Australian Journal of Basic and Applied Sciences, 10(15) October 2016, Pages: 167-176

AUSTRALIAN JOURNAL OF BASIC AND APPLIED SCIENCES

ISSN:1991-8178 EISSN: 2309-8414
Journal home page: www.ajbasweb.com

Production Nanoparticles by Chemical Precipitation for Use as Flame Retardant of PVC

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A R T I C L E I N F O

Article history:
Received 26 August 2016
Accepted 10 October 2016
Published 18 October 2016

Keywords:
Polyvinyl chloride, polyvinyl alcohol, magnesium hydroxide, aluminum tri-hydrate, nanoparticle, burning rate, flame retardant.

A B S T R A C T

Magnesium hydroxide(MH) and Aluminum tri-hydroxide (ATH) nanostructure as an effective flame retardant were synthesized by chemical precipitation route. This paper study the effect of the Magnesium hydroxide and Aluminum tri-hydroxide nanoparticles on flame retardancy and mechanical properties of polyvinyl chloride (PVC). (1) Phr of (MH),(ATH) and (2) Phr of (MH+ATH) nanoparticles are individually added to PVC and mixed well. The composite is synthesis by use co-rotating twin screw extruder at (145-160) °C and at screw speed (25 and 38 rpm). Burning rate of nanocomposite calculate according to (ASTM D 635-03). Different mechanical techniques are used to evaluate the characteristics of polymer nanocomposites: Tensile strength, Creep, hardness. The results of PVC/ MH, PVC/ATH and PVC/MH/ATH nanocomposite showed that burning rate decreasing with addition (MH),(ATH)and(MH+ATH) nanoparticles, temperature is lower with addition. The tensile strength decreasing with nano (MH),(ATH) and (MH+ATH) addition for PVC. The hardness increasing with addition (MH),(ATH) and (MH+ATH)and the creep is more improved.

INTRODUCTION

The most commonly used mineral flame retardants are aluminum tri-hydroxide and magnesium hydroxide. As the temperature rises magnesium hydroxide shows an endothermic decomposes (1.356 kJ/g) about 330◦C and absorbs energy. Moreover, it releases nonflammable water which dilutes combustible gases. residual magnesium oxide also provides heat insulation by reflecting heat when it accumulates on the surface (Hollingbery, L.A. and T.R. Hull, 2010).

$$Mg(OH)2(s) \rightarrow MgO(s) + H2O(g) \qquad (1)$$

Aluminum tri- hydroxide shows endothermic decomposes (1050 kJ/kg) about 220 ^{5}C, also it releases nonflammable water that dilutes combustible gases and Residual aluminum oxide protect the surface.

$$2Al(OH)3(s) \rightarrow Al2O3(s) + 3H2O(g) \qquad (1)$$

PVC is a thermoplastic polymer that can be processed by a variety of techniques like injection molding, extrusion, blow molding, and compression molding. PVC is an amorphous, rigid polymer due to the large side group (Cl, chloride) with a T_g of 75 to 105ºC and softens at about 85°C. Also in rubbers, (Cato Brede, Ingun Skjevrak and Per Fjcldal, 2003; Miley, J., 1996; Sherif D. El Wakil, 1998). PVC is one of the largest volume

To Cite This Article: Zuhair Jabbar Abdul Ameer and Diyar Hussein Habbeb., Production Nanoparticles by Chemical Precipitation for Use as Flame Retardant of PVC. ***Aust. J. Basic & Appl. Sci.,*** *10(15): 167-176, 2016*

commodity plastics produced in the world and is expected to continue with a good high growth rate. PVC is a rigid plastic in un-plasticized state, but, in the presence of plasticizers, PVC is a flexible plastic. PVC is used in a wide range of applications because of its combined properties of high modulus, ease of fabrication, low flammability and low cost (Xinliang Yu, 2010), Nanoparticles are particles with at least one dimension at 100 nanometers or less. The properties of many conventional materials change when converted to nanoparticles; this is because nanoparticles have a greater surface area per weight than larger particles, which causes it to be more reactive to other molecules (Joseph H. Koo, 2006).

2. Experimental:

2.1 Nanoparticles preparation:

2.1.1 Magnesium hydroxide nanoparticles preparation:

-Materials Used:

Magnesium nitrate hex hydrate $Mg(No_3)_2.6H_2O$ was obtain from Himedia, India company. using the basic material to prepare magnesium hydroxide nanoparticles, Ammonia (NH_3)was obtain from Central Drugs House company (CDH), using in preparation process of nanoparticles for formation suspension from solution, Polyethylene glycol (PEG) was obtain from Sinopharm Chemical Reagent company. Using as surfactant material and Deionized water.

-The procedure of Synthesis of $Mg(OH)_2$ nanoparticles:

(1)g $Mg(NO_3)_2$ $6H_2O$ was dissolved in (200)mL deionized water by using magnetic stirrer at (50) ̊C for (15)min ,(0.25) g of polyethylene glycol (PEG)was added to the solution at (50) ̊C for (30)min. (20) mL of ammonia was slowly added into the solution under magnetic stirrer ,The white precipitate was centrifuged and washed with deionized water to removing the surfactant, and later dried at 70°C for (24)h in a drying furnace, see figure (2-1).

