

## Room Temperature Preparation of Aluminum Hydroxide Nanoparticles and Flame Retardant Poly Vinyl Alcohol Nanocomposite

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### Abstract

Al(OH)<sub>3</sub> nanoparticles were synthesized by a simple precipitation reaction. The effect of various amines like ethylene diamine, propylene diamine, triethylenetetramine and tetraethylenepentamine as precipitating agents on the morphology of Al(OH)<sub>3</sub> nanostructures was investigated. The influence of Al(OH)<sub>3</sub> nanoparticles on the flame retardancy of the poly vinyl alcohol (PVA) matrix was studied using UL-94. Nanostructures were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. Flame retardancy of the nanocomposites enhanced in the presence of Al(OH)<sub>3</sub> nanostructures. This improvement of nanocomposites is due to the endothermic decomposition of Al(OH)<sub>3</sub> and release of water which dilutes combustible gases.

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## 1. Introduction

Beside numerous advantages that synthetic polymeric matrices have to society in everyday life, there is one obvious drawback related to the high flammability of many of them. Polymers are used not only bulk parts but also films, fibers, coatings, and foams, and these thin objects are even more combustible than molded parts. Fire hazard is a combination of factors, including ignitability, ease of extinction, flammability of the volatile products generated, amount of heat released on burning, rate of heat release, smoke obscuration, flame spread,

and smoke toxicity. One of the main disadvantages of bulk aluminum hydroxide is that for appropriate flame retardancy tests, 30 to 65 wt% of aluminum hydroxide is required. Enhancement the loading of hydroxides will result in a significant decrease in physical properties. Aluminum hydroxide is the most known and commonly used mineral flame retardants. As the temperature rises Al(OH)<sub>3</sub> shows an endothermic decomposes (1.17 kJ/g) around 220°C and absorbs energy [1-5]. Some flame retardants show almost exclusively a physical mode of action like aluminum hydroxide. On the other

hand, there is no single flame retardant that will operate exclusively through a chemical mode of action. Chemical mechanisms are always accompanied by one or several physical mechanisms, most commonly endothermic dissociation or dilution of fuel. Combinations of several mechanisms can often be synergistic. Applying of halogen-free flame retardants is widespread due to the increasing concern about the health and environmental risks [1]. Another mechanism could be the catalytic effect of anhydrous alumina, which will help acid-catalyzed dehydration of some polymers and as a result can enhance charring. In addition aluminum hydroxide is an important precursor for synthesis of alumina and alumina-derived ceramics. Alumina has many desired properties such as high surface area, good mechanical and especially thermal and chemical stability etc. So alumina has various industrial applications, and can be widely used as absorbent, catalyst, heat transfer and catalyst support [6-8]. The high purity nanocrystalline alumina powders were synthesized as yet by variety methods such as precipitation, hot-air spray pyrolysis, sol-gel and hydrothermal. It releases non-flammable water which dilutes highly flammable gases.  $\text{Al}(\text{OH})_3$  is used as halogen-free flame-retardant for polymers.  $\text{Al}(\text{OH})_3$  can 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 [9-11]. Poly vinyl alcohol is a biodegradable and water soluble polymer with applications in paper coating, packaging films and adhesives. [4]. In this work a facile and rapid method for preparation of aluminum hydroxide was used.  $\text{Al}(\text{OH})_3$  was then added to the poly vinyl alcohol in order to increase the flame retardancy.

All polymer fires start with an ignition event, where a source of heat comes into contact with a fuel generated by the heating of the polymer. This event initiates a flow of flammable degradation products, which react with oxygen from the air to produce a flame and heat. Some of the heat is transferred back to the surface of the fuel, maintaining the flow of flammable volatile degradation products. Low ignitability of the polymers is the first line of defense against fire. Although all organic polymers do ignite, the higher the temperature that a material has to reach before it ignites, the safer it is. For most materials, the ignition temperature is in the range 275 to 475°C. Ignitability is assessed via time to ignition or minimum heat input for ignition. Fire performance improves if either of these increases. Ignitability depends to a large extent on how quickly the surface can be raised to the ignition temperature. Special consideration has to be given to polymers that melt before thermal decomposition. Usually, at a low heat exposure, melting precedes ignition and the polymer can flow or drip, removing heat from the surface. This phenomenon is beneficial for flame retardancy of uncharable polymers. At a higher heat exposure, ignition may occur before the surface is heated to sufficient depth for the melted material to flow, and such polymers may ignite relatively easy [1]. Aluminum hydroxide is used primarily in wire and cables in poly(vinyl chloride), polyethylene, and

various elastomers. combinations with red phosphorus, silicones, boron compounds, nanoclays (treated montmorillonites), and charring agents have been explored. Surface treatment of metal hydroxides also helps to improve physical properties and sometimes improves flame retardancy, due to better dispersion.

