PREPARATION AND PROPERTIES OF ALPHA NAPHTHOL-FORMALDEHYDE RESIN WITH NANO-HYDROXY APATITE

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ABSTRACT

In this work, the preparation of resin material and reinforcing materials were discussed and then composite preparation was made. Then alpha naphthol-formaldehyde polymer was synthesized and mixed with nano-hydroxyapatite for increasing the properties of material like melting and boiling point. Then, to check the mechanical property like hardness of the composite. Though, the behavior of the polymer composites will be changed due to the addition of hydroxyapatite. While preparing the composites, epichlorohydrin was blended in order to epoxidied through the hydroxyl group. Then the composite material were taken and shaped into ASTM standard with the help of compression molding machine for testing the mechanical property of the material. In this, hexamethylene tetramine was used for curing the composite in the machine. The composite powder was taken to find the morphological characters with the help of SEM and XRD analysis. Finally the mechanical property like hardness were discussed for the composite and melting and boiling point were measured and compared with matrix material.

Key words: *Epichlorohydrin, Hydroxyapatite, Hexamethylenetetramine, naphthol-formaldehyde.*

1. INTRODUCTION

Generally the polymer materials have bad mechanical properties when compared to metals but the importance of polymer is gradually increased due to less weight and corrosion less. Here naphthols are monohydric alcohols which are derived from naphthalene and this is belongs to phenol family. So, only naphthol was used as matrix material for enormous application similar to phenol.

Generally, these are positioned isomers which are 1-naphtha and 2- naphthol from hydronaphthalene. In this 1- naphthol was made by heating naphthalene with sulphuric acid and caustic soda and 2-naphthol was formed from fusing process. Naphthols were slightly soluble in water but completely soluble with alcohols, ethers and caustic alkalis. But in general, there were enormous changes in the properties of the material by small amount of reinforcing material in the composite materials. For example, with the addition of nanotubes of carbon has made improvement in mechanical and thermal properties. Similarly there were several types of nano materials were added in the composites through which electrical, strength, optical, mechanical and heat properties were changed[Habaib a. al taee et.al [19] (2009)]. So, in to increase the properties the material, the reinforcement with other materials is done. Here, polymer matrix used is naphthol-formaldehyde. [D.R. Paul el.al[1] (2008)]

2. MATRIX MATERIAL

Naphthol-formaldehyde, which was called as naphtha-methanol, because it was based on the structure and synthesis manner. This was one type of thermosetting resin which was non- transparent, made from naphthol and formaldehyde heated with the source

of ammonia or pyridine. These resins are used as dyes. Like phenolic and melamine resins, naphthol- formaldehyde polymers are now employed primarily as dye chemical in textile industries and hair dyes. Naphthol-formaldehyde resins are lighter in color than phenol-formaldehyde resins.

3. REINFORCING MATERIAL

Hydroxyapatite (HA) is a member of the apatite family of calcium phosphates whose chemical formula is Ca_{10} (PO_4) $_6$ (OH) $_2$, with the CA/P stoichiometric ratio of 1.67. Hydroxyapatite has been used in biomedical applications like preparation of bones and teeth. Then by using this specific property of hydroxyapatite, there were several research done in biomedical application with polymer composites. Because these types of composites have produced increased properties like mechanical, bioactivity, biodegradation, ect. [Kacey G. Marra et.al, 8 (1999)]. Generally hydroxyapatite has been produced into nano sized particle with some known methods like wet chemical method, hydrothermal micro emulsion, ect. In this hydrothermal microemulsion method was best known for preparing the particle into nano- wires, nano-needles, ect [Raksujarit et.al [9] (2010)].

4. EXPERIMENTAL DETAILS

Materials Used

40% Formaldehyde solution, naphthol, benzene, oxalic acid, calcium nitrate, di-ammonium phosphate, ammonia

Synthesis of naphthol-formaldehyde

In a 2 L three-necked, round bottom flask a-naphthol (1 mol), formaldehyde (40 % w/v, 0.5 mol), oxalic acid (2 .0 g) and benzene (500 ml) were agitated on magnetically stirred for 1 h. The contents were then refluxed at 80 C for 3 h. The reaction mixture was then filtered under reduced pressure (10–15 mm Hg). at 90–100 ºC to remove benzene and water . The liquid was washed with a large volume of petroleum ether (40–60 ºC). The NF was collected as a thick liquid. [Desai K.R. et.al[1] (2001)]

Than 1:6 ratio of moles of alpha naphthol-formaldehyde resin and epichlorohydrin were dissolved and the mixtures were heated in a boiling water bath. The mixture was stirred continuously for 1 day. Then, with this mixture 3 moles of sodium hydroxide in the form of 30 % aqueous solution was added drop wise. The resulting organic layer was separated, dried under vacuum [Jenish Paul et.al [10] (2010)].