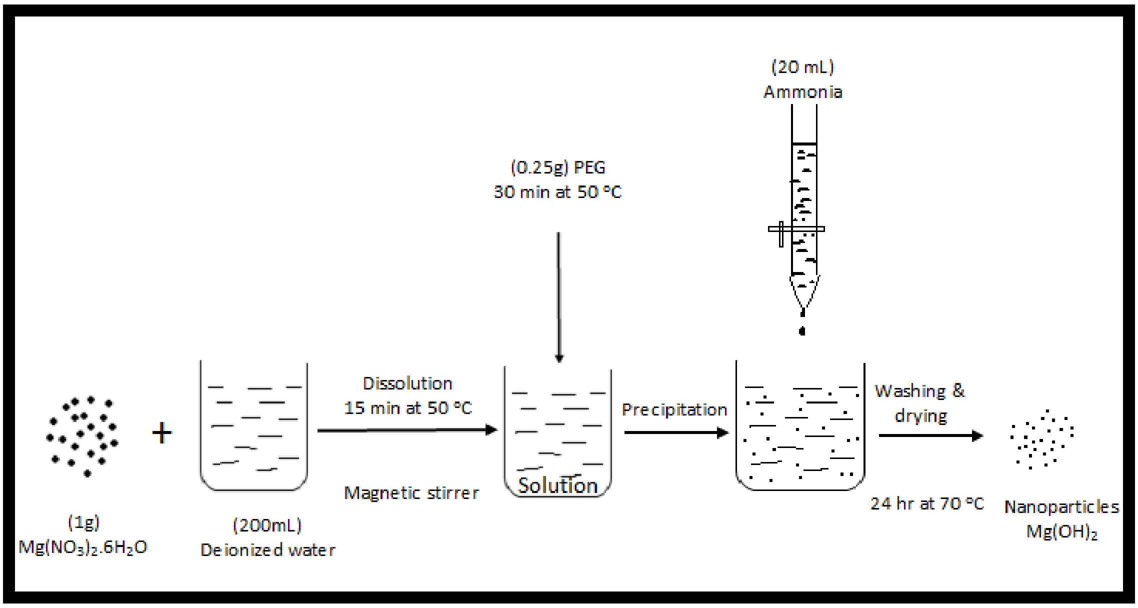

Fig. 2-1: Schematic diagram of Mg(OH)2 nanostructures Preparation.

2.1.2Aluminum tri-hydroxide Nanoparticles Preparation:

-Materials used:

Aluminum tri- hydrate (ATH) powder was obtained from Himedia company, India, used as basic material in process preparation of nanoparticles ,Sodium hydroxide (NaOH) was obtained from Reagent World (USA) company ,Polyethylene glycol (PEG) was obtain from Sinopharm Chemical Reagent company using as surfactant material , Ethanol and deionized water.

-The procedure of Synthesis of $Al(OH)_3$ nanoparticles:

At the first , prepared sodium hydroxide solution by dissolved (39.6)g form NaOH in (110)mL of deionized water. (66g) from $Al(OH)_3$ raw material was dissolved in sodium hydroxide solution on magnetic stirrer at (115) 5C for (30)min to get the sodium aluminum solution. The solution was then cooled down to room temperature and diluted with(220)mL of deionized water. (1.43)g of (PEG) was added to the diluted sodium aluminum solution. The sodium aluminum solution was aged for (5) h to fabricate the Al(OH)3 precipitate. Then, the Al(OH)3 precipitate was washed by deionized water and ethanol and dried at 100° C for (8) h, see figure (2-2).

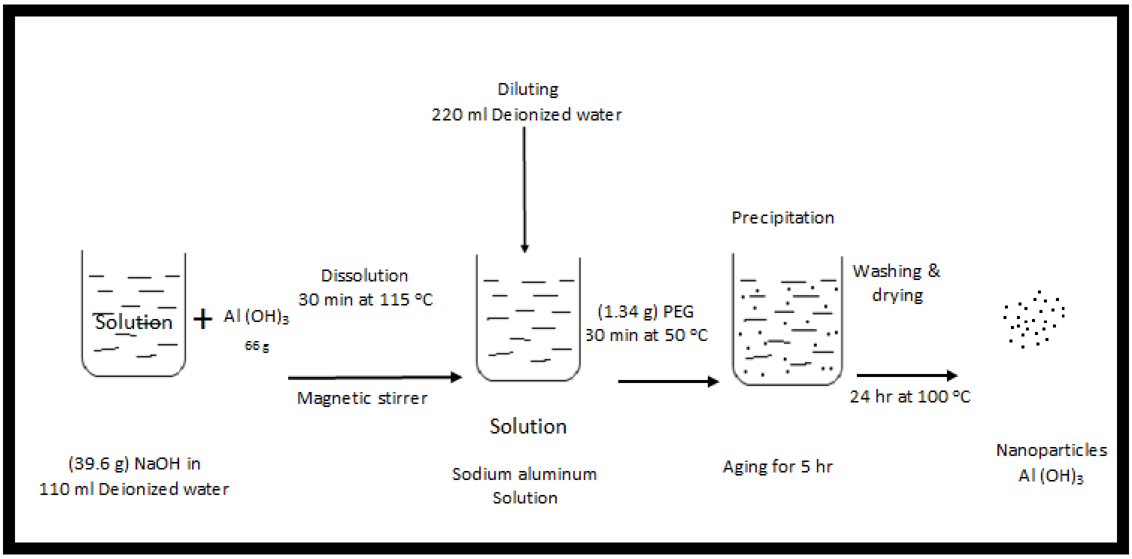

Fig. 2-2: Sketch of $Al(OH)_3$ nanostructures Preparation.

2.2 X-ray Diffraction:

Figure(2-3) and (2-4) illustrate the XRD patterns of prepared magnesium hydroxide and aluminum tri-hydrate. Figure (2-3) show the result of (MH) Nano powder that compared with stander XRD pattern of MH (07-0239) , the peaks appear at 2ɵ= 18.57° at intensity 90 , 2ɵ= 38.016° at intensity 100, 2ɵ= 50.8° at intensity 55and 2ɵ= 58.6° at intensity 35.

