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Sonochemical Synthesis of $Ca(OH)_2$ Nanoparticles and Its Application in Preparation of MWCNT-Paraloid Nanocomposite

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Abstract

In this work at the first step calcium hydroxide nano-particles were synthesized via sono-chemical method at room temperature. At the second step aminated multi-walled carbon nano-tubes was prepared via chemical modification of surfaces of CNT. Finally modified-MWCNT and $Ca(OH)_2$ were added to paraloid matrix by aid of ultrasonic irradiation. Paraloid-modified-MWCNT-$Ca(OH)_2$ nanocomposite was used as a protection agent applicable in cultural heritage preservation. This nanocomposite can be used against acid rain that is destructive agent in historic monuments. One of the main advantages of paraloid as a consolidant is that it is stronger and harder than polyvinyl acetate without being extremely brittle. Nanostructures were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). Thermal stability behavior of paraloid filled with calcium hydroxide was investigated by thermogravimetric analysis (TGA). Our results show that the MWCNT-$Ca(OH)_2$ nanostructure can enhance thermal stability property of the paraloid matrix. Nano-additives like a barrier slow down volatilization of paraloid chains against heat.

1. Introduction

Paraloid is a thermoplastic resin that was created by Rohm and Haas for use as a surface coating and as a vehicle for flexographic ink. Paraloid is commonly being used as an adhesive by conservator-restorers, specifically in the conservation and restoration of ceramic objects and glass objects. It is a long lasting and non-yellowing acrylic resin, which can be defined chemically as an ethyl-methacrylate copolymer. It is soluble in acetone, ethanol, toluene and xylenes, among other solvents and solvent mixtures.

This adhesive is more flexible than many of the other conventionally used adhesives, also it tolerates more stress and strain on a join than most others. The major disadvantage to its using is related to its handling properties, as in the case of other acrylic resins it is difficult to apply as an adhesive and to operate with exactness.

Dissimilar cellulose nitrate, paraloid doesn't need additives like plasticizers to stabilize its permanence. Fumed colloidal silica was added to help with the workability of the resin. Research shows that the silica better distributes the stress and strain that occurs during evaporation of a solvent and during the setting of the adhesive film [1-4].

Solvent mixtures with various proportions of acetone, ethanol, and toluene are frequently used to alter the working time of the resin and to produce slightly different properties (hardness and flexibility) in the based resin.

Acid rain is a rain or any other form of precipitation that is unusually acidic, meaning that it possesses elevated levels of hydrogen ions. It looked at the effects of acid rain and funded research on the effects of acid precipitation on freshwater and terrestrial ecosystems, historical buildings, monuments, and building materials.

It can have harmful effects on plants, aquatic animals and infrastructure. Acid rain is caused by emissions of sulfur dioxide and nitrogen oxide, which react with the water molecules in the atmosphere to produce acids. Governments have made efforts since the 1970s to reduce the release of sulfur dioxide into the atmosphere with positive results. Nitrogen oxides can also be produced naturally by lightning strikes and sulfur dioxide is produced by volcanic eruptions. The chemicals in acid rain can cause paint to peel, corrosion of steel structures such as bridges, and erosion of stone statues [5-11].

For example Harvard University wraps some of the bronze and marble statues on its campus with waterproof covers every winter, in order to protect them from erosion caused by acid rain and acid snow.

Scientists for improvement properties of composite materials investigate composites with nano-fillers, leading to the development of nanocomposites.

Nanoparticles disperse into the polymeric matrix homogeneously and hence leads to formation of a condensed char during the combustion. Metal hydroxides provide water which dilutes combustible gases. Metal oxide also provides heat insulation by reflecting heat when it accumulates on the surface[12-14].

Recently, Baglioni et al. prepared different metal hydroxide nanoparticles by various chemical reactions. One of the main disadvantages of the paraloid is its low thermal stability; therefore there is a need to increase its thermal stability[15-17].

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. Sonochemistry 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 handle many chemical reactions [18].

In this work, paraloid-MWCNT-$Ca(OH)_2$ nanocomposites were synthesized via sonochemical method for application in cultural heritage conservation. Results show that the $Ca(OH)_2$ nanostructure can enhance the thermal stability of the paraloid matrix.

2. Experimental

2.1 Materials and characterization

$Ca(NO_3)_3 \cdot 4H_2O$, and sodium hydroxide 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 CuK_α 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 $Ca(OH)_2$ nanoparticles

$Ca(NO_3)_2$ $4H_2O$ (1 g) is dissolved in 20 mL of water. NaOH solution (5 mL, 1 M) is then slowly added to the mentioned solution under radiation (75 W) for 15 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.