## 2 Experimental

### 2.1 Materials and characterization

All the chemicals were used as received without further purifications.  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , ethylenediamine (ED), propylene diamine (PD), triethylenetetramine (TET), tetraethylenepentamine (TEP) and poly vinyl alcohol (PVA: 20000) were purchased from Merck Company.

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 Au (BAL-TEC SCD 005 sputter coater) to make the sample surface conducting obtain better contrast and prevent charge accumulation. X-ray diffraction (XRD) patterns were recorded by a Philips X-ray diffractometer using Ni-filtered  $\text{CuK}_\alpha$  radiation. For preparation of nanocomposite, a multi-wave ultrasonic generator (Bandline MS 73) 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. The effect of nanostructure on flame retardant properties has been considered using UL-94 test. In UL-94 a bar shape specimen of plastic  $130 \times 13 \times 1.6$  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. Materials are ranked as N.C. in UL-94 tests when the maximum total flaming time is above 50 s. The sample is classified HB when slow burning on a horizontal specimen; burning rate  $< 76$  mm/min [12,13].

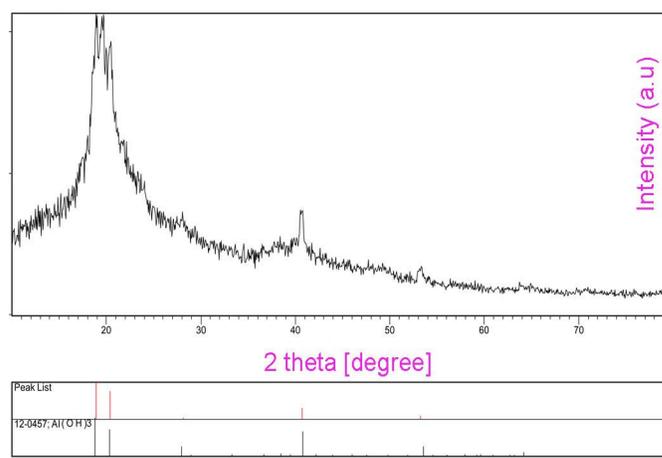


Fig. 1. XRD pattern of  $\text{Al}(\text{OH})_3$  nanoparticles

### 2.2. Synthesis of $\text{Al}(\text{OH})_3$ nanoparticles

1g  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  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  $\text{Al}(\text{OH})_3$ . The white precipitate was centrifuged and washed with distilled water to removing the surfactant, and later dried at  $70^\circ\text{C}$  for 24h in a vacuum dryer.

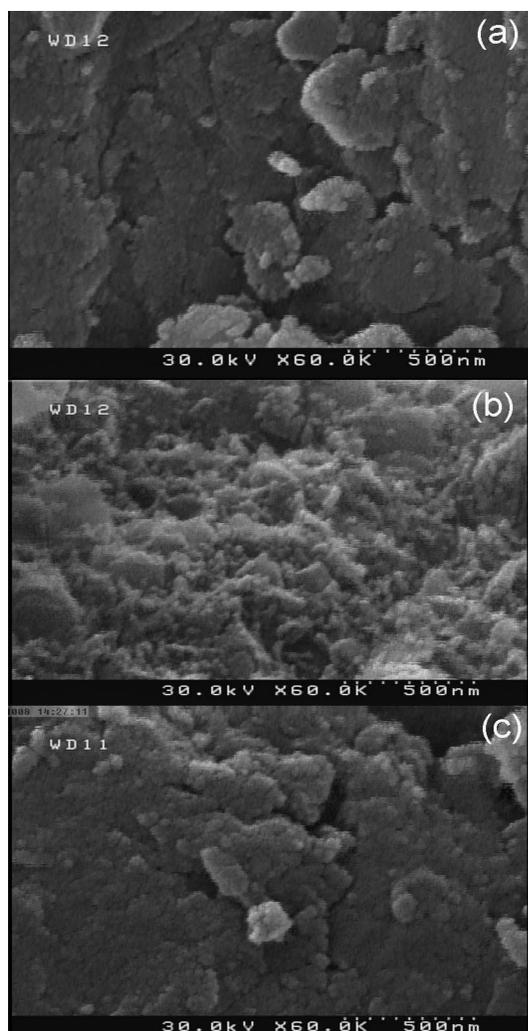
### 2.3. Synthesis of PVA- $\text{Al}(\text{OH})_3$ nanocomposite

4 g of PVA was dissolved in 15 mL of water and then  $\text{Al}(\text{OH})_3$  (1 g) was dispersed in 5 mL of water with ultrasonic waves (60W, 30 min). The dispersion of  $\text{Al}(\text{OH})_3$  was then added slowly to the polymer

solution. The solution was mixed under stirring for 6 h. The product was casted on a template with dimension  $130 \times 13$  mm and after about 48 h of solvent evaporation.