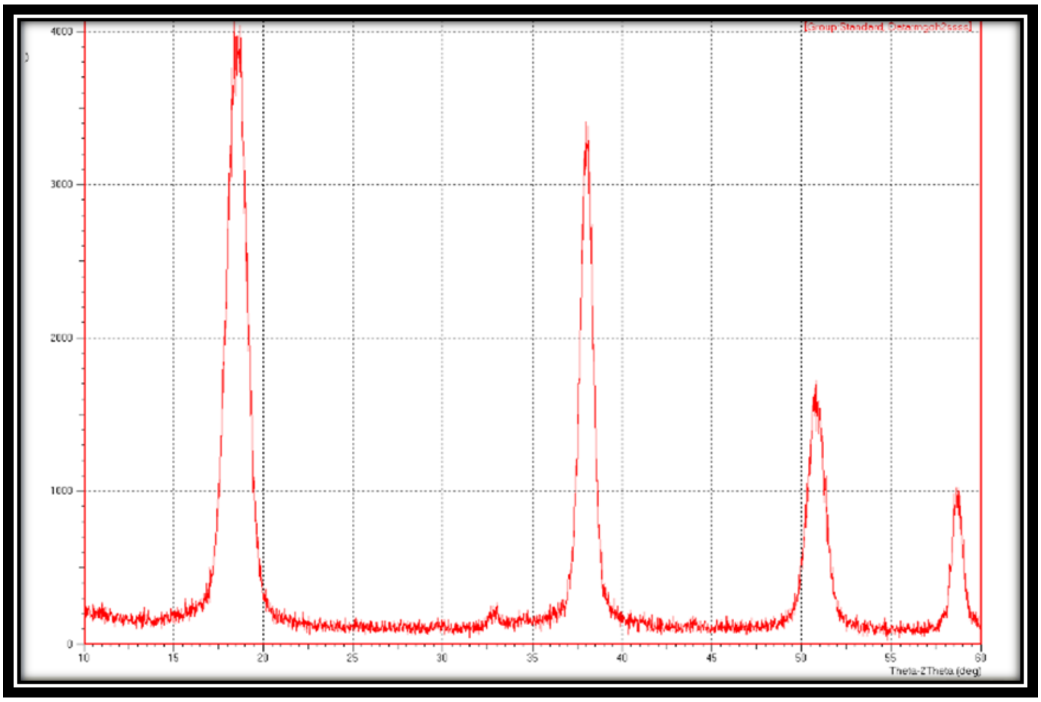

Fig. 2-3: XRD of (MH) Nano powder.

Figure (2-4) show the result of (ATH) Nano powder that also compared with stander XRD pattern of ATH (33-0018) , the peaks appear at 2ɵ= 18.3° at intensity 100 , 2ɵ= 20.2° at intensity 70, 2ɵ= 38.3° at intensity 4, and 2ɵ=54.4° at intensity 30.

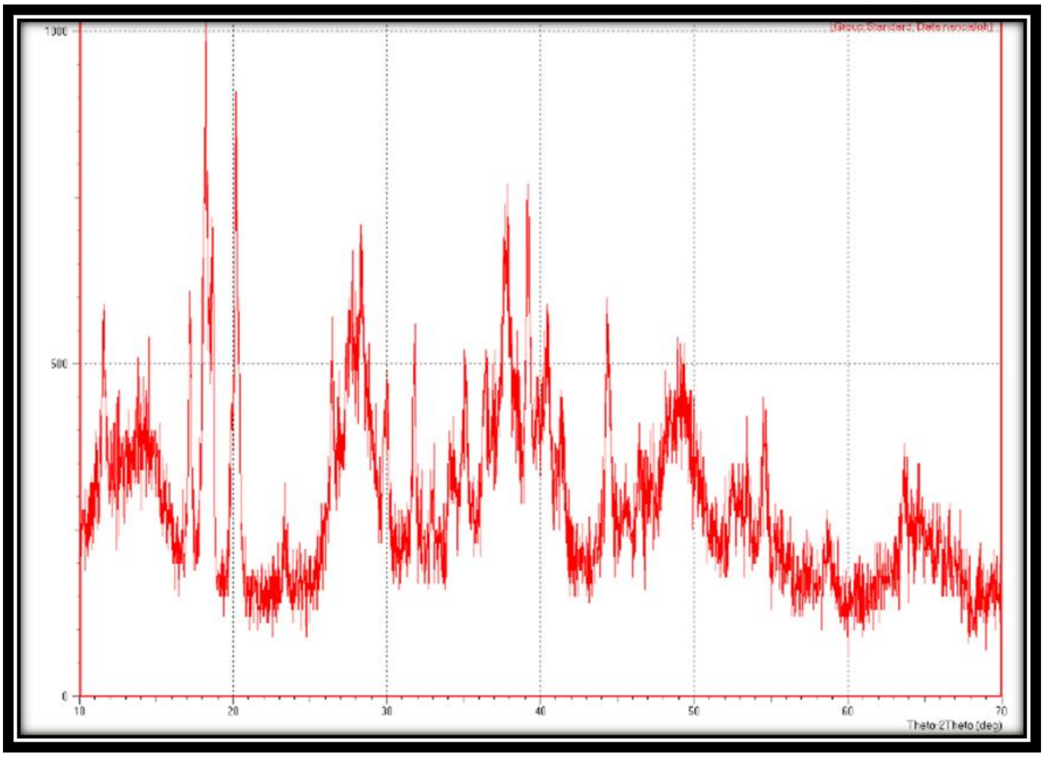

Fig. 2-4: XRD of (ATH) Nano powder.

2.3 Particle Size:

Figure (2-5) and (2-6) show the SEM image that limiting the particle size of prepared nano (MH) and (ATH) powder. Figure (2-5) show the particle size of Nano (MH), that explain the magnesium hydroxide nanoparticle has particle size ranging about (90-100)nm. Figure (2-6) show the particle size of Nano (ATH), which explain it has particle size ranging about (60-80)nm.