2.3. Functionalization of multi-walled carbon nanotubes

Aminated multi-walled carbon nanotube was prepared via chemical modification of surfaces according to Naeimi et al [19]. Oxidation of MWCNTs was performed with ozone in aqueous phase. Amidation of generated carboxylic groups, was occurred with amines in the presence of 2-(7-Aza-1H-benzotriazole-1-yl)-1,1,3,3-tetramethyl uronium hexafluorophosphate as a coupling agent. Obtained functionalized MWCNTs are soluble in many common organic solvents. The functionalized MWCNTs were characterized in detail using FTIR and SEM methods.

2.4. Preparation of nanocomposite

For synthesis of nanocomposite, paraloid (3g) is first dissolved in acetone (15 mL). The $Ca(OH)_2$ nanoparticles (1 g) MWCNT (0.2 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.

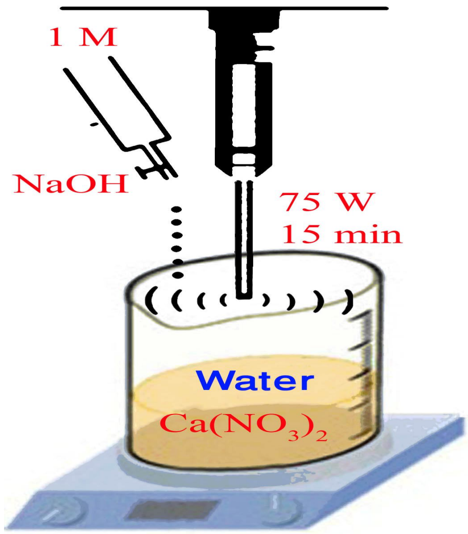

Fig. 1. Schematic diagram of preparation of $Ca(OH)_2$ nanoparticles.

3. Results and discussion

XRD pattern of $Ca(OH)_2$ nanoparticles is shown in Fig. 2 which is indexed as a hexagonal phase (space group: P-3m1). The experimental values are very close to the literature (JCPDS No. 84-1265). A little amount of calcium carbonate is observed.

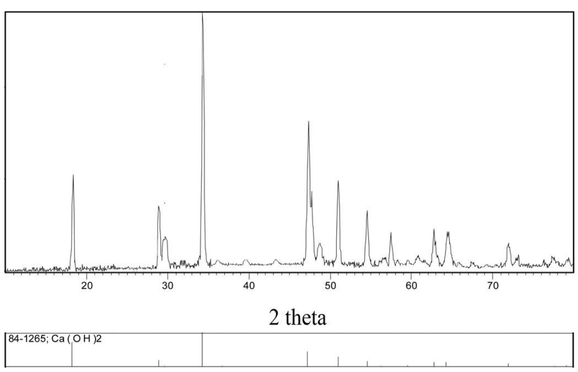

Fig. 2. XRD pattern of $Ca(OH)_2$ nano-particles.

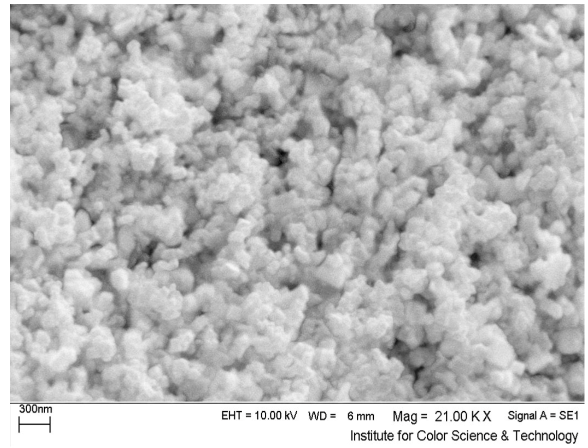

Fig. 3. SEM image of $Ca(OH)_2$ nano-particles.

The crystallite size measurements were carried out using the Scherrer equation,

$$Dc=0.9\lambda/\beta\cos\theta$$

where β is the width at half maximum intensity of the observed diffraction peak, and λ is the X-ray wavelength (CuK_α radiation, 0.154 nm). The estimated crystallite size is about 17 nm.

SEM images of the $Ca(OH)_2$ under ultrasonic waves 75W at 15 min is shown in Fig. 3 Nanoparticles with average diameter of 60nm are obtained. SEM image of the modified multiwall carbon nanotubes is displayed in Fig 4. The average diameter of MWCNTs is about 90 nm.

Transmission electron microscope image of the $Ca(OH)_2$ under ultrasonic waves 75W at 15 min is shown in Fig. 5 that confirm particle with average diameter less than 100 nm. We studied interaction between the $Ca(OH)_2$ nanoparticles and modified nanotubes surrounded by paraloid chains.

