The Effect of Mg(OH)$_2$ Nanoparticles on the Thermal Stability and Flame Retardancy of Paraloid Nanocomposites

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Abstract

Paraloid-Mg(OH)$_2$ nanocomposites were synthesized via sonochemical method. Nanostructures were characterized by XRD and SEM. Thermal stability behavior of paraloid filled with magnesium hydroxide was investigated by thermogravimetric analysis (TGA). The influence of Mg(OH)$_2$ nanostructures on the flame retardancy of the paraloid matrix was studied using UL-94 analysis. Our results show that the Mg(OH)$_2$ nanostructure can enhance the flame retardant property of the paraloid matrix. The enhancement of flame retardancy of nanocomposite is due to endothermic decomposition of Mg(OH)$_2$ that absorbs energy and simultaneously releases of water (dilutes combustible gases). Photo-catalytic activity of the nanoparticles was evaluated by monitoring the degradation of methyl orange (MeO) in an aqueous solution.

1. Introduction

Scientists for improvement properties of composite materials investigate composites with nano-fillers, leading to the development of nanocomposites. Improvement the fire retardant behavior of polymers is a major challenge for extending their use for most applications. 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. As 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. Metal oxide also provides heat insulation by reflecting heat when it accumulates on the surface. One of the main problems of magnesium hydroxide is that for successful flame 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]. Nanoparticles disperse into the polymeric matrix homogeneously and hence leads to formation of a

condensed char during the combustion. Recently, Baglioni et al. prepared different metal hydroxide nanoparticles by various chemical reactions [10-14]. These products were used as consolidants for wall paintings (frescoes), paper, stone and wood, as reported in the remarkable scientific papers of the Baglioni group. Paraloid is a commercial material with good chemical resistance properties. It is widely used as an important polymer for cultural heritage application because of its desirable properties. One of the main disadvantages of the paraloid is its low thermal stability; therefore there is a need to increase its thermal stability [15-18].

A variety of synthesis strategies for metal hydroxides nanostructure materials have been described. Sonochemical method as a simple, effective and novel route has been developed to prepare nanostructures. Sonochemical method operated under ambient conditions. Ultrasonic waves propagate through the solution causing alternating high and low pressure in the liquid media. Ultrasonic irradiation caused cavitation in a liquid medium where the formation, growth and implosive collapse of bubbles occurred. The collapse of bubbles with short lifetimes produces intense local heating and high pressure. These localized hot spots can generate a temperature of around 5000 °C and a pressure of over 1800 kPa and can drive many chemical reactions [1].

In this work, paraloid-$Mg(OH)_2$ nanocomposites were synthesized via sonochemical method. Results show that the $Mg(OH)_2$ nanostructure can enhance the flame retardancy and thermal stability of the paraloid matrix.

2 Experimental

2.1 Materials and characterization

Mg(NO3)3.6H2O, poly ethylene glycol (MW:20000), cethyl tri methyl ammonium bromide

and NaOH were purchased from Merck Company. All the chemicals were used as received without further purifications. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered CuKα radiation. A multiwave ultrasonic generator (Bandeline MS 72) equipped with a converter/transducer and titanium oscillator operating at 20 kHz with a maximum power output of 100 W was used for the ultrasonic irradiation. Scanning electron microscopy (SEM) images were obtained using a LEO instrument (Model 1455VP). Prior to taking images, the samples were coated by a very thin layer of Pt (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation.

2.2. Synthesis of $Mg(OH)_2$ nanoparticles

$Mg(NO_3)_2$ 6H_2O (1 g) is dissolved in 20 mL of water. NaOH solution (10 mL, 1 M) is then slowly added to the mentioned solution under radiation (60 W) for 20 minutes. The white precipitate is then centrifuged and rinsed with distilled water and left in an atmosphere environment to dry. A schematic diagram for experimental setup used for this sonochemical reaction is given in Fig. 1.