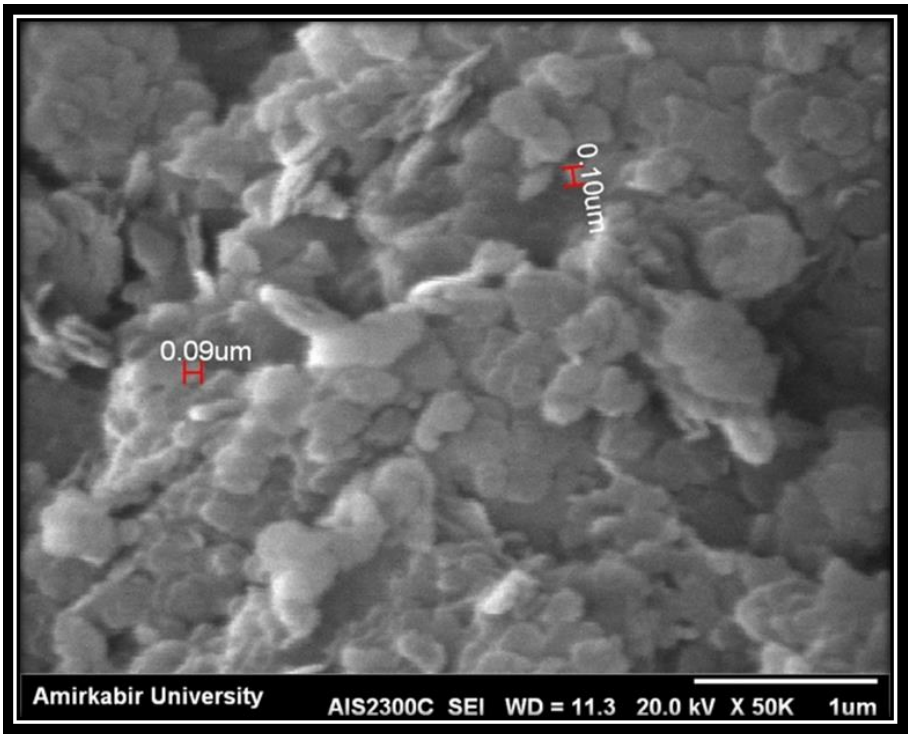

Fig. 2-5: Particle size of magnesium hydroxide nanoparticle.

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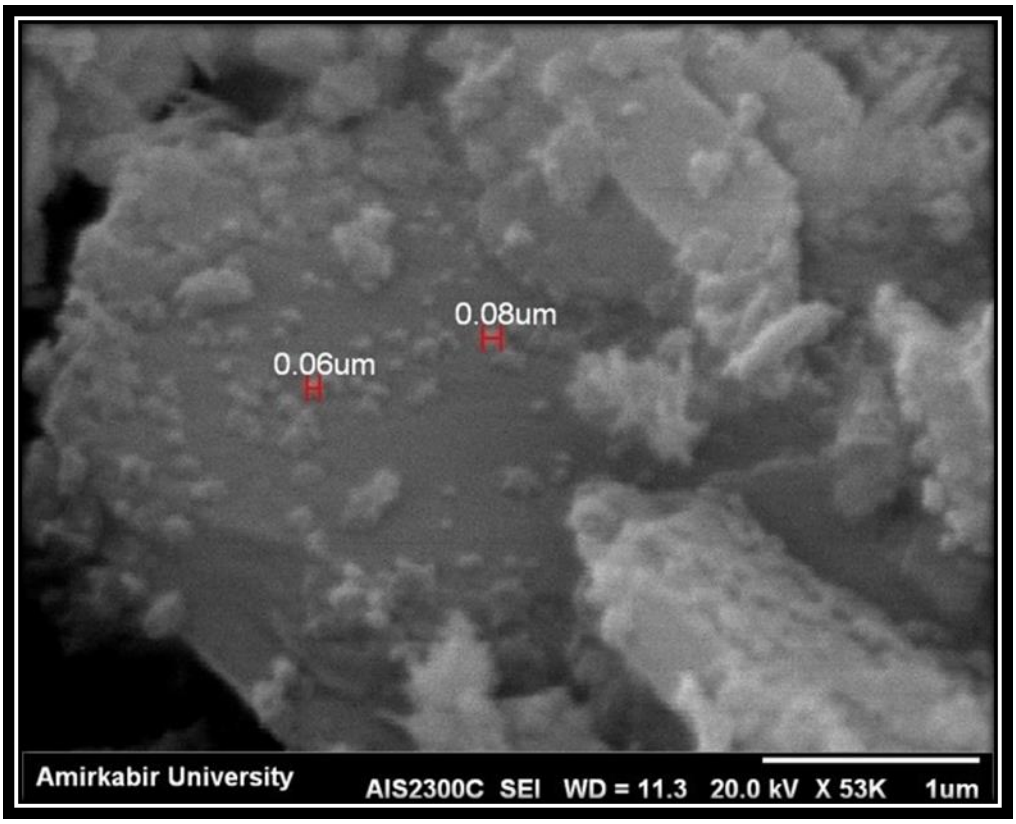


Fig. 2-6: Particle size of aluminum tri-hydroxide nanoparticle.

3- PVC Nanocomposite Preparation:

Materials used:

Polyvinyl chloride (PVC),N,N-Dimethylformamide solvent (DMF),Magnesium Hydroxide Nanoparticles, Aluminum tri-hydroxide Nanoparticles. Samples preparation in percentage according to tables down:

Table 2-1: polyvinylchloride and magnesium hydroxide nanoparticles .

PVC (Phr)	MH Nanoparticles (Phr)
100	1

Table 2-2: Polyvinyl chloride and aluminum tri-hydroxide nanoparticles.

PVC (Phr)	ATH Nanoparticles (Phr)
100	1

Tables 2-3: polyvinyl chloride ,magnesium hydroxide nanoparticles and aluminum tri-hydroxide nanoparticles.

PVC (Phr)	MH Nanoparticles (Phr)	ATH Nanoparticles (Phr)
100	1	1

Preparation the samples of PVC Nanocomposite were achieved at percentage that shown in tables above, by using co-rotating twin screw extruder model (SIJ-30A). To obtain a homogeneous distribution of the nanoparticles was performed the following procedure, Polyvinyl chloride (PVC) was dissolved in (200)ML of(DMF)solvent, by using magnetic stirrer at (125) ^{5}C for (30)min.