Fig. 4. SEM image of modified-MWCNT

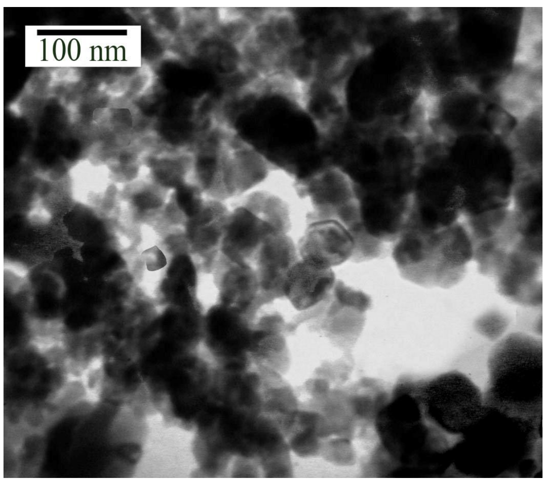

Fig. 5. TEM image of $Ca(OH)_2$ nano-particles.

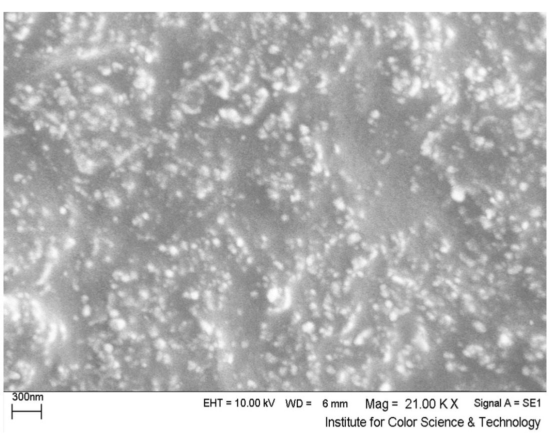

Fig. 6. SEM images of Paraloid-$Ca(OH)_2$ nanocomposite (high loading additives).

SEM image of the paraloid-$Ca(OH)_2$ nanocomposite under ultrasonic waves 60W at 20 min is shown in Fig. 6 Image of pure paraloid show smooth and flat surface so this scanning electron microscope confirm highly mono-dispersed and suitable dispersion in polymer matrix.

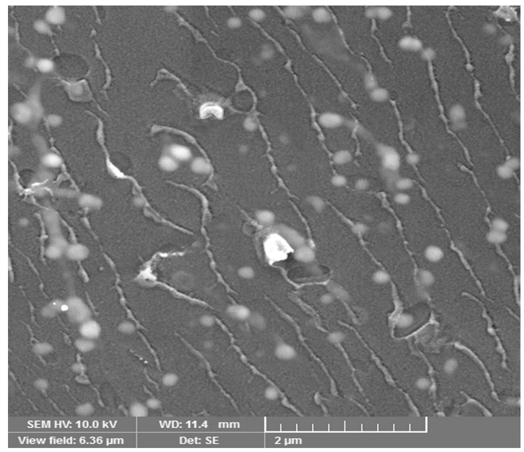

Fig. 7. SEM image of Paraloid-MWCNT-$Ca(OH)_2$ nanocomposite.

SEM image of the surface paraloid-modified MWCNT-$Ca(OH)_2$ nanocomposite prepared under ultrasonic waves 60 W at 20 min is shown in Fig. 7. Image of pure paraloid show smooth and flat surface so this scanning electron microscope approve appropriate dispersion in polymer matrix.

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 [15-18]. TGA curves of pure paraloid and paraloid-MWCNT-$Ca(OH)_2$ nanocomposites are illustrated in Figs. 8a and 8b respectively.

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

$Ca(OH)_2$ has barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. So the initial degradation temperature (Tonset) increases.

$Ca(OH)_2$ nanostructure can enhance the fire resistant property of the paraloid matrix. The enhancement of thermal stability of nanocomposite is due to endothermic decomposition of $Ca(OH)_2$ that absorbs energy and simultaneously releases of water.

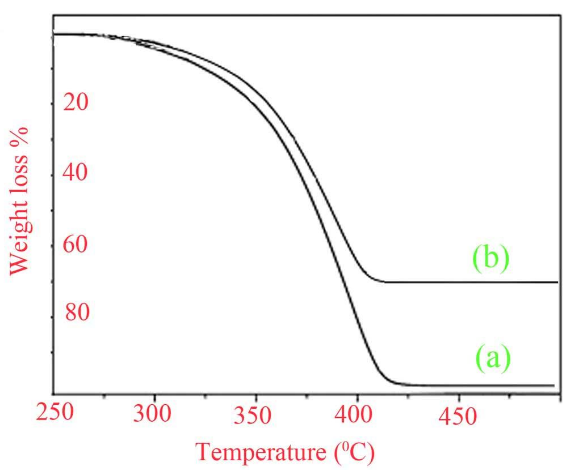

Fig. 8. TGA curves of (a) pure paraloid (b) paraloid-MWCNT-$Ca(OH)_2$ nanocomposite.

