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Enhanced fire retardancy of poly methyl methacrylate by combination with aluminium hydroxide and magnesium hydroxide

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ABSTRACT

The use of polymeric materials in life, due to their unique properties such as low weight and easy process, significantly increased. But polymers are relatively high combustibility and most of them produce smoke and toxic and corrosive gases during burning. As a result of modification of the polymer behavior against fire is the main challenge to make them more useful. Retardant additives reduce the risk of fire and release of it. The performance of this class of materials is by increase in combustion time, improve in inflammability of polymer, reduce in heat release rate and prevent of dripping during burning. In this study, it is tried to improve thermal resistance of polymethyl methacrylate PMMA by synthesis and characterization of nanoparticles of magnesium hydroxide and aluminum hydroxide nanoparticles by SEM and XRD and use it as fillers for polymers, which is highly used in Industry. 4 composite samples with ratios of 10/90, 20/80, 30/70 and 40/60 of PMMA and $Mg(OH)_2$ and 4 composite samples with ratios of 5/5/90, 10/10/80, 15/15/70 and 2/20/40 of PMMA and $Mg(OH)_2$ and $Al(OH)_3$ were prepared and their thermal behavior was studied. The results show that increasing the percentage of magnesium hydroxide in the composites, heat resistance of polymer and the melting temperature and the percentage of residual mass in composite increased. The addition of aluminum hydroxide to composite increased the thermal resistance and increased the percentage of residual mass in some of them.

KEY WORDS: FIRE RETARDANCY, NANO ALUMINUM HYDROXIDE, POLY(METHYLMETHACRYLATE), NANO MG(OH)2, NANO COMPOSITE

INTRODUCTION

The research and developments on new engineering materials belong to the important fields of material science. One can see the continuous competition between the traditional inorganic engineering materials and polymers. Since polymeric materials (including composites) are promising, due to their economic versatile applicability, they are widely used in many applications, such as housing materials, transport and electrical engineering (Almeras *et al.* 2003; Anna *et al.* 2002; Bourbigot *et al.* 1996a; Bourbigot *et al.* 1996b). These commercial polymers are easily flammable. The flame retardant can act in various ways i.e. physically or chemically. Many types of flame retardants are used in consumer products (Troitzsch, 1990; Sain, 2004; Zhu, 2003). They are mainly phosphorus, antimony, chlorides and bromides, magnesium and boron-containing compounds (Seymour *et al.* 1978).

Al(OH)3can act also as a reinforcing agent and smoke suppressant additive with low or zero emissions of toxic or hazardous substances. The main advantages of polymeric materials over many metal compounds are high toughness, corrosion resistance, low density and thermal insulation. Improvement of the flame retardancy and thermal stability of polymers is a major challenge for extending their use for most applications. The higher level of flame retardancy of nanoparticles is due to their bigger surface to volume fractions which let them disperse into the polymeric matrix homogeneously, and hence leads to formation of a compact char during the combustion (Grigsby *et al.* 2005; Wang *et al.* 2007; Kuljanin *et al.* 2006).

Poly(methyl methacrylate) (PMMA) isa highly flammable polymer, improving its thermal stability is very important. There are several fire retardants available in the market. Although they improve the fire resistance of PMMA, they have a lot of disadvantages. Many additives are effective only at high loadings, generally from 10 wt% to 40 wt%, which changes the physical properties of the polymer. Most flame retardants additivesare halogenated compounds (Bundersek *et al.* 2012a). On the other hand, metaloxides are halogen-free products, which can also be used for improving thermal stability and fire properties of PMMA. Aluminum hydroxide (Al(OH)3) and magnesium hydroxide (Mg(OH)2) are environmentally benign, butneed to be added in high concentrations to be effective (Beyer, 2002). Transparency of PMMA in the visible region is reason that PMMA is an importantthermoplastic for numerous uses (Beyer, 2005; Beyer, 2002; Chiang *et al.* 2009; Bundersek *et al.* 2012b).

Inorganic compound magnesium hydroxide [Mg(OH) 2] as a smoking- and toxic-free additive has been exten-sively used in halogen-free flame-retardant polymeric materials. However, its fatal disadvantages are low flame-retardant efficiency and thus very large usage amount, which lead the mechanical properties of a flame-retardant polymeric material to drop down sharply. The surface modification of magnesium hydroxide in order to increase the compatibility between Mg(OH)2 particles and polymers can enhance the mechanical strength of composites (Wang *et al.* 2001).