Nanoparticles of (MH),(ATH)and (MH+ATH),are mixed in (DMF) solvent by ultrasonic device at 40% of total energy (1200 W) for 10min and 50ºC. Solution of (MH),(ATH)and (MH+ATH), were mixed with dissolver PVC. solution of (PVC) and (MH), (ATH), (MH+ATH), were spilled in cold deionized water, after freezing it exited and filtered from water and, then cutting it to pieces and placed it in a drying furnace at 90 ºC for (24)h. After drying, we cutting it to small pieces, then feed to extruder at (145-160) ºC, (25 – 38) rpm. The extruded material pass through the rolls to obtain sheets from it at thickness (3)mm, then the sheets were cut and mechanically machined. Cutting is performed according to the international standard specifications for each test used.

RESULTS AND DISCUSSION

- Flame test:

Figure (3.1) shows the burning rate that obtained from the flame test (ASTM D 635-03) for PVC composite that contain Nanoparticles from magnesium hydroxide, aluminum tri-hydroxide and the mix of it. see table(3.1)

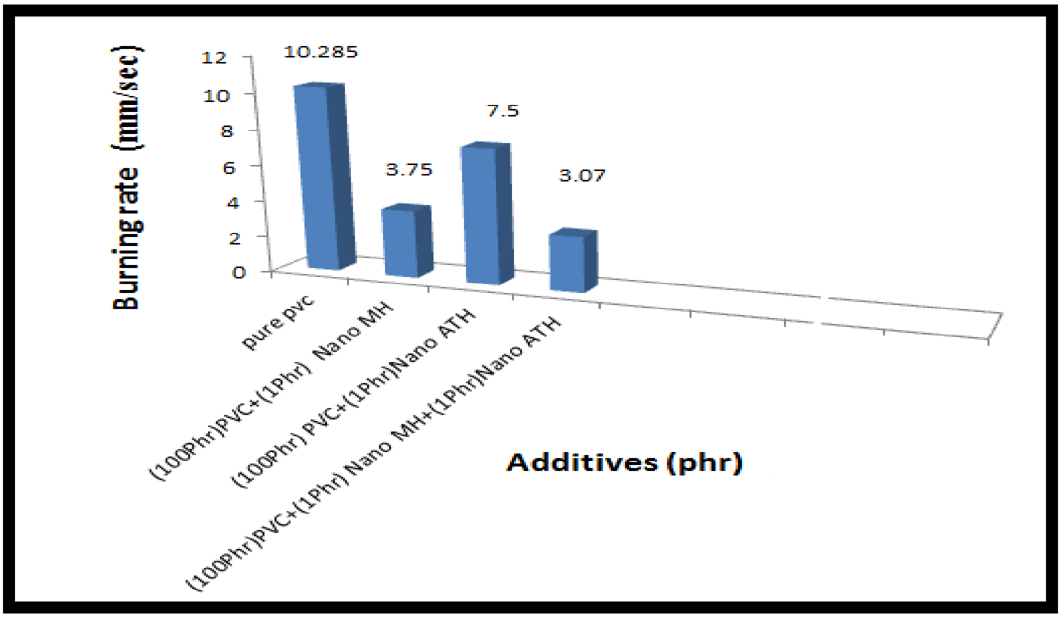
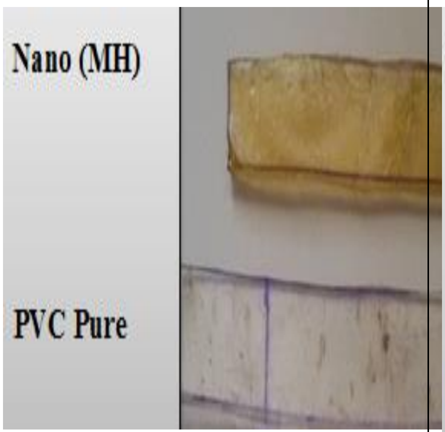
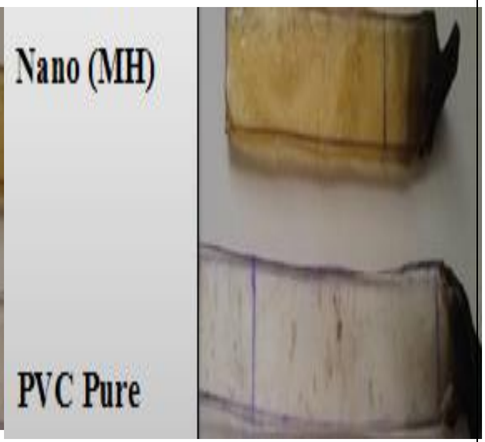


Fig. 3.1: burning rate of PVC nanocomposite, that contain(MH),(ATH)and (MH+ATH).

Table 3.1: photographic image of the flame test samples before and after test.

PVC nanocomposite composition	Before test	After test
PVC+ Nano MH		
PVC+ Nano ATH		

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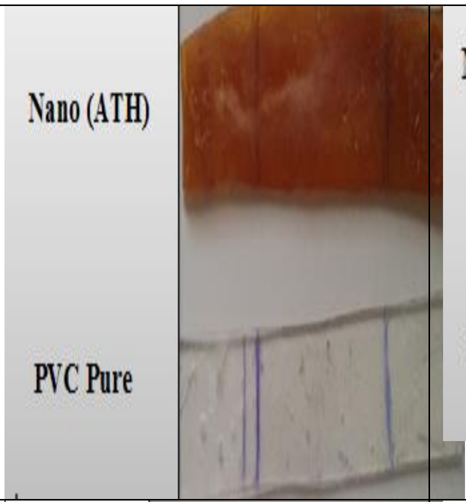
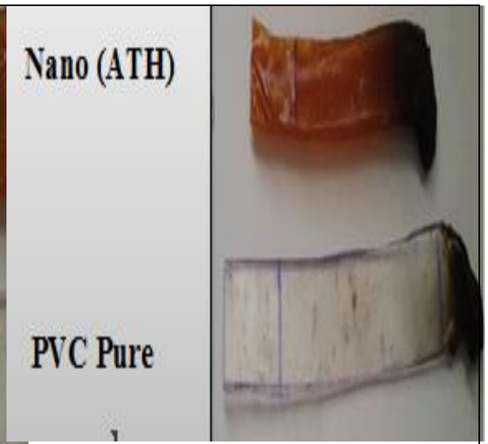
<tr><td></td><td>
</td><td>
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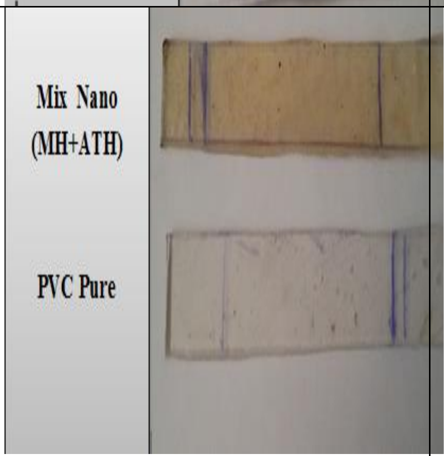
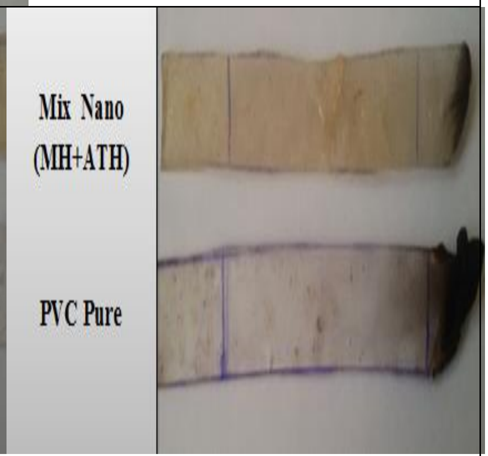
<tr><td>PVC+ Nano (MH+ATH)</td><td>
</td><td>
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Burning rate for PVC is lowered obviously from (10.285)to (3,75) mm/sec, when added (1g) magnesium hydroxide nanoparticles, and to (7.5) mm/sec when added (1g) aluminum tri-hydroxide nanoparticles. Metal hydroxide nanoparticles act as flame retardant through absorbing heat from the system in dehydration and evaporation process, where before the breakdown it absorbed the energy from the fire, this energy begin to increase until reach to the energy required to breakdown of MH to (H_2O) and (MgO), and ATH to (H_2O) ,(Al_2O_3), that cool the region of fire and formation the char, which lead to self-extinguish, magnesium hydroxide is more effective than aluminum tri-hydroxide , this may be arise from higher temperature decomposition of magnesium hydroxide. also this behavior attributed to good dispersion of MH,ATH nanoparticles inside the PVC matrix. where best burning rate of PVC composite is recorded when use the mix nanoparticles, this lowering in burning rate is attributed to synergy between MH-ATH in flame retardancy effect, that lead to liberate much more quantity of water in vapor phase and char in region of the fire.

- Scan Electron Microscope (SEM) Test:

Figure (4-1) and (4-2) show the SEM image of PVC composite that contain nanoparticles from metal hydroxide, figure (4-1) show the morphology of PVC composite containing nano MH, that appears homogeneous of distribution nanoparticle inside PVC matrix, this is due to using ultrasonic device which produce uniform distribution and less agglomeration of nanoparticles.

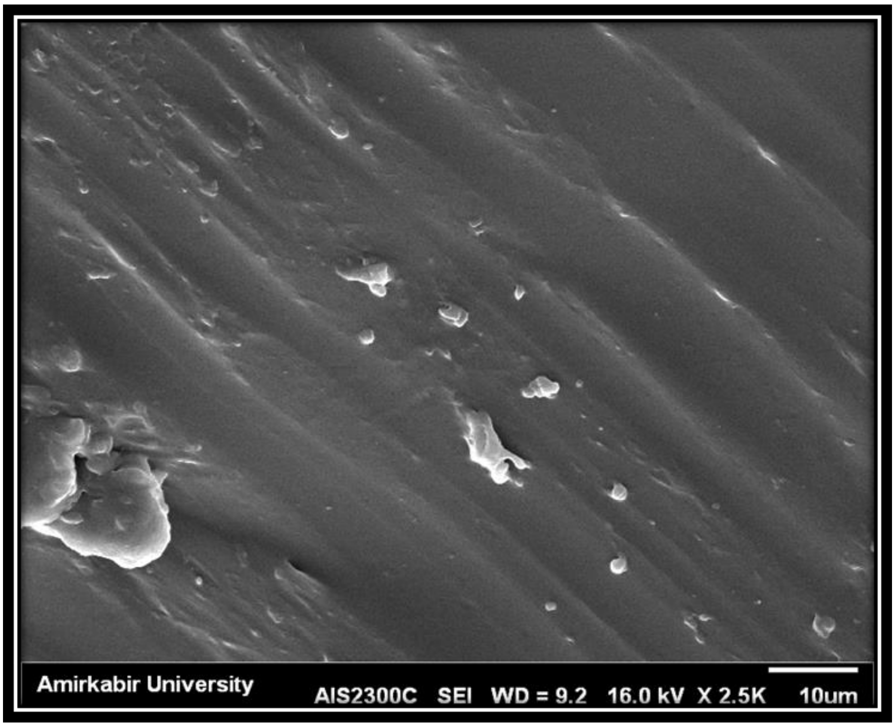

Fig. 4-1: SEM image of PVC composite containing MH nanoparticles.

figure (4-2) show the morphology of PVC composite containing nano ATH, that appears homogeneous of distribution nanoparticle inside PVC matrix, this is due to using ultrasonic device which produce uniform distribution of nanoparticles, also appear roughness on the surface this lead good mechanical adhesion between ATH and PVC and give good mechanical properties of the composite.