Composite Preparation

Prepared naphthol-formaldehyde powder was taken 20gm in which calcium nitrate was added 20ml. Then similarly 20ml of di-ammonium phosphate was added slowly with constant stirring. To maintain pH value greater than 11, ammonia was added during the process. Then the composite material was prepared and this was filtered and dried at 105°C. Through these the composite material was prepared with few quantities. Similarly, the process was continued for preparing the powder with maximum quantity for the preparation of specimens

Then the composite material was taken and shaped into ASTM standard with the help of compression molding machine for testing the mechanical property of the material. In this, hexamethylene tetramine was used for curing the composite in the machine. The specimen was prepared with ASTM D785 with the dimension of (length ×width × thickness = 120×13×3) mm and placed in a vacuum oven at a temperature of 120°C and a pressure of 10 Torr for 1 h. Specimens were cured using a compression molding machine. Five specimens were prepared, tested to determine mechanical property. [Sang Chul Roh et.al [12] (2012)].

5. CHARECTERIZATION AND ANALYSIS OF POLYMER COMPOSITE

SEM image was used to examine the morphology of NF-n-HA in the slurry and in the composite [Akihiro Matsumoto et.al [13] (2007)]. The XRD analysis was taken to determine the thermal stability of composites. So, to test the material, the powder was dried in a oven at 80°C for 24 h before testing. The thermal stability was checked on the composite material of alpha-naphthol-nano hydroxyl apatite with the help of thermo gravimetric analyzer (Perkin Elmer, Diamond TG/DTA) over a temperature range of room temperature of 50° to 900°C at a heating rate of 20°C/min. The particle size of alpha naphthol formaldehyde and n-HA powder was found by Debye-Scherrer formula. In this, CuKα radiation from a Cu X- ray tube was used. The samples were measured in the 2θ range from 10° to 90°.

6. RESULTS AND DISCUSSION

SEM Analysis

SEM image (Zeiss Evo 40XVP) was used to determine the particle scattering in the nano- composite and structure of composite. In this, the powder was prevented with the gold coating for charging before the observation by SEM.

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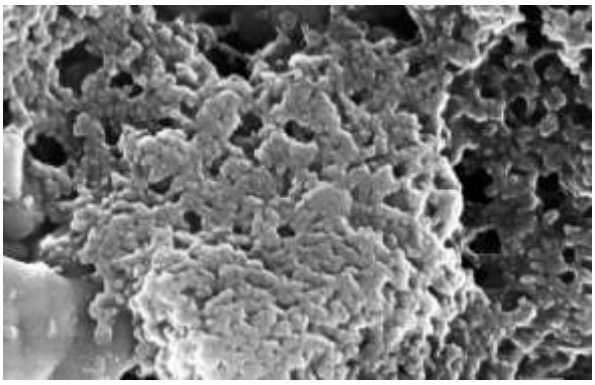
Figure 1 n-HA scattered on composite material



The figure 1 shows that nano-hydroxyapatite was scattered on the naphthol formaldehyde and nano particles were gathered in a group over naphthol formaldehyde. The particle size n- HA could be below 100 nm. This phenomenon reveals the good miscibility between polymer and n-HA phases.

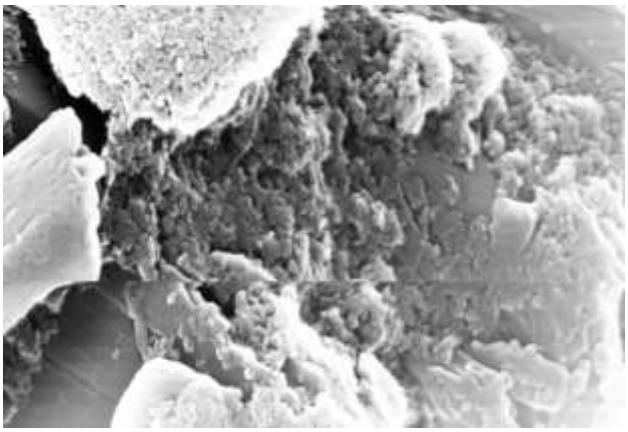


Figure 2 SEM image of composite material in which the nano-hydroxyapatite is magnified