Finally, to improve the properties of composites made of PMMA, some changes in proposed structures are necessary. Therefore, in this study, Nano-magnesium hydroxide and aluminum hydroxide nanoparticles as mineral retardant fillers are synthesized and identified by XRD and SEM. Then, composites of PMMA with different ratios of Mg (OH) 2 were built DSC-TGA and LOI test were carried out on them. At the end, composites composed of PMMA with different ratios of Mg(OH)2 and Al(OH)3 were made and the same tests with the previous composites were done on them and thermal behavior of composites containing aluminum hydroxide and composites lacking aluminum hydroxide were compared.

MATERIALS AND METHODS

All materials and solvents used in the synthesis of Nano magnesium hydroxide and Nano aluminum hydroxide were purchased from Sigma Aldrich and Merck and used without any further purification. the melting points (ºC) of the complexes were recorded on a Kruss instrument and TG/DSC curves were obtained from a Diamond TGA PerkinElmer 60 Hz. Poly methyl methacrylate (PMMA) was obtained from I Tech polymer company Iran with melt mass flow rate (MFR) of 0.9 – 27 g/10 min at 125ºC and density 1.15 - 1.19 g/cm3.. Infrared spectra were recorded as KBr disks on Tensor 27 Bruker spectrophotometer. The evaluation of Al(OH)3oxide and synthesized Nano composites were monitored by powder X-ray diffraction Philips PW 1800 diffractometer with Cu Kα radiation. Atomic force microscopy was carried out on a Denmark Dual scope/Raster scope C26, DME microscope. Scanning electron microscopy measurements was performed on a VEGA\\TESCAN at an accelerating voltage of 15 kV. The LOI values were measured using a ZRY type instrument (made in China) on the sheets of120 · 60 ·3 mm3 according to ASTM D2863-77 standard.

2.1 Synthesis of Nano magnesium hydroxide

To prepare magnesium hydroxide nanoparticles, first 5 g (MgSO4.7H2O) was solved in 40 ml of deionized water and 5 ml of sodium hydroxide was added to it. Then, the obtained solution was stirred with 1600 rpm for 1 hour

in 60 ºC. The obtained solution was passed from Nano filter paper by Buchner funnel and then was rinsed with deionized water in order to completely rinse the Ammonia. The remaining sediment was put in an oven with 105 ºC for 8 hours and finally magnesium hydroxide nanoparticles will be synthesized.

2.2 Synthesis of Nanoaluminum hydroxide

1g Al(NO3)2 9H2O were dissolved 33 ml of water. Then various precipitation agents ethylenediamine, propylene diamine, triethylenetetramine, tetraethylenepentamine were added until the pH of the solution adjust to 8. A white precipitate is obtained confirming the synthesis of Al(OH)3. The white precipitate was centrifuged and washed with distilled water to removing the surfactant, and later dried at 70°C for 24h in a vacuum dryer.

Preparation of PMs composites

In this study, 4 samples with different percent of magnesium hydroxide and PMMA were prepared to study thermal properties that were named as follows:

To prepare the composite samples, a two-armed mixer device was used and its temperature and speed were adjusted respectively as 110ºC and 60 rpm and then 10 minutes was considered for the formation of composites.

2.4 Preparation of PMAs composites

To study the effect of aluminum hydroxide nanoparticles in retardaning PMs composite samples, 4 samples of PMAs composite were prepared with different percent of aluminum hydroxide, magnesium hydroxide and PMMA and then were named as follows:

To prepare the composite samples, a two-armed mixer device was used and its temperature and speed were adjusted respectively as 110ºC and 50 rpm and then 15 minutes was considered for the formation of composites.

