Synthesis and Mechanical Characterization of C.N.F Reinforced PCU Composite

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***Abstract*—**Polymeric composites reinforced with carbon nanofiber (C.N.F) and hydroxyapatite (HA) are found to have improved bio compatibility, bone adhesion properties resulting lesser problems in the long term safety. Thermo Plastic Polyurethane (Polycarbonate Urethane, PCU) which is identified for biomedical applications increasingly is used as the polymer base in the present study. Solution processing is used to prepare polymer composites having good quality films. Flexural and tensile tests were carried out to predict the influence of various constituents and combinations of CNF-PCU reinforcements on the mechanical characteristics of the test specimen. Flexural tests predict that CNF has more influence on flexural strength than HA and PCU. Whereas, the tensile test reveals that PCU has higher influence on tensile strength than CNF and HA.

***Keywords*—** Hydroxyapatite, Polycarbonate Urethane, Carbon Nanofibers, Solvent Casting.

I. INTRODUCTION

A NUMBER of new materials are being manufactured and tested for use as implant materials that have good biocompatibility compared to stainless steel and titanium. One such material is Polycarbonate Urethane which is found to have better osteoblast and fibroblast adhesion properties when reinforced with Carbon Nanofibers. The tests are carried out on films made using solvent cast method with Chloroform as the solvent.[1] Also Hydroxyapatite is a bone mineral and when used in the composites *in vivo* helps in bone formation. [2] Among the nanoscale reinforcements used it is found that Carbon nanofibers are having lesser cellular toxicity as compared to Single Walled Nanotubes and Multi Walled Nanotubes.[3] Polycarbonate Urethane material has good compatibility with natural tissue and its modulus is similar to cartilage. [4]

Solvent cast process is a unique method of production of composites without the application of excess temperature and pressures. Other advantages of this process include homogenous thickness distribution, free of gel specks, isotropic orientation, processing of thermally sensitive materials. The solvent cast products are more expensive compared to extruded ones due to slower production rates, extra energy costs of solvent recovery and investment in facilities for handling solvents. But the high quality of solvent cast films cannot be achieved in any other process.[5] Any solvent which can dissolve the polymers and can aid in dispersion of reinforcements can be used as a solvent in the solvent cast process. Dimethyl Formamide is one such solvent which can dissolve Polycarbonate Urethane and can effectively help in dispersion during ultrasonic dispersion. Dimethyl Formamide is used as a suspension medium for Hydroxyapatite as it is known to stabilize the Hydroxyapatite crystals effectively because of polarity and possibly due to its specific molecular structure. [6]

The average ultimate tensile strength, loaded in the direction of long axis of the compact bone of 15specimens taken from parietal bone of adult human embalmed cadavers was 10230lb/in^2 (70.3MPa) with a minimum of 6030 lb/in^2 (41MPa) and a maximum of 15800lb/in^2 (108MPa).[7] Poly Urethane (PU) composite with Multi Walled Carbon Nanotubes (MWCNT) loaded with 0%, 0.2%, 0.5% and 1% when tested with tension under ASTM D638 Type V sample resulted in ultimate tensile strengths of 1.71MPa, 4.2MPa, 7.79MPa, 10.18MPa and corresponding Elastic Modulus are 3.65GPa, 6.24GPa, 6.6GPa, 7.0GPa. The addition of MWCNTs increased the tensile strength and Elastic modulus.[8] Polymer Composites with reinforcements of HAP in 0%, 25% and 50% are tested for tensile strength and modulus. Increase in HAP content increases the elastic modulus and decreases the tensile strength of the composite. [9] In the current study the reinforcement levels of CNF are set at 0-5% to achieve optimal cell adhesion characteristics and strength properties and that of HAP are set at 20-40% for increased elastic modulus.

II. SYNTHESIS OF COMPOSITE

A. Raw Material specification

Medical Grade aliphatic Thermoplastic Polyurethane or Polycarbonate Urethane (PC3572D) supplied by Lubrizol in granules form is used. The rated ultimate tensile strength is 74MPa (max) tested according to ASTM D412 standards. Synthetic Nano Hydroxyapatite particles supplied by IFGL Bio Ceramics Ltd with particle size Ø100-200nm are used. Pyrolytically Stripped Carbon nano fibers of Ø100 x 20-200μm length supplied by Aldrich are used.

