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## Mechanical Analysis of Bio Nanocomposite Prepared from *Luffa cylindrica*

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### Abstract

*Luffa cylindrica* (LC), a tropical vegetal product, consists of highly vascular system. It has been modified by calcium phosphate and calcium carbonate separately to produce composites of Ca-salts. The modified form of LC has been reinforced with novolac resin at 30 °C to provide cross linked polymer composites. The composites have been further sonicated at 40 °C for 1 h to produce bio nano composites. The final yield is more than 80% of the raw materials used. The physical and chemical analysis of the composites have been done. Incorporation of resin in to the inner fiber surface of LC which is rich in cellulose is confirmed from ultra-violet spectroscopy (UV), and Fourier transform infrared (FTIR) analysis. Thermal studies of the composites done in an inert atmosphere reveals that the composites decompose within a temperature range of 250 - 550 °C. The tensile parameters such as maximum stress, Young's modulus and yield strength were measured. The compressive and flexural strength of the LC fiber- reinforced composites were also studied by varying the weight of fiber in the resin.

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*Keywords:* *Luffa cylindrica*; nanocomposite; tensile stress; compressive stress.

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### 1. Introduction

The persistence of plastics in the environment, concerns over emission hazards to human beings as well as to animals and birds or ingestion of these materials have spurred the efforts to find more environment friendly alternative materials. Natural fibers are now emerging as viable alternatives to synthetic fibers either alone or as composite materials for various applications such as building materials,

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automotive parts, packaging industries, biomedical applications etc. The advantage of natural fibers are low cost, low density, improved mechanical properties, recyclability and biodegradability.

The fruit of sponge gourd which is popularly known as *Luffa cylindrica* (LC) is a tropical forest product of India. It belongs to Cucurbitaceae family [1]. It has thick peel which has a three dimensional array of fibers. It is reported that LC possess a high content of celluloses, pentosans and other fibrous organic materials. Its characteristic properties, chemical composition and reactivity of different sites have been investigated by many workers [2-3]. Their bio degradability nature can contribute to a healthier ecosystem and low cost production for which authors of the present paper have made an attempt on this product, by modifying its surface by inorganic polymers. The modern society is now facing challenge to develop new biodegradable material for bio medical applications. Calcium phosphate and calcium carbonate are two important biomaterials. Amorphous calcium phosphate comprises nearly 80% of human bone. These are extensively used in bone replacement, dental filling, bone tissue engineering etc[8]. In view of this it has been attempted to explore the possibilities of using LC fibers by modifying their surface by calcium phosphate and calcium carbonate.

The modified LC fibers are then polymerized with novalac resin to produce bio- composites. Furthermore the prepared composites have been converted to nanocomposites by sonication. Also it has been attempted by taking different weight ratio of the LC fibers and resin. The thermal stability and mechanical parameters like maximum stress, Young's modulus and yield strength of the composites are studied.

## 2. Experiment

### 2.1. Materials

The chemicals such as calcium chloride ( $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 97%), di-sodium hydrogen phosphate di-hydrate ( $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ , 99.5%), resorcinol ( $\text{C}_6\text{H}_4\text{O}_2$ ), formaldehyde (HCHO), maleic anhydride [ $\text{C}_2\text{H}_2(\text{CO})_2\text{O}$ ], ethylene diamine [ $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ], commercial divinyl benzene (45% ethyl vinyl benzene and 55% divinyl benzene), methanesulphonic acid and 2N HCl all of analytical grade were procured from Merck and used without further purification.

### 2.2. Experiment

The fibers of LC were cut into small discs washed thoroughly with deionized water to remove impurity. These LC fibers are then dried at 70 °C in oven (vacuum). Aqueous solution of  $\text{CaCl}_2$  (3 mol  $\text{L}^{-1}$ , pH = 9),  $\text{Na}_2\text{CO}_3$  (2 mol  $\text{L}^{-1}$ , pH = 10), and  $\text{Na}_2\text{HPO}_4$  (2 mol  $\text{L}^{-1}$ , pH = 10), were prepared separately. The fibers were immersed in  $\text{CaCl}_2$  solution for 12 h at room temperature. The modified fibers were reimmersed in  $\text{Na}_2\text{HPO}_4$  solution for 12 h at room temperature to deposit compounds of calcium phosphate over them. Another set of the modified fibers were reimmersed in  $\text{Na}_2\text{CO}_3$  solution for 12 h to deposit compounds of calcium carbonate over it. Thus two separate sets of modified fibers were prepared [4].

Resorcinol-formaldehyde resin was synthesized by using the standard procedures [5]. Four samples such as B1, B2, B3, B4 were prepared using modified LC fibers and resin. In sample B1 and B2, LC fibers modified with calcium carbonate and resin are in weight proportion 1:1 and 2:1 respectively. In sample B3 and B4 LC fibers modified with calcium phosphate and resin are in weight proportion 1:1 and 2:1, respectively. Maleic anhydride and ethylene diamine were used as cross linkers. All the samples were heated separately at temperature of 70 °C for 9 h and then powdered. The powdered composite was then

exposed to ultrasonic vibration at 30 kHz for 1 h at room temperature using a sonicator (1.5 L50 H/Deluxe, India).