For synthesis of nanocomposite, paraloid (4.5g) is first dissolved in acetone (20 mL). The $Mg(OH)_2$ nanoparticles (0.5 g) are dispersed in acetone (10 mL) by ultrasonic waves. The nanoparticles dispersion is then slowly added to the paraloid solution. The new solution is then stirred for 8 hours. To evaporate the solvent, the product is casted on a glass plate and left for 24 hours.

3. Results and discussion

XRD pattern of $Mg(OH)_2$ nanoparticles is shown in Fig. 2 which is indexed as a pure cubic phase (space group: P-3m1). The experimental values are

very close to the literature (JCPDS No. 44-1482). The crystallite size measurements were carried out using the Scherrer equation (Eq. 1),

$$D_c = 0.9\lambda/\beta\cos\theta \qquad (1)$$

where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK$_\alpha$ radiation, 0.154 nm). The estimated crystallite size is about 15 nm.
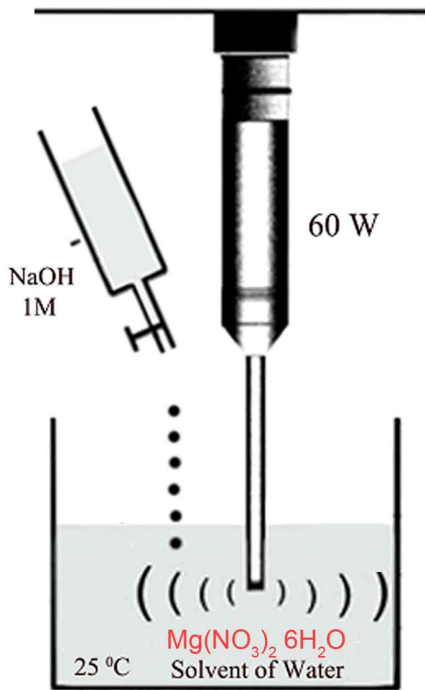

**Fig. 1**. Schematic diagram of preparation of Mg(OH)$_2$ nanoparticles
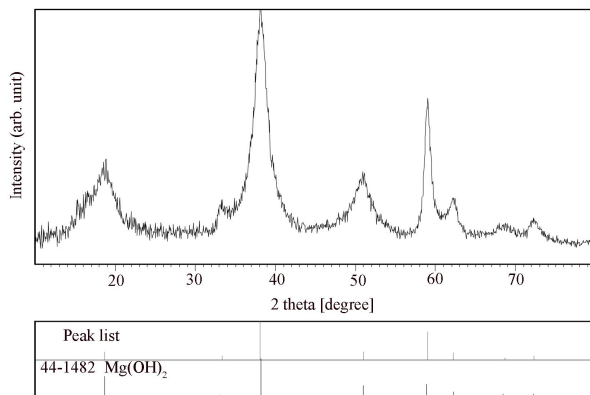
Fig. 2. XRD pattern of Mg(OH)$_2$ nanoparticles