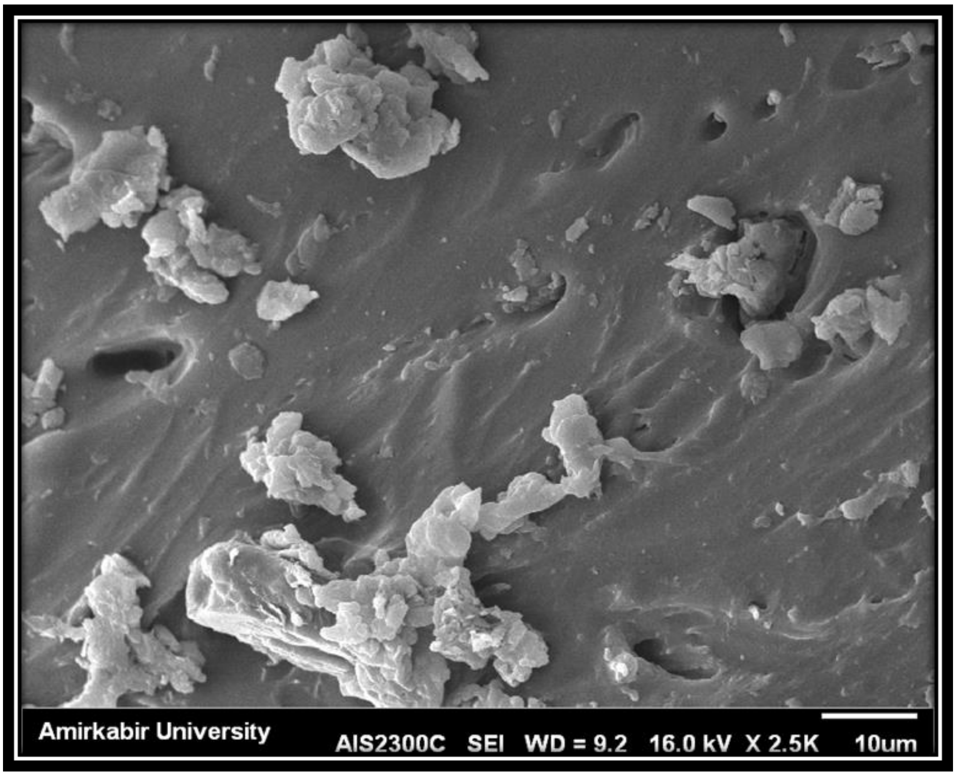

Fig. 4-2: SEM image of PVC composite containing ATH nanoparticles.

-Tensile strength:

In this test used micro computer controlled electronic universal testing machine model (WDW-5E) made in China, Figures (4-3) show the addition's effect of metal hydroxide nanoparticles (MH) and (ATH) on the value of tensile strength for polyvinyl chloride, The results show that the tensile strength decreases with the addition nanoparticles , due to the poor interfacial adhesion between the metal hydroxide nanoparticles surface and the PVC matrix, resulting in poor stress transfer across the interface. When addition mixture from (MH+ATH), noted improvement in tensile properties, because formation hydrogen bond that reinforce secondary bond for PVC which is increase the stability of polymer chains that lead to increase tensile strength.

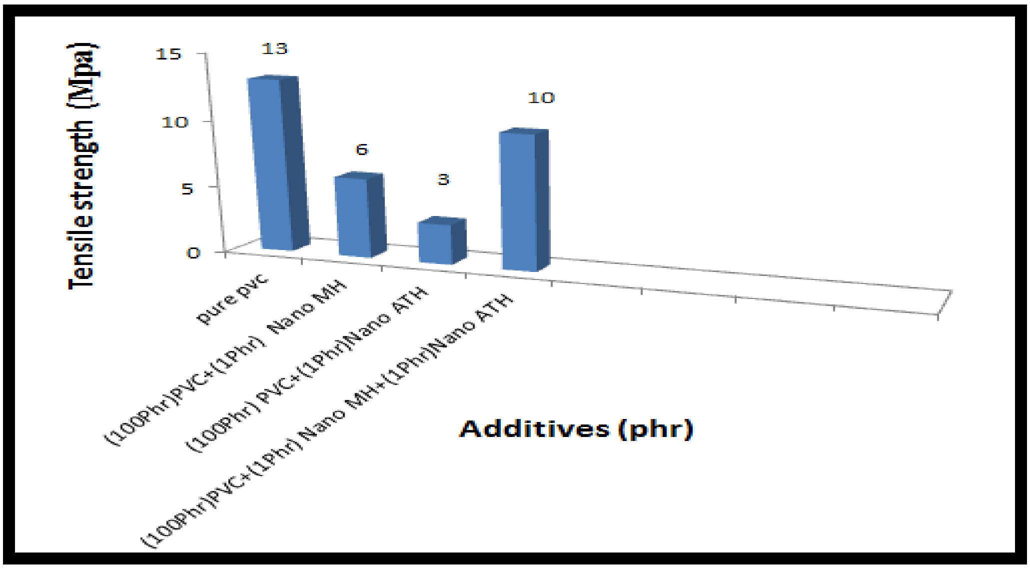

Fig. 4-3: Tensile strength for PVC nanocomposite that contain (MH),(ATH) and (MH+ATH).

-Hardness Test:

Shore D hardness device model (TH 210 FJ) made in Germany, which is available in laboratory of Materials Engineering college /University of Babylon use to inspect hardness of PVC nanocomposite, Shore D hardness for PVC nanocomposite is shown in figure (4-4). The results showed that the hardness of PVC increases with addition nanoparticles(MH),(ATH)and (MH+ATH). good dispersion of nanoparticles by use the ultrasonic that prevent particles from agglomeration inside PVC matrix that lead to increase the interaction between filler-matrix so increased the hardness of nano-composite, where the (MH,ATH) nanoparticles fill the holes and orient the chain therefore hardness increasing. Best hardness of PVC nanocomposite when added mix from (MH+ATH).