### 2.3. Composite fabrication

A 10 g of powdered sample was mixed with 10 g of commercial divinyl benzene and kept for 12 h. The sample was swollen as it absorbed sufficient divinyl benzene in to it. This facilitates the sample to be softened and a paste like material was obtained. This material can easily be shaped and moulded. The material was made acidic by addition of 0.25 mL of methanesulphonic acid. The paste was kept in a small mould (10 cm × 2 cm).The mould was heated for 4 h at 60 °C and was cured to get cross linked composite. The composite was found to be relatively stronger and was not brittle.

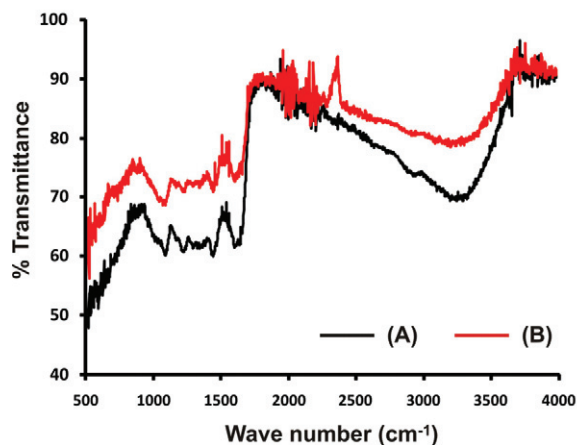


Fig.1. (A) FTIR spectra of B 1(composite of LC fibers modified with calcium carbonate and resin in equal weight proportion) and (B) FTIR spectra of B3 (composite of LC fibers modified with calcium phosphate and resin in equal weight proportion)

### 2.4. Test methods

The powdered samples were examined by FTIR spectroscopy (FTIR Nicolet 6700 / Thermofisher Scientific) using KBr pellet technique in the region 500 - 4000  $\text{cm}^{-1}$  to identify the functional groups in the composites. The UV- visible spectral analysis of all the composites were carried out by Shimadzu UV 1600 visible spectrometer in the wavelength range 240 - 800 nm. X-Ray diffraction (XRD) analysis of the samples was carried out for structural phase identification using WXR/ Shimadzu/Japan at room temperature. The voltage and current setting of the diffractometer was at 40 kV and 30 mA respectively. XRD patterns were obtained in the scan angle range of  $10^\circ$  and  $80^\circ$ . Thermal stability of the composites was studied in nitrogen atmosphere on TGA Q50 V20.10/TA instruments, USA at a heating rate of 10  $^\circ\text{C}/\text{min}$  in temperature range of 50  $^\circ\text{C}$  to 800  $^\circ\text{C}$ . Testing of sample for compressive strength, tensile strength and flexural strength was done in Universal testing machine (Lloyd Instruments, UK).

## 3. Results and Discussion

### 3.1. FTIR analysis

The presence of 4 vibrational modes due to the tetrahedral symmetry of phosphate groups such as  $\nu_1$  ( $640 \text{ cm}^{-1}$ ),  $\nu_2$  ( $500.4 \text{ cm}^{-1}$ ),  $\nu_3$  ( $1087 \text{ cm}^{-1}$ ),  $\nu_4$  ( $570 \text{ cm}^{-1}$ ) confirms the presence of calcium phosphate and

its polymorph in B3 and B4 sample. Furthermore, the existence of calcite ( $821.3\text{ cm}^{-1}$ ), vaterite ( $837.2\text{ cm}^{-1}$ ), aragonite ( $800.5\text{ cm}^{-1}$ ) are observed in the sample B1 and B2 [6-8]. The FTIR spectra of the calcium phosphate based composite and calcium carbonate based composite are shown in Figure 1.

### 3.2. UV–Vis spectral analysis

The UV absorption spectrum of B1 sample shown in Figure 2 reveals two large peaks at 286 nm and 353 nm. The peaks show the presence of  $\text{CO}_3^{2-}$  in the composite. The same is further attributed by a small visible spectral peak at 535 nm.

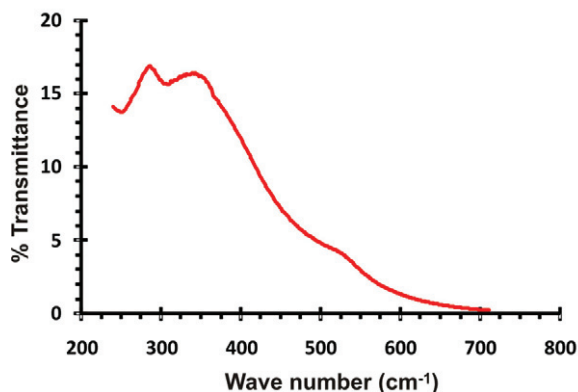


Fig. 2. UV spectrum of B1 (composite of LC fiber modified with calcium carbonate and resin in equal weight proportion)

### 3.3. XRD analysis

XRD pattern of B1 sample is shown in Figure 3 which contains resin and LC fibers modified with calcium carbonate in weight proportion 1:1. Diffraction peak at  $45.09^\circ$  indicates presence of vaterite, whereas  $29.2^\circ$ ,  $64.55^\circ$  for calcite and  $44.2^\circ$  for aragonite. Furthermore diffraction peaks at  $22.46^\circ$ ,  $23.70^\circ$ ,  $32.50^\circ$ ,  $77.85^\circ$  shows presence of hydroxy apatite (HAP) and peaks at  $44.21^\circ$ ,  $64.55^\circ$  gives evidence of presence of  $\beta$  tricalcium phosphate ( $\beta$  TCP) in sample B3 and B4 [6-8]. The presence of diffraction peaks around  $22^\circ$  and  $23^\circ$  in all the samples indicate the presence of cellulