Mechanical And Thermal Behavior of Novolac Reinforced With Nano - Hydroxy Apatite

N.Pugazhenthi[1], D.Mohanraj[2], D.Shivalingappa[3], K.Sivakumar[4], K.Suresh[5]

[1,5] PG Scholar, Department of Mechanical Engineering, Adhiyamaan College of Engineering, India.

2,3 Professor, Department of Mechanical Engineering, Adhiyamaan College of Engineering, India.

[4] Professor, Department of Chemistry, Adhiyamaan College of Engineering, India.

Abstract— In this report, a novolac polymer matrix was synthesized and melt blended with nano-hydroxyapatite in order to quantify their effect on thermal and mechanical behaviour of the resulting polymer composites. In this, complete preparation of nanocomposite were discussed. Here novolac resins are epoxidised through the phenolic hydroxyl groups by treatment with epichlorohydrin. Nanocomposites were mixed with hexamethylenetetramine (HMTA) which was used as curing agent. The composites were shaped through compression moulding machine according to the ASTM std. The morphological characters were found through the synthesized powder using SEM and XRD analysis. Thermal stability was characterized using TGA. The mechanical properties like tensile strength, hardness were discussed for the composite.

Keywords — Epichlorohydrin, Hydroxyapatite, Hexamethylenetetramine, Novolac,

1. INTRODUCTION

The large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nano particulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage [Habaib a. al taee et.al [9] (2009)]. The properties of high performance nanocomposites may be mainly due to the high aspect ratio and/or the high surface area of the fillers, since nano particulates have extremely high surface area to volume ratios when good dispersion is achieved. Phenolic resin is a common synthetic resin that is used in a broad range of applications such as paints, adhesives, and composites. Phenolic resin is a thermoset polymer and has two types, the resole type and the novolac type, depending on the method of synthesis and the catalysts used. Here polymer matrix used is novolac. Novolacs (originally Novolak, the name given by Leo Baekeland) are phenol-formaldehyde resins made where the molar ratio of formaldehyde to phenol is less than one. Already many nanoparticles were used to change the properties of novolac in the field of thermal and mechanical. Here we use novolac polymer matrix which is blended with nano-hydroxyapatite.

1. MATRIX MATERIAL

Phenolic resin is a common synthetic resin that is used in a broad range of applications such as paints, adhesives, and composites. Phenol-Formaldehyde resin is a highly crosslinked thermosetting material that is produced by the poly-condensation of phenol and formaldehyde in the presence of either acidic or basic catalyst. The novolac resin has various applications. It can be used in resin form as a bonding agent. Subsequently, the liquid resin can be dried and ground into moulding powder, which is usually used in moulding electrical fittings. Buttons, television and computer housing and the other household articles for the purpose of the paper, emphasis will be on the preparation, processing and characterization of P-F resin and moulding powder [Yan-min Pei et.al [23] (2011)].

2. 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. Hap has been used in biomedical applications in conjunction with many compounds since it is a major constituent of bones and teeth. In biomedical applications, HA/biocompatible polymer nanocomposites have been extensively studied, since such materials provide the ability to control biodegradability, bioactivity, and mechanical properties [Kacey G. Marra et.al [13] (1999)]. Several synthetic techniques have been introduced to prepare nano-sized HA particles including solid state reactions, wet chemical methods, and hydrothermal microemulsion techniques. Among these, hydrothermal microemulsion techniques lend themselves for the synthesis of nanopowders, nanoneedles, and nanowires [Raksujarit et.al [18] (2010)].

3. EXPERIMENTAL DETAILS

3.1 Materials Used

Glycial acetic acid, 40% Formaldehyde solution, Phenol, Con.HCl, calcium nitrate, diammonium phosphate, ammonia

3.2 Synthesis of Novolac

Taking 5ml of glycial acetic acid and 2.5ml of formaldehyde solution in 250ml beaker. Then 2gm of phenol and 1ml of conc.HCl solution in it. Heat slowly with constant stirring for 5min. A large mass of pink color plastic is formed. The residue obtained is washed several time with distilled water. 1 mole of the novolac resin was dissolved in 6 moles of epichlorohydrin and the mixture heated in a boiling water bath. The reaction mixture was stirred continuously for 16 hours. while 3 moles of sodium hydroxide in the form of 30 % aqueous solution was added drop wise. The resulting organic layer was separated, dried and then fractionally distilled under vacuum [Jenish Paul et.al [10] (2010)].

3.3 Composite Preparation

Prepared novolac powder is taken 20gm in which calcium nitrate is added 20ml. Then equal amount of diammonium phosphate is added slowly with constant stirrering. To maintain ph value greater than 11, ammonia is added during the process. The material is filtered and dried at 105°c. Through which 25gm of composite material is prepared. Similarly the process is continued for preparing 500gm of powder. In which novolac is reinforced with nano-hydroxyapatite.

To prepare specimens for tensile strength (ASTM D638) and hardness tests (ASTM D785), melt blended composites were ground into fine powder and then mixed with HMTA (mixing ratio: composite/HMTA=10/1), which was used as a curing agent. The mixture was poured into a mold (length ×width ×thickness=120mm×13mm×3mm) and was 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 moulding machine. The tensile properties were tested on a Schimadzu Autograph Universal Testing Machine (ASTM D 638-89). Five specimens were tested and the results were averaged to determine mechanical properties [Sang Chul Roh et.al [20] (2012)].

4. CHARECTERIZATION AND ANALYSIS OF POLYMER COMPOSITE

Scanning electron microscopy was used to examine the microscopy morphology of n-HA in the slurry and in the composite [Akihiro Matsumoto et.al [2] (2007)]. The samples for XRD and TGA analysis were dried in a vacuum oven at 80°C for 24 h before testing. In order to determine the effect of n-HA crystals on the thermal stability of the neat and modified cured resin samples was determined using thermo gravimetric analyser (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 mean grain size of n-HA powder was determined by Debye-Scherrer formula from XRD analysis. In this case CuKα radiation from a Cu X- ray tube was used. The samples were measured in the 2θ range from 10° to 90°.

5 RESULTS AND DISCUSSION

5.1 SEM ANALYSIS

Scanning electron microscope (Zeiss Evo 40XVP) was used to investigate the microstructures and the fracture surfaces of composites Samples were coated with a thin layer of gold to prevent charging before the observation by SEM.

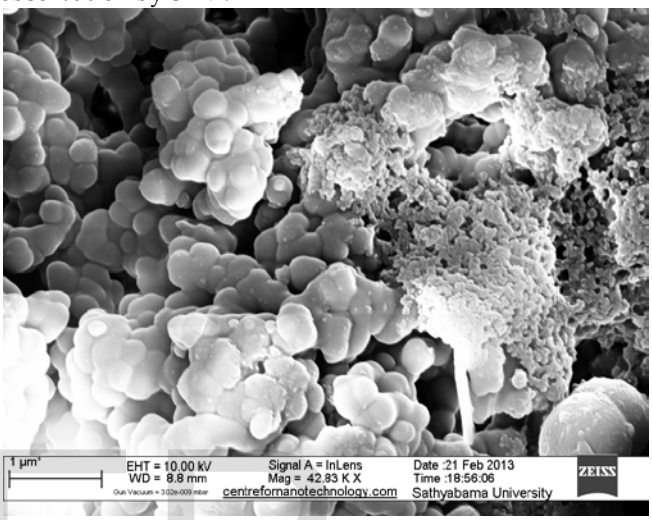

Fig 1 cluster of n-HA in composite material

The figure 1 shows size of the n-HA cluster decreased and the phase separation improved. The size of the cluster of n-HA could be controlled below 100 nm. This phenomenon reveals the good miscibility between organic (polymer) and inorganic n-HA phases.

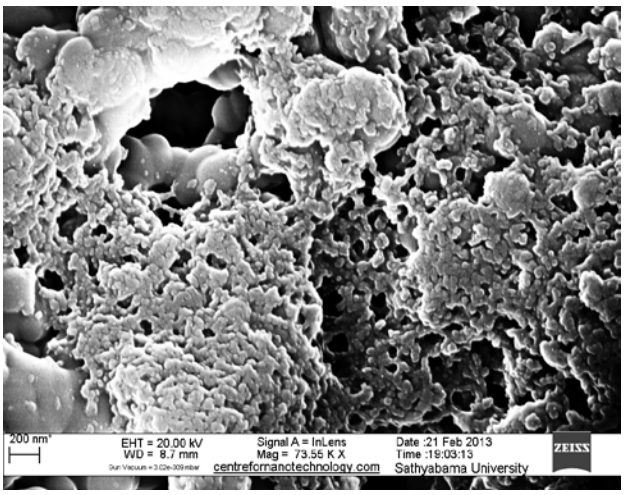

Fig 2: SEM image of composite material in which the nano-hydroxyapatite is magnified

5.2 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 mean grain size of HAP powder was determined by Debye-Scherrer formula

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

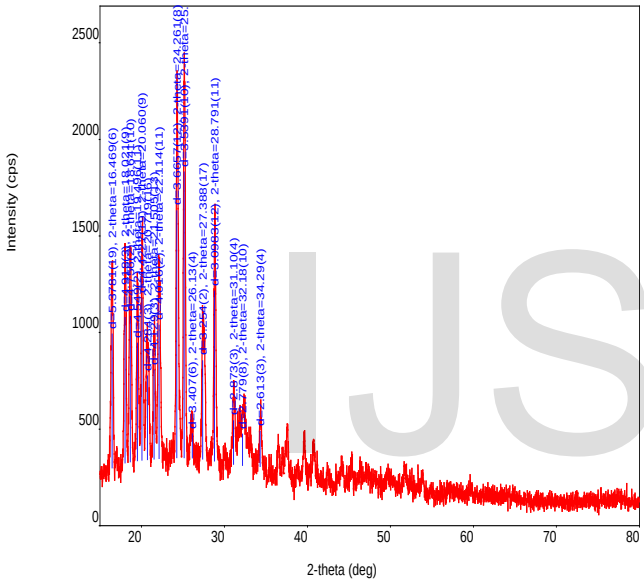

Fig 3: XRD pattern of nano-hydroxyapatite in the composite

where, D is the average crystallite size (nm); K is the shape factor ($K = 0.9$); λ is the wavelength of the X-rays ($\lambda = 1.54056$ Å for Cu Kα radiation); B is the full width at half maximum (radian) and θ is Bragg's diffraction angle (degree). The diffraction peak at 24.261° corresponding to the (008) Miller plane family was chosen for calculation of the crystallite size. The data indicates that the mean grain size of n-HA in the composite is 3.66 nm [S.Sasikumar et.al [19] (2006)].

5.3 Effect of n-HA on the thermal stability of novolac polymer

Thermal degradation of polymer ia a major problem at temperatures above the melting point and inevitably occurs in polymer melts during processing.

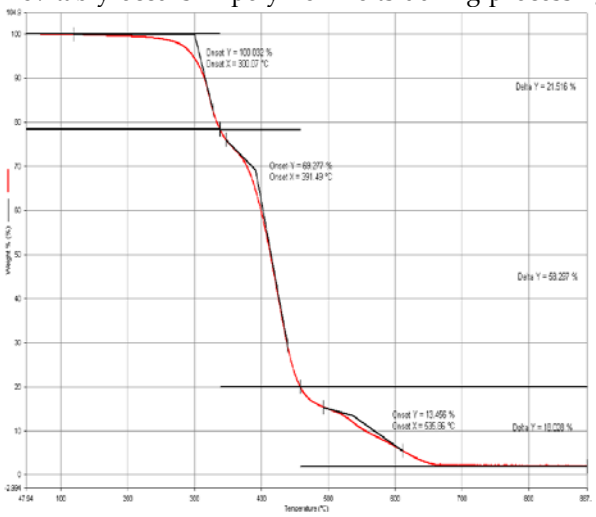

Fig 4 shows TGA curve for composite material

The study of thermal degradation can be best complicated or corroborated by such techniques as thermogravimetric analysis (TGA), which measures the weight loss as a function of temperature. Therefore, we have investigated the effect of n-HA on the thermal decomposition characteristics of novolac polymer.

Figure 4 shows TG curves for neat novolac polymer with n-HA nanocomposites in heating rate between 10° to 900°C at 20°c/min. The next section considers the implications. The temperature of degradation at which the weight loss is 5 and 10% of the neat novolac-type phenolic resin were 281.8 and 365.3 °C, respectively [Chin-lung chiang et.al [3] (2002)]. The temperature of material increased to 321.13 and 430.57 °C, respectively. The char yield of the composite materials increased from 36.13 to 58.25 wt %. The inorganic components of the silica enhanced the thermal stability of the hybrid materials. In which the temperature stability of composite material is higher than novolac polymer.

5.4 Mechanical Properties of The Composite

Table-1: mechanical property polymer and composite

material	Tensile strength (MPa)	Hardness (Shore D)
Novolac	27	84
Novolac – n-HA	35	97

Table-1 gives the mechanical properties of novolac and novolac with nano-hydroxyapatite. Specimens for tensile strength and hardness test were prepared from composites mixed with HMTA used as a curing agent by compression molding. It can be seen that the tensile strength and hardness of nanocomposite which is

prepared by in situ polymerization has increased considerably by the incorporation of n-HA, indicating a good reinforcing effect of n-HA. The improvement in tensile strength and hardness over that of the base resin is due to a higher degree of cross-linking as well as chain extension.

6 CONCLUSION

The present work describes the synthesis of novolac with nano-hydroxyapatite polymer composite. Through which the morphological characteristics were studied by SEM analysis and particle size of nano material can be calculated using XRD analysis. The mechanical properties of polymer composite have done. In this tensile strength and hardness value of composite is tested, through which property value is increased for composite material when compared to polymer material. The thermal stability of polymer composite also increased when compared to pure polymer. So, I conclude that hydroxyapatite was used as reinforcing material for thermosetting polymer and also for thermoplastic polymer. It is anticipated that this study may open the way for future investigations in the use of n-HA in fiber board so that the range of n-HA potential applications can be widened.

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