XRD Analysis

Fig 3 shows the XRD pattern of hydroxyapatite crystal. This means that n-HA was completely dispersed on the surface of polymer material. The particle size of nano hydroxyapatite powder was determined by Debye-Scherrer formula

$$D = \frac{K * \lambda}{B * \cos\theta}$$

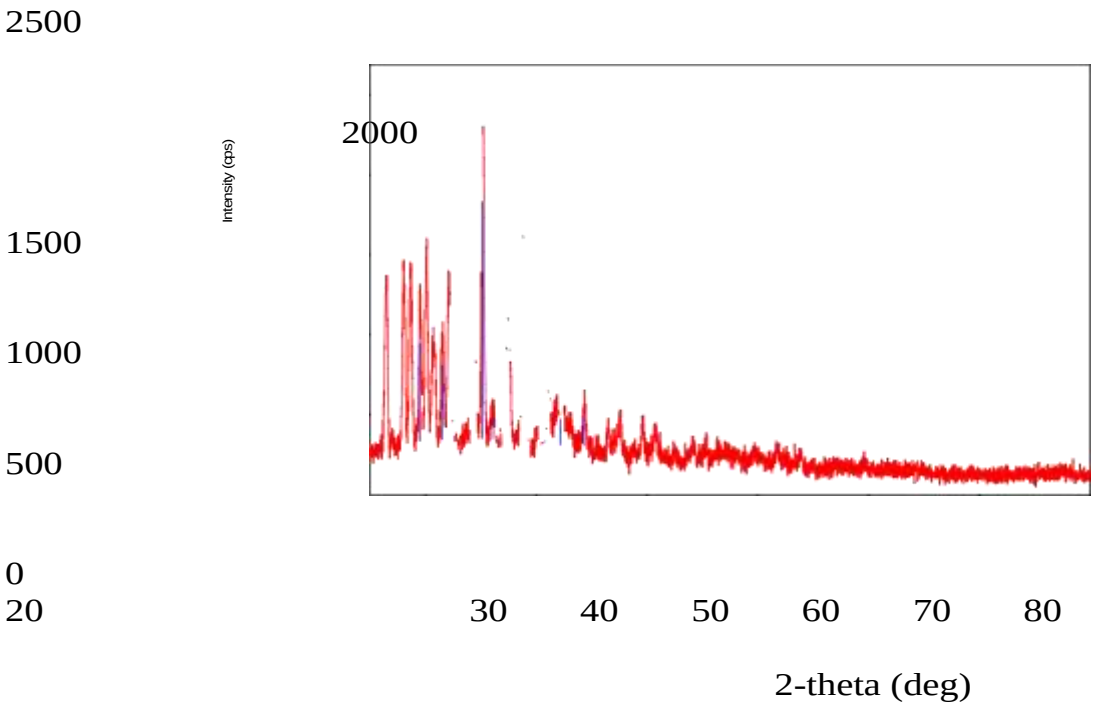


Figure 3 XRD pattern of nano-hydroxyapatite in the composite

where,

D means the average crystallite size (nm)

K means the shape factor (*K* = 0.9)

λ means the wavelength of the X-rays (λ = 1.54056 Å for Cu Kα radiation)

B is the full width at half maximum

(radian) θ is Bragg's diffraction angle

(degree).

The diffraction peak at 24.261° corresponding to the (008) Miller plane family was chosen for the calculation of the crystallite size. The data indicate that the mean grain size of n-HA in the composite is 3.66 nm [S.Sasikumar et.al [10] (2006)].

7. PROPERTIES OF THE COMPOSITE MATERIAL

Generally alpha- naphthol was considered with the properties of naphthol-formaldehyde with nano-hydroxyapatite. Specimens for the melting point of the composites were taken and done with the help of fisher-John melting point apparatus. Through which the melting point of alpha NF resin has low when compared with alpha NF composites. Similarly the boiling point of the material was also measured, through which composite has increased property. Then the materials were prepared from composites mixed with HMTA used as a curing agent by compression molding.

It can be found that the hardness of the nanocomposite material has increased when compared to the source material.

8. CONCLUSION

The present work describes the preparation of alpha naphthol-formaldehyde with nano- hydroxyapatite polymer composite. Through this composite, the morphological characteristics were studied by SEM analysis and particle size of nano material can be calculated using XRD analyses. The mechanical property of polymer composite has done. In this, hardness value of composite was tested, through which property value increases for composite material when compared to polymer material. The boiling and melting point of the composite was increased when compared to alpha-NF. So, I conclude that hydroxyapatite was used as reinforcing material for thermosetting polymer. Because, the material has increased mechanical property. It is anticipated that this study may open the way for future investigations in the use of n-HA.

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