Calcium hydroxide were used as consolidants for wall paintings (frescoes), paper, stone and wood, as reported in the remarkable scientific papers of the Baglioni group (Fig 9). 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. Its nanocomposite with $Ca(OH)_2$ and modified-carbon nano tubes can be used as a protective agent against ultraviolet and visible light which are destructive for natural colors that were used in historic graphics and schemes.

Because of its transparency and versatility conservators, led by Stephen Koob of the Corning Museum of Glass, have recently begun to use cast sheets of paraloid as a fill material in glass objects. The most suitable solvent for paraloid is acetone.

Acid rain can damage buildings, historic monuments, and statues, especially those made of rocks, such as limestone and marble, that contain large amounts of calcium carbonate.

$$NO_2 + OH\cdot \rightarrow HNO_3$$
$$SO_3\ (g) + H_2O \rightarrow H_2SO_4\ (aq)$$

Paraloid-modified-MWCNT-calcium hydroxide nanocomposite was used as a protection agent applicable in cultural heritage preservation. This nanocomposite can be used against acid rain that is destructive agent in historic monuments (Fig10). One of the main advantages of paraloid as a consolidant is that it is stronger and harder than polyvinyl acetate without being extremely brittle.

Lime or limestone in slurry form is also injected into the tower to mix with the stack gases and combine with the sulfur dioxide present. The calcium carbonate of the limestone produces pH-neutral calcium sulfate that is physically removed from the scrubber. That is, the scrubber turns sulfur pollution into industrial sulfates.

The effects of this are commonly seen on old gravestones, where acid rain can cause the inscriptions to become completely illegible. Acid rain also increases the corrosion rate of metals, in particular iron, steel, copper and bronze.

Fig. 9. Images of historic schemes by natural colors

Acids in the rain react with the calcium compounds in the stones to create gypsum, which then flakes off.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$$

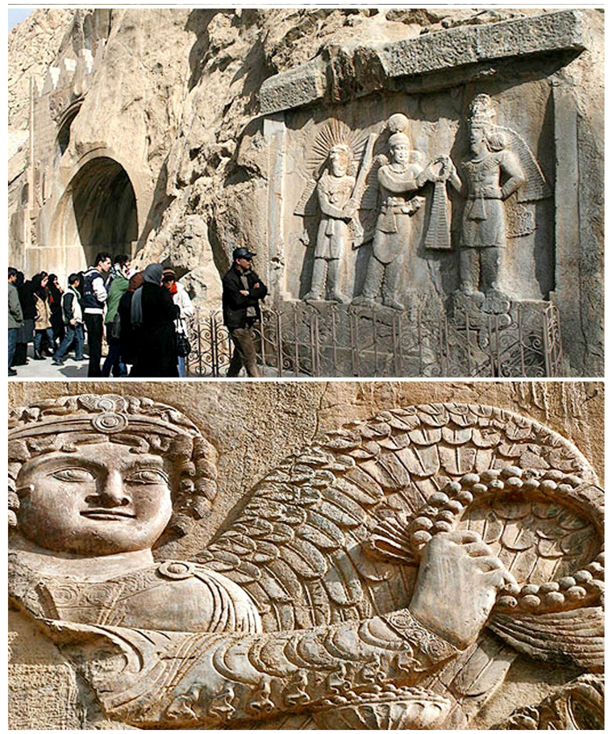

Fig. 10. Images of historic monuments (Taq Bostan, Kermanshah, Iran)

4. Conclusion

$Ca(OH)_2$ nanoparticles were prepared by a simple sonochemical process at room temperature. Nanoparticles and nanotubes were then added to paraloid matrix. The influence of additives phase on the thermal properties of paraloid matrix was studied. The results show that the MWCNT-$Ca(OH)_2$ can enhance the thermal stability property of the paraloid matrix. MWCNT-$Ca(OH)_2$ have barrier effect to slow down the product volatilization and thermal transport during decomposition of the polymer. Paraloid-modified-MWCNT-calcium hydroxide nanocomposite was used as a protection agent applicable in cultural heritage preservation. This nanocomposite can be used against acid rain that is destructive agent in historic monuments

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