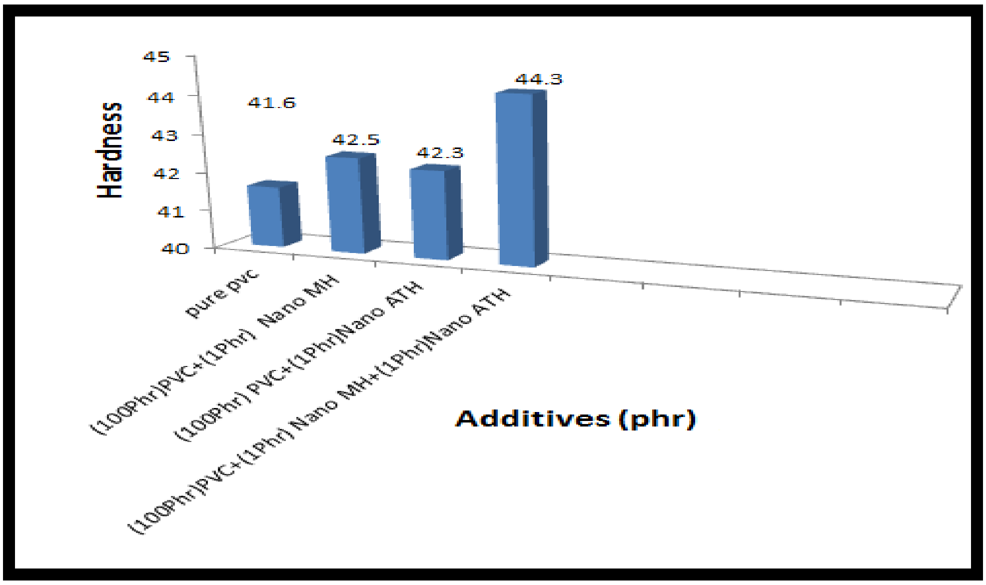

Fig. 4-4: Hardness for PVC nanocomposite that contain (MH),(ATH) and (MH+ATH).

-Creep Test:

Laboratory device used in this test model (WB 600) made in Germany , located in the laboratory of Materials Engineering college /University of Babylon, Figure (4-5), explain addition 's effect of metal hydroxide nanoparticles (MH),(ATH)and (MH+ATH) on creep property of PVC, result shown that creep decreases with addition (MH),(ATH) nanoparticles. because good dispersion of nanoparticles inside PVC matrix by using ultrasonic which is lead to homogeneous distribution of it, so it lead to increase the force interaction between nanoparticle and PVC matrix and restricted the chains mobility and increase the stability of it . Result shown the creep of PVC is more decreases when added mix from (MH,ATH) nanoparticles, because contain of nanoparticles inside the matrix is high which is (2 Phr) than (1Phr) to the (MH),(ATH), this quantity is more restricted to movement of chains of polymer by filling the holes.

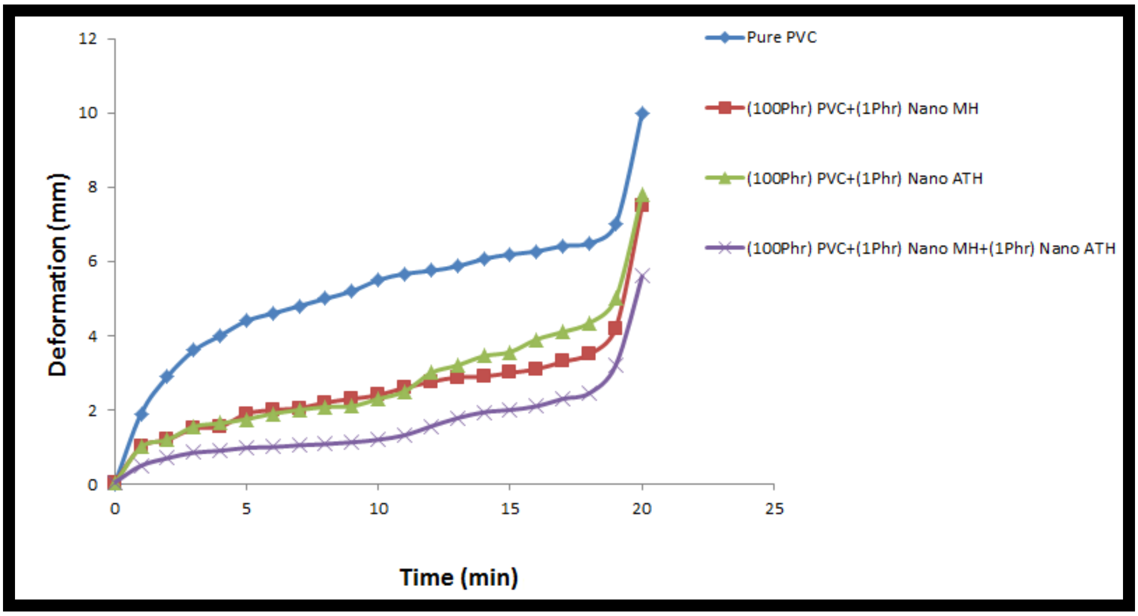

Fig. 4-5: creep of PVC nanocomposite that contain (MH),(ATH) and (MH+ATH) nanoparticles.

Conclusions:

Magnesium hydroxide (MH) and Aluminum tri-hydroxide(ATH) nanostructures were prepared by chemical perspiration route. MH, ATH nanoparticles were then added to Polyvinyl chloride matrix. The influence of the inorganic phase on the thermal, mechanical properties of polymer matrixes was studied. Burning rate of the PVC nanocomposite is decreases in the presence of (MH), (ATH) nanoparticles. The enhancement of burning rate of the nanocomposites is due to endothermic decomposition of MH and ATH release of water which dilutes combustible gases. Also have barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. The tensile strength decreasing with Nano MH and ATH addition for PVC. The hardness increasing with addition and the creep is more improved.

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