SEM images of the Mg(OH)$_2$ without using ultrasonic waves is shown in Fig. 3a which approve bulk product is achieved. SEM image of the Mg(OH)$_2$ obtained at 60W at 30 min is illustrated in Fig.3b. Nanoparticles with average diameter of 80nm are obtained. The effect of different surfactants such as polymeric, anionic and cationic on the morphology of magnesium hydroxide nanostructures are displayed in Fig 4a-c. By using poly ethylene glycol (PEG) bulk product was obtained, it seems PEG remained on the surface of product. In presence of cethyl tri methyl ammonium bromide (CTAB) nanoparticles were synthesized and image show nanoparticles tending to form nanorods. By applying sodium do decyl benzene sulfonate (SDBS) nanoparticles were achieved.
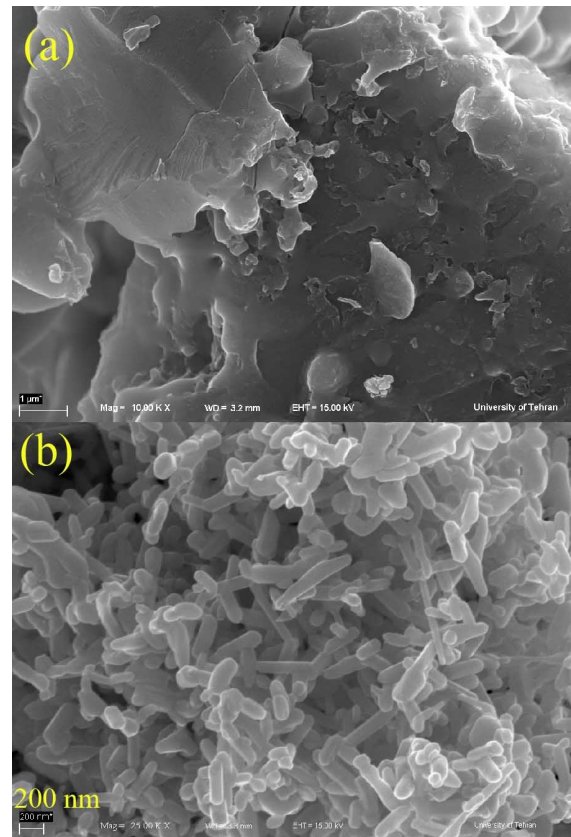
Fig. 3. SEM images of Mg(OH)$_2$ (a) without (b) under ultrasonic waves
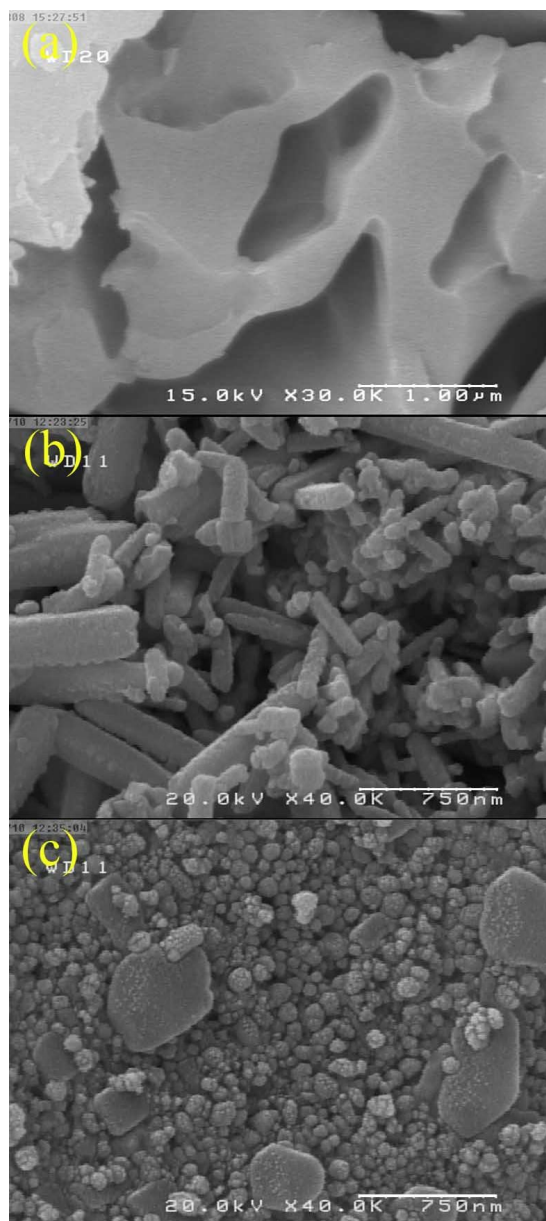
Fig. 4. SEM images of Mg(OH)$_2$ (a) PEG (b) CTAB (c) SDBS

The influence of CTAB (cationic) and SDBS (anionic) surfactant on the morphology of the product is schematically depicted in Fig.5. We studied the Mg(OH)$_2$ interaction between the nanoparticles surrounded by paraloid chains.