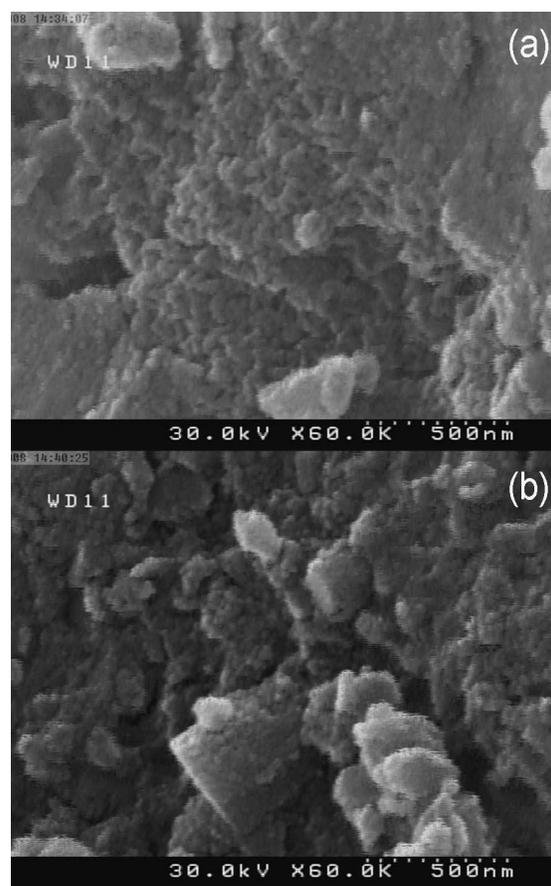
### 3. Results and discussion

XRD pattern of  $\text{Al}(\text{OH})_3$  nanoparticles is illustrated in Fig. 1. It shows a pure hexagonal structure with suitable agreement to literature value (reference peaks are also depicted in the XRD pattern, JCPDS card no. 12-0457).



**Fig. 2.** SEM images of nanoparticles synthesized with (a,b) ethylene diamine (c) propylene diamine  
Scanning electron microscope images of nanoparticles synthesized with ethylene diamine

and propylene diamine are illustrated in Fig 2a,b and 2c respectively. Nanoparticles with average diameter less than 100 nm were obtained. SEM images of nanoparticles synthesized by triethylenetetramine and tetraethylenepentamine are shown in Fig 3a and 3b respectively. By applying new amines also nanoparticles with average diameter lower than 100 nm were obtained. SEM image of PVA- $\text{Al}(\text{OH})_3$  nanocomposite is illustrated in Fig 4 that confirms presence of nanoparticles in the polymeric matrix while pure polymers show smooth and flat surfaces.