Table 1. The properties of PMs composite samples	
Compounds	Composite
PMMA 90% - Mg(OH)210%	PM-10
PMMA80% - Mg(OH)220%	PM-20
PMMA70% - Mg(OH)230%	PM-30
PMMA60% - Mg(OH)240%	PM-40

Table 2. The properties of the produced composite samples	
Compounds	Composite
PMMA90% - Mg(OH)25%–Al(OH)35%	PMA-10
PMMA80% - Mg(OH)210%–Al(OH)310%	PMA-20
PMMA70%- Mg(OH)215%–Al(OH)315%	PMA-30
PMMA60% - Mg(OH)220%–Al(OH)320%	PMA-40

Thermal gravimetric

The tests related to differential thermal analysis were performed by TGA device under ASTM-E1131 standard. Thermal analysis, changes in the sample weight (losing the weight of the sample that is controlled under a heating program) is considered as the basis of Thermogravimetry analysis (TG) and test conditions are similar for all produced composites and the temperature increases to 10 centigrade per minute and the temperature range from ambient conditions is to 600 ºC.

Characterization of Mg(OH)2 Nanoparticlesand of Al(OH)3Nanoparticles

The typical powder XRD pattern of Mg(OH)2 nanoparticlesis given in Fig. 1. All diffraction peaks canbe indexed as the hexagonal structure of Mg(OH)2 with the lattice constants comparable to the values of JCPDS7-239. No XRD peaks arising from impurities such as NaCl and MgO were detected. Moreover, the peaks of the samples are significantly broadened. This indicates that the Mg(OH)2 particles have a very small grain size, which can be calculated from the broadened XRD peaks by means of Scherrer formula (Staudenmaier, 1898).

XRD pattern of Al(OH)3 nanoparticles is shown in Fig. 2. The pattern of as prepared Al(OH)3 nanoparticles is indexed as a pure monoclinic phase (space group:P21/n) which is very close to the literature values (JCPDS No. 33-0018), the narrow sharp peaks indicate that Al(OH)3 nanoparticles are well crystallized.

The crystallite size measurements were also carried out using the Scherrer equation, $D_c = K\lambda/\beta\cos\theta$, Where b is the width of the observed diffraction peak at its half maximum intensity (FWHM), K is the so-called shape factor, which usually takes a value of about 0.9, and λ is the X-ray wavelength (CuKα radiation, equals to 0.154 nm). The estimated crystallite size is about 8 nm.
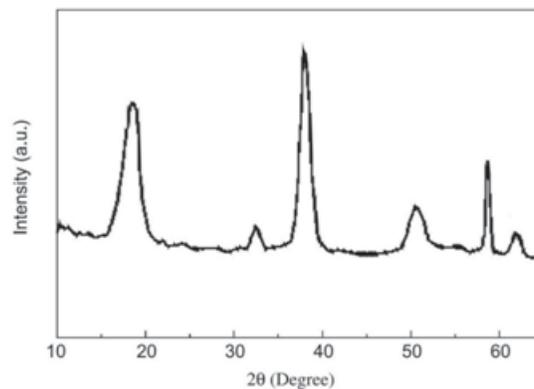
FIGURE 1. Effect of vemicompost and azotobacter on kernel weight

FIGURE 2. Effect of vemicompost and azotobacter on kernel weight

FIGURE 3. Effect of vemicompost and azotobacter on kernel weight
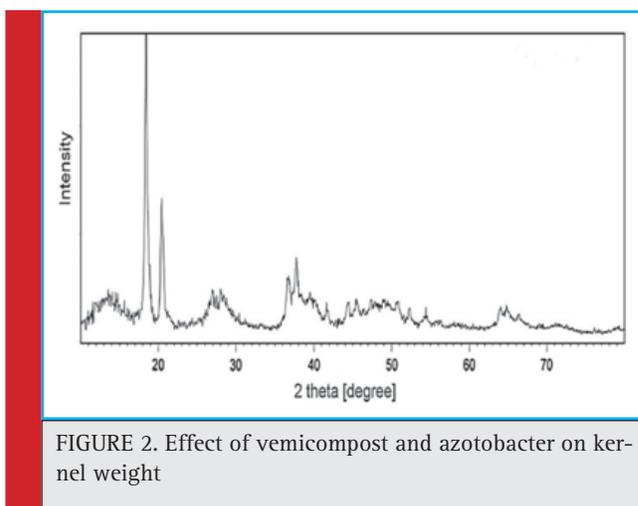
Scanning electron microscopic analysis (SEM) on magnesium hydroxide nanoparticles was shown in figure 3.and Scanning electron microscopic analysis (SEM) on aluminum hydroxide nanoparticles was shown in figure 4. As is clear, the magnesium hydroxide nanoparticles like aluminum hydroxide nanoparticles have a good and uniform distribution.

Thermal analysis

The results of the thermal behavior of composites PMs in Table 4 and the results of the thermal behavior of PMAs composites are shown in Table 5. Degradation began in PMs series of composite with increasing $Mg(OH)_2$ nanoparticles in three samples are almost identical an at the final sample due to changes in the physical structure of PMMA it was decreased. The peak temperature of degradation and thermal resistance of composites in

FIGURE 4. Effect of vemicompost and azotobacter on kernel weight
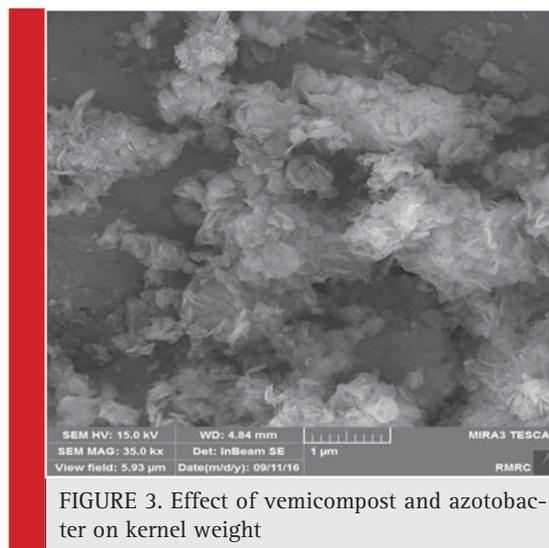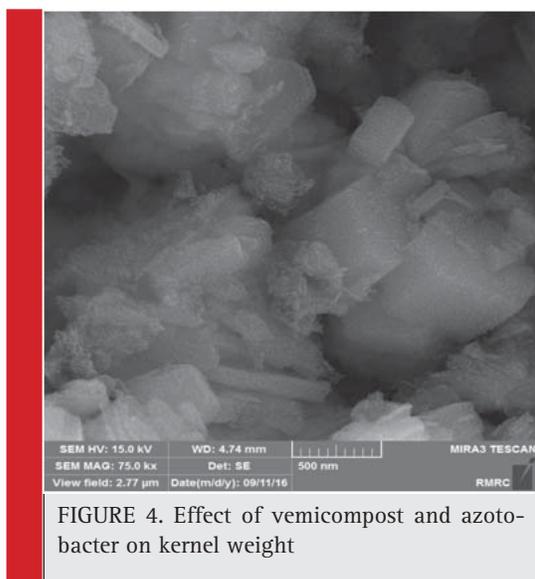
Table 4, increases from top to bottom that shows the effect of Nano-$Mg(OH)_2$ nanoparticles in burning behavior of composites this series. In Table 5, thermal behavior of composites of PMAs series is provided and the difference over PMs series is the nanoparticles of $Al(OH)_3$ in produced composites structure. It is well shown that the temperature composites. Degradation temperature in PMAs series is not much different from PMs composite series but peak temperature of degradation in PMAs composite series improved by average of 7 ° C in PMs series.

Analysis of the residual mass of the composite material

The results of the composite residual mass after thermal analysis is provided in Table 6 for composites of PMs Series and in Table 7 it is provided for composites of PMAs. It is well shown that by increasing the amount of retardant in the composite structure, a smaller percentage of them disappears. By comparing Tables 6 and 7 it clear that apart from PMA-20 composite that its percentage of residual mass compared to composite of PM-20 is significantly improved, the percentage of residual mass of other composites in Tables 6 and 7 are almost the same in comparison.

Limited Oxygen Index (LOI) analysis

LOI test results of PMs composites and PMAs composites series are respectively shown in Figure 5 in Figure 6. It is well shown that by increasing the percentage of $Mg(OH)_2$, the amount of oxygen required for combustion of samples has increasing trend. LOI of pure PMMA sample was 17 % and with an increase of $Mg(OH)_2$ in PMMA it had a rising trend so that LOI of PM-40 that 40% of composite products is $Mg(OH)_2$ is 30. In the case of Figure 6, the same trend is visible and LOI of PAM-

Table 3. Thermal behavior of PMs composites Series			
End Temperature of demolition ºC	Peak Temperature of demolition ºC	First Temperature of demolition ºC	Sample
425	301	199	PM-10
430	300	198	PM-20
442	330	200	PM-30
490	420	190	PM-40