In the last two decades polymer matrix nanocomposites have also been extensively investigated, since just a small amount of

nanoparticles as an additive leads to production of novel materials with excellent physicochemical properties [2-4]. TGA curves of pure paraloid and paraloid-Mg(OH)$_2$ nanocomposites are illustrated in Figs. 6a and 6b respectively.
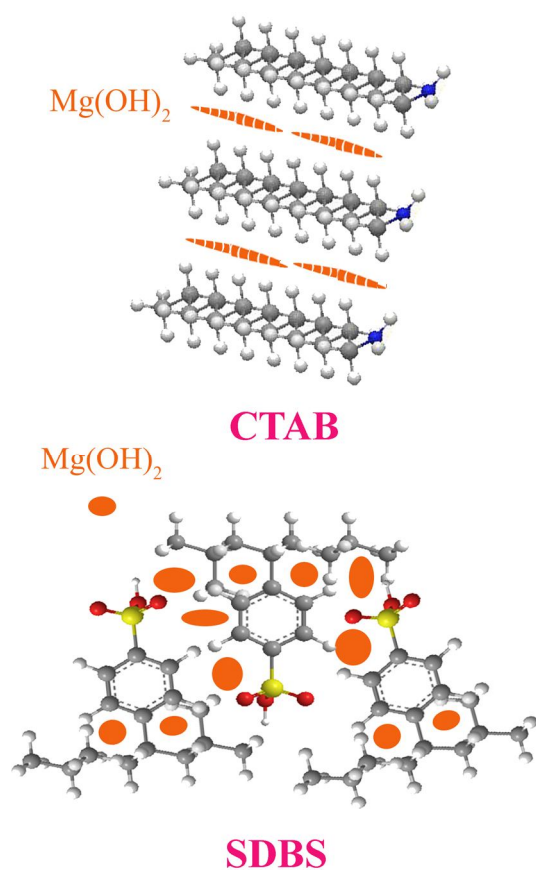
**Fig. 5.** Effect of cationic and anionic surfactant on the morphology of the product

Thermal decomposition of the paraloid nanocomposite shift towards higher temperature in the presence of Mg(OH)$_2$ nanostructures.

Mg(OH)$_2$ has barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. So the initial degradation temperature (Tonset) increases. The effect of nanostructure on the flame retardant properties has been considered using UL-94 test. In

UL-94 a bar shape specimen of plastic 127 × 13 × 1.6 mm is positioned vertically and held from the top. A Bunsen burner flame is applied to the specimen twice (10 s each). A V-0 classification is given to material that is extinguished in less than 10 s after any flame application, drips of particles allowed as long as they are not inflamed. A V-1 classification is received by a sample with maximum combustion time < 30 s, drips of particles allowed as long as they are not inflamed.

The sample is classified V-2 if it satisfies the combustion time criteria of V-1, but flaming drips are allowed [3]. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s.
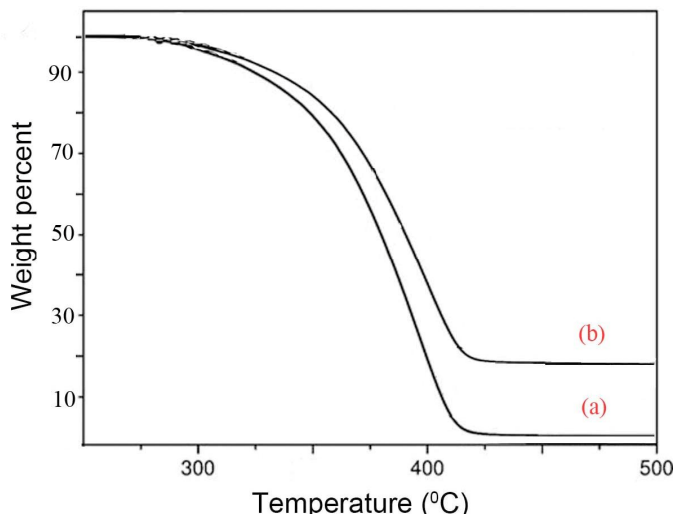

Fig. 6. TGA curves of (a) pure paraloid (b) paraloid-$Mg(OH)_2$ nanocomposite

The results of UL-94 tests for paraloid and paraloid-$Mg(OH)_2$ nanocomposites are N.C and V-0 respectively. The results show that the $Mg(OH)_2$ nanostructure can enhance the flame retardant property of the paraloid matrix. The enhancement of flame retardancy of nanocomposite is due to endothermic decomposition of $Mg(OH)_2$ that

absorbs energy and simultaneously releases of water (dilutes combustible gases).