B. Synthesis of composite

Solvent casting process is employed to produce composite

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sheets in the thickness range of 1.5±0.3mm. The polymer granules are dissolved in the solvent using magnetic stirring at 80°C. The dissolved polymer solution and the suspended reinforcements is homogenized using ultrasonic energy using prod type sonicator. This solution is then put in a vacuum maintained 120°C. The degassed solution is poured in a glass mould or petri dish and then put in the oven maintained at 120°C for the evaporation of the solvent. The composite material is allowed to cool to room temperature in the oven and then the sheet is stripped from the glass mould and then cut to required shape for conducting the tests.

A nomenclature is used for identifying of the composite materials. The composite material is referred as CXXHXX where in C represents Carbon Nano Fibers, H represents Nano Hydroxyapatite; XX gives an idea of the amount of component present in percentage. For example a composite referred as C03H35 implies presence of 3% CNF and 35% HAP. The balance 60% constitutes the matrix material i.e., Poly Carbonate Urethane (PCU) The experimental design given in **Table I** is used as a reference to prepare composites for mechanical characterization.

TABLE I
COMPOSITION OF COMPOSITES

Composite Nomenclature	**Wt. % of CNF**	**Wt. % HAP**	**Wt. % of PCU**
C00H00	0	0	100
C00H20	0	20	80
C00H40	0	40	60
C01H25	1.25	25	73.75
C02H30	2.5	30	67.5
C03H35	3.75	35	61.25
C05H40	5	40	55
C03H23	3.0	23	74.0

III. MECHANICAL CHARACTERIZATION

A. Flexural Testing

The test is also called 3point Bend test and is carried according to Procedure A of ASTM D790 and according to which the strain rate is to be maintained at 0.01mm/mm/min. For every specimen the rate is calculated and given as input for calculation purposes. The specimen's width and depth are measured using a digital vernier.

$$R=ZL^2/6d \quad (1)$$

Where R = Rate of cross head motion, mm
L = Support span, mm
d = Depth of beam, mm
Z = rate of straining of the outer fiber, mm/mm/min.

Two specimens of each specification of composite are tested using the method explained above. The flexural strength of the composite material under study increases with increase in HAP content up to 20% and then decreases with further addition of HAP up to 40%. With addition of CNF to the composite the flexural strength increases with increase in both CNF and HAP but above 3%CNF and 23%HAP the increase the material property is very less. **Figure I** show the flexural strength for various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Flexural strength is 0.83, 0.51,-0.58 indicates CNF has more influence on flexural strength as compared to HAP and PCU.

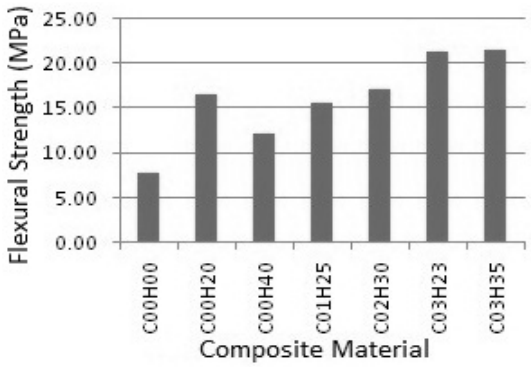

Fig. 1 Flexural Strength for Composite Materials

The flexural modulus is the ratio of flexural stress to the strain in flexural deformation. The flexural modulus of the composite material increases with increase in HAP content upto 20% and then decreases with further addition of HAP up to 40%. With increasing addition of CNF to the composite the flexural modulus increase**s. Figure II** shows the Flexural modulus for various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Flexural Modulus are 0.92, 0.53, -0.61 indicates CNF has more influence on the Flexural modulus than HAP. The pure polymer C00H00 has very flexural modulus and the specimen did not fail within the 5% limit. The material C03H35 failed at 4.2% strain and this material is not as flexible compared to the other materials prepared. The higher modulus of C05H35 is mainly due to presence of both CNF and HAP contents, because the C00H40 material with higher content of HAP was found to be having lesser modulus indicating the ability to deform/bend under load.

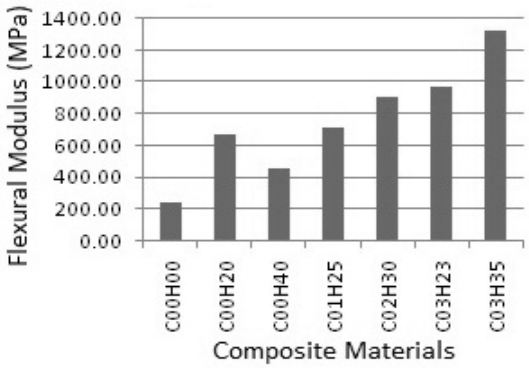

Fig.2 Flexural Modulus for Composite Materials

The flexural deflection of the composite material decreases with increase in HAP content upto 20% and then increases with further addition of HAP up to 40%. With the increasing addition of CNF the deflection of the composite material increases upto 3.125% CNF and 23%HAP and further increase in reinforcements reduced the deflection. The material found to be brittle. Figure III shows the flexural deflection of various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Flexural deflection is -0.27, -0.64, 0.64 indicates that higher the PCU content more is the deflection in the composite and negative coefficient for HAP indicates a inverse relation.

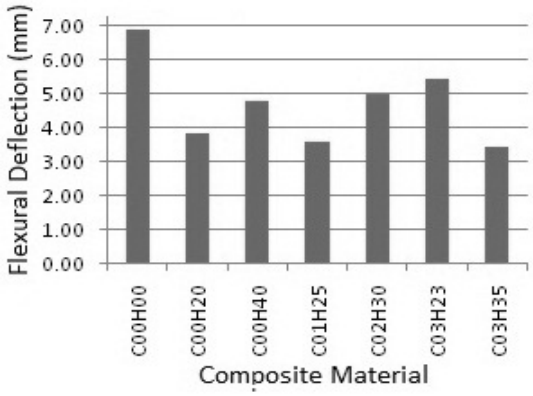

Fig. 3 Flexural Deflection for Composite Materials

B. Tensile Testing

The ASTM D638 is the reference standard for conducting the test. The specimen is cut to dumbbell as per Type A according to the standard. The edges of the specimen are polished to remove any nips and burrs that could affect the end results. When load is applied, the movable jaw move at a predetermined rate selected according to the ASTM D638 standard. The ultimate tensile strength or tensile stress at break of the material decreases with increase in HAP content up to 40% and with addition of CNF there is increase in tensile strength and above 30% of HAP even with higher CNF content the tensile strength decreases. As observed, the C03H35 material is brittle in nature, but C00H40 is ductile. The increase in brittleness of C03H35 is due to the action of both CNF and HAP in the material. **Figure IV** shows Tensile strength of various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Tensile Strength is -0.29, -0.93, 0.92 indicates CNF content has less influence on the tensile strength and higher content of PCU gives more tensile strength to material. The HAP reduces the tensile strength more effectively than CNF as is evident from the high correlation coefficient. The higher the content of the PCU more will be the ultimate tensile strength of the material. Thus for the higher tensile strength in the composite the reinforcement content should be reduced or the polymer grade should be having higher tensile strength.

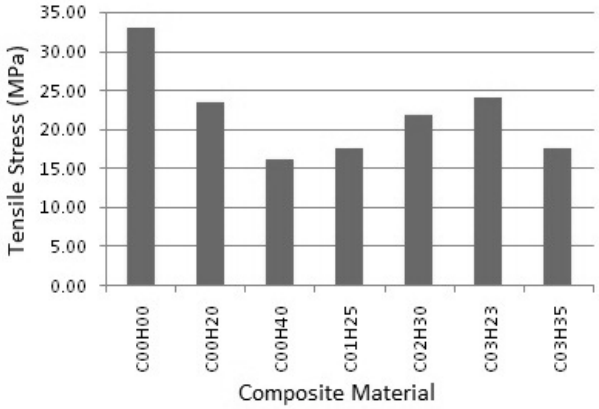

Fig. 4 Tensile Stress at break for Composite Materials

The elastic modulus increase drastically with increase in HAP content from 0 to 20% and then the increase is lesser up to 40%. With addition of CNF to the composite the modulus increases up to 30% HAP and 2.5% CNF and above which there is decrease in the elastic modulus with increase in reinforcements. **Figure V** shows the elastic modulus for various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Elastic Modulus is 0.51, 0.66, -0.68 indicates CNF has lesser influence on elastic modulus. The pure polymer is flexible in tension and the addition of reinforcement increases the modulus of the material and as the amount of PCU increases in the composite the modulus decreases.

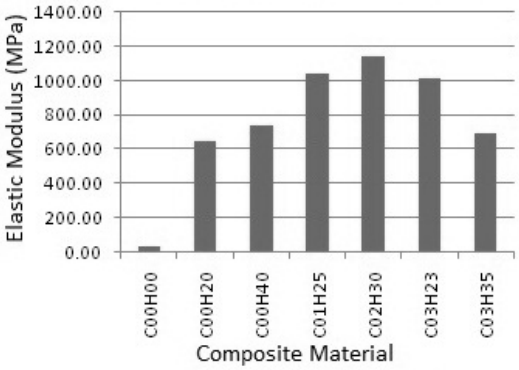

Fig. 5 Elastic Modulus for Composite Materials

The Nominal strain at break is the ratio of change in the grip length to the initial grip length measured using crosshead

extension indicator at break. The Nominal strain of pure polymer if very high compared with the composite material with both CNF and HAP reinforcements. In the absence of CNF, the addition of HAP reduces the strain loading of the composite material, but with the addition of CNF the elongation is reduced drastically even at low percentages. **Figure VI** shows the Nominal strain at break of various composite materials. The coefficient of correlation between amount of CNF, HAP, PCU and Nominal Strain is -0.65, -0.84, 0.88 indicates as HAP content increases nominal strain decreases.

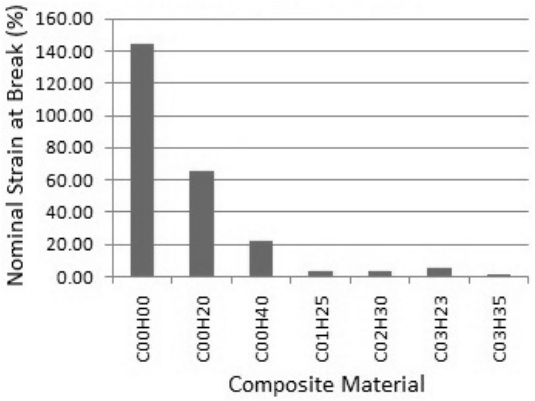

Fig. 6 Nominal Strain at break for Composite Materials

C. SEM Images and Analysis

Prepared composites materials are imaged using SEM. **Figure VII** shows the section of the composites C00H20 and C03H23.

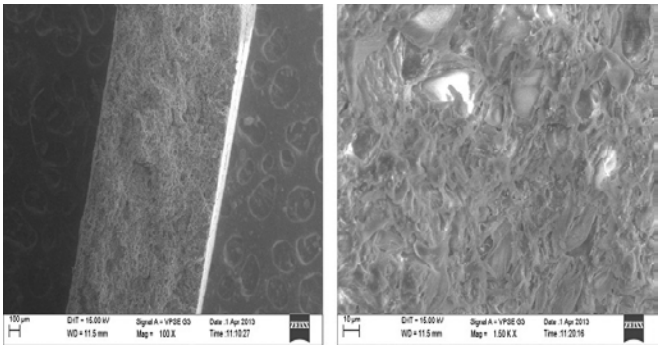

Fig.7 SEM Image of C03H23

From the images it is clear that the dispersion of the reinforcement phase is uniform within the composite. There are no cavities present in the cross section of the composite, indicating that there is no entrapped solvent. The solvent is evaporated from the composite material and the process capability is good enough to produce composites without porosity.

IV. CONCLUSIONS

From the manufacturing methods, it is clear that PCU (PC3572D) can be reinforced with Carbon Nanofibers and Hydroxyapatite using Solvent Cast method and good dispersions can be obtained using ultrasonication methods as confirmed by the SEM images.The absence of porosity in the SEM images also indicates the complete evaporation of solvent. The method is relatively simple and thus can be used for make composites in sheets of 1.5mm thick.

From the composites manufacturing, C00H23 has the better properties with tensile strength at break 24.18MPa, elastic modulus 1012.67MPa, flexural strength of 21.35MPa and flexural modulus 977.19MPa. The properties C00H23 though not sufficient for use as bone plates as envisaged, is well below the 70MPa of compact bone found in humans. The manufactured composite materials are highly flexible and hence can be used in areas like replacement for cartilages and also in places where there is lesser load.

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