Table 4. Thermal behavior of PMAs composites Series			
End Temperature of demolition ºC	Peak Temperature of demolition ºC	First Temperature of demolition ºC	Sample
430	298	200	PMA-10
436	301	200	PMA-20
450	331	220	PMA-30
495	410	188	PMA-40

Table 5. Amount of residual mass after the thermal Analysis in PMs composites Series	
The Remaining Percentage	Sample
3.22	PM-10
8.70	PM-20
24.67	PM-30
49.33	PM-40

Table 6. Amount of residual mass after the thermal Analysis in PMAs composites Series	
The Remaining Percentage	Sample
4.38	PMA-10
21.05	PMA-20
26.56	PMA-30
49.19	PMA-40

40 composite is 31.5 that 20% of produced sample is $Mg(OH)_2$ and 20% is $Al(OH)_3$.

By comparing Figures 5 and 6, the close test results of LOI between PMAs and PMs series composites is realized and it is clear that except PMA-20composite, which had about 22.5 % favorable performance than PM-20 composites, other sample results are almost the same.

RESULTS AND DISCUSSION

Given the importance and high consumption of poly methyl methacrylate (PMMA) in different industries including construction, automotive, electronics, etc. in this project we tried to improved thermal resistance of PMMA using magnesium hydroxide and aluminum hydroxide nanoparticles as additives. Although the addition of fillers weakens the mechanical and physical properties and behavior of the polymer. According to
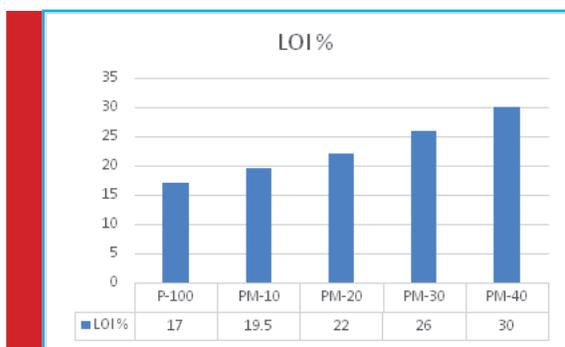
FIGURE 5. Effect of vemicompost and azotobacter on kernel weight
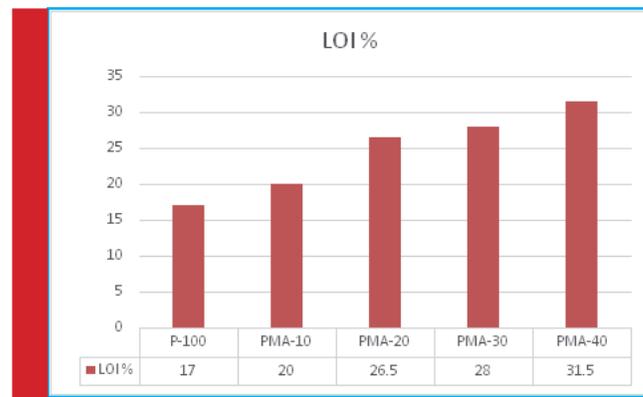
FIGURE 6. Effect of vemicompost and azotobacter on kernel weight

the results, resistance of composite made from magnesium hydroxide particles against fire increased and melt rate increased as well. Increase in the amount of magnesium hydroxide in composite improved the residual mass of composite. The LOI test results show that composite had achieved a good resistance against fire and smoke of process of burning is reduced. By comparing the degradation temperature magnesium hydroxide and aluminum hydroxide nanoparticles it can be concluded that the degradation temperature was between 180° C -200 ° C and given the degradation reaction reduced the flammability of polymer and produced Al2O3 provides a thermal insulation coating and the resulting water vapor diluted the flammable gases and provided a thin protective gas layer. However, due to lower degradation point compared to magnesium hydroxide, when it was used in PMAs composites it decreased the peak degradation temperature of the composite compared to degradation temperature of PMs series. It is because of Magnesium hydroxide nanoparticles degradation temperature, which is about 350° C. The residual mass percentage of composite and LOI test results indicated an improvement in polymer properties of PMAs series.

Generally, by comparison of eight composites, average degradation temperature is more favorable in PMAs series and according to initial thermal resistance against the destruction of the best examples of PAM-30 is made of composite.

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