The photo-catalytic activity of the nanoparticles was evaluated by monitoring the degradation of methyl orange (MeO) in an aqueous solution.

0.05 g of nanoparticles was dispersed in 10 ml of MeO solution (3ppm). Pure methyl orange and MeO in the presence of $Mg(OH)_2$ nanoparticles (30 and 60 min) are illustrated in Fig 7a-c.
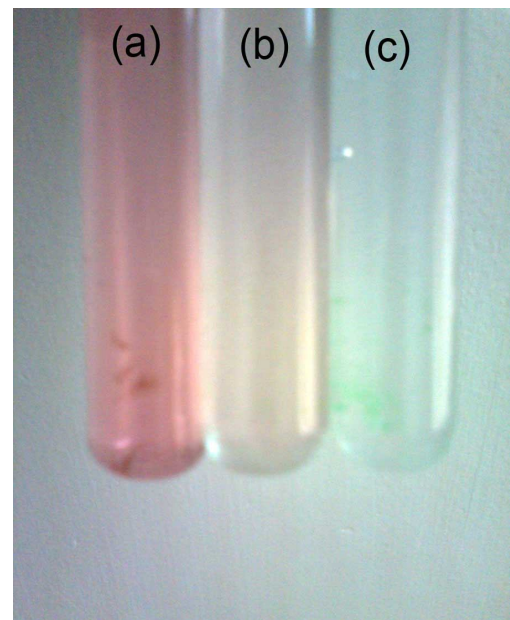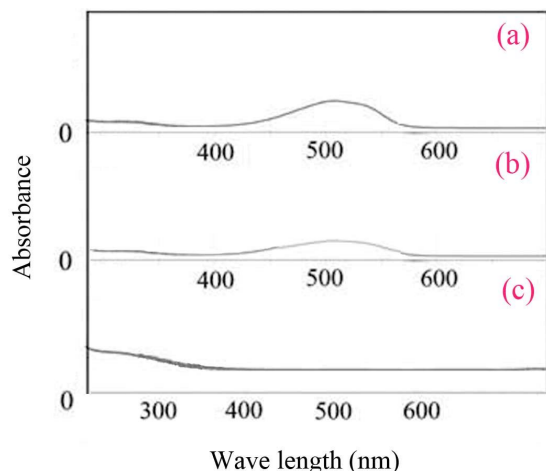

Fig. 7. (a) pure MeO (b) 30 min (c) 60 min.

4. Conclusion

$Mg(OH)_2$ nanoparticles were prepared by a simple sonochemical process at room temperature. Nanoparticles were then added to paraloid matrix. The influence of the inorganic phase on the thermal properties and flame retardancy of paraloid matrix was studied. The results show that the $Mg(OH)_2$ can enhance the thermal stability and flame retardant property of the paraloid matrix. The enhancement of flame retardancy of nanocomposite is related to endothermic decomposition of $Mg(OH)_2$ that absorbs energy and simultaneously

dilutes combustible gases. $Mg(OH)_2$ has also barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer.

Fig. 8. Absorption spectra (a) pure MeO (b) 30 min (c) 60 min.

As time increased, more and more MeO were adsorbed on the nanoparticles catalyst, until the absorption peak (λ = 510 nm) vanish. The MeO concentration decreased rapidly with increasing time, and the peak almost disappeared after 60 min. Uv-visible spectra of pure methyl orange and methyl orange in presence of nanoparticles are shown in Fig 8a-c respectively.

Acknowledgements

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