**Fig. 3.** SEM images of nanoparticles synthesized (a) triethylenetetramine (b) tetraethylenepentamine

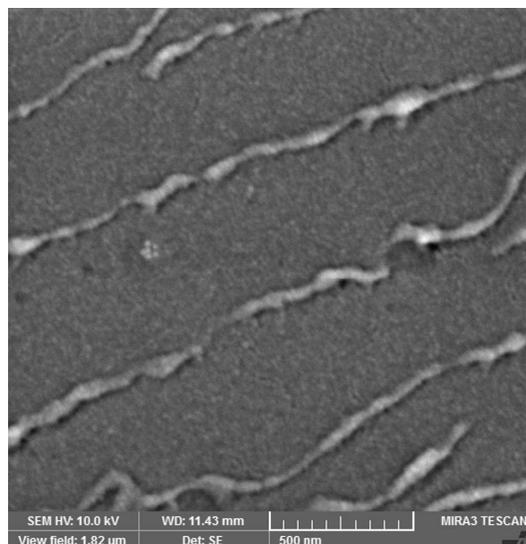


Fig. 4. SEM image of PVA-Al(OH)<sub>3</sub> nanocomposite

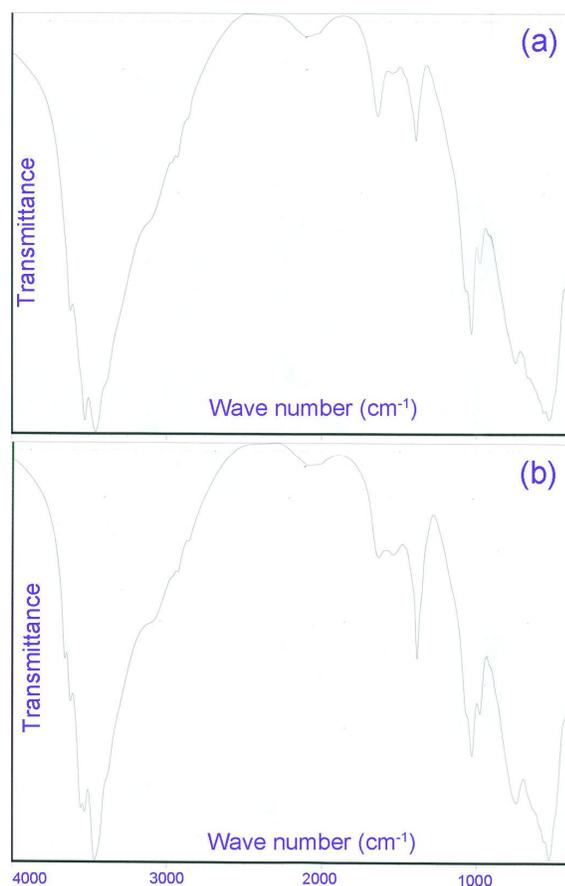


Fig. 5. FT-IR of Al(OH)<sub>3</sub> nanoparticles (a) ethylene diamine (b) propylene diamine

FT-IR of Al(OH)<sub>3</sub> nanoparticles synthesized with ethylene diamine and propylene diamine are depicted in Fig 5a and 5b respectively and exhibit peaks at 523 and 1026 cm<sup>-1</sup> correspond to the Al–O bonds in Al(OH)<sub>3</sub>. Absorption peak at 3455 cm<sup>-1</sup> is because of OH groups that are adsorbed on the surface of nanoparticles. Peak at 3525 cm<sup>-1</sup> is responsible to OH groups of nanoparticles. Interaction between Al(OH)<sub>3</sub> and PVA are depicted in Fig 6. Adsorption of polymer chains on the surface of Al(OH)<sub>3</sub> nanoparticles results in a confinement of the segmental motions and suppress chain-transfer reactions [2,12].

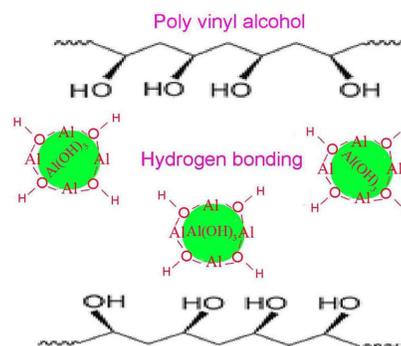
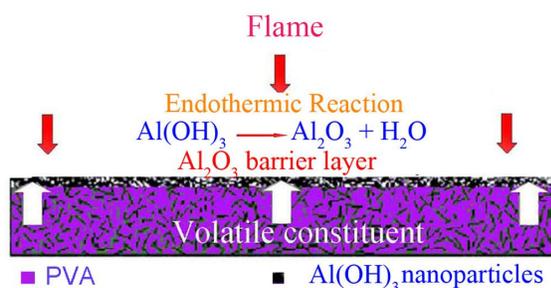


Fig. 6. Interaction between Al(OH)<sub>3</sub> and PVA

In PVA-Al(OH)<sub>3</sub> nanoparticles have been appropriately distributed in PVA matrix and because of hydrogen bonds between them a suitable barrier layer of nanoparticles is formed that slows evaporation of polymeric segments and prevents oxygen and flame arriving to polymer (Fig 7). UL-94 outcomes for PVA and PVA-Al(OH)<sub>3</sub> nanocomposites are HB and V-0 respectively. The results approve that the Al(OH)<sub>3</sub> nanostructure can enhance the flame retardant property of the PVA matrix. The enhancement of flame retardancy of nanocomposites is because of endothermic decomposition of Al(OH)<sub>3</sub> that absorbs energy. It simultaneously releases water which dilutes

combustible gases. Dispersion of  $\text{Al}(\text{OH})_3$  have also a obstruction effect to decrease product volatilization and thermal transport among decomposition of the polymer.



**Fig. 7.** Scheme of  $\text{Al}(\text{OH})_3$  performance against flame

#### 4. Conclusion

$\text{Al}(\text{OH})_3$  nanostructures were prepared by a simple precipitation method. The effect of various amines on the morphology of  $\text{Al}(\text{OH})_3$  nanostructures was investigated.  $\text{Al}(\text{OH})_3$  nanoparticles were then added to poly vinyl alcohol matrix. The increase in flame retardancy of the nanocomposites is due to endothermic decomposition of  $\text{Al}(\text{OH})_3$  and release of water which dilutes combustible gases.  $\text{Al}(\text{OH})_3$  have also obstruction effect to decrease the polymer volatilization and heat transport during decomposition of the polymer. In PVA- $\text{Al}(\text{OH})_3$ , nanoparticles have been appropriately distributed in PVA matrix and because of effective hydrogen bonding between aluminum hydroxide and poly vinyl alcohol a suitable interaction was observed.

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