. Fabrication and characterization of Fe 3 O 4 @SiO 2 @TiO 2 @Ho nanostructures as a novel and highly efficient photocatalyst for degradation of organic pollution. Journal of Energy Chemistry. 2017;26(1):17-23.

18. Starnes WH. Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride). Progress in Polymer Science. 2002;27(10):2133-70.

19. Ito M, Nagai K. Analysis of degradation mechanism of plasticized PVC under artificial aging conditions. Polymer Degradation and Stability. 2007;92(2):260-70.

20. Ma H, Fang Z, Tong L. Preferential melt intercalation of clay in ABS/brominated epoxy resin–antimony oxide (BER–AO) nanocomposites and its synergistic effect on thermal degradation and combustion behavior. Polymer Degradation and Stability. 2006;91(9):1972-9.

21. Nguyen C, Kim J. Thermal stabilities and flame retardancies of nitrogen–phosphorus flame retardants based on bisphosphoramidates. Polymer Degradation and Stability. 2008;93(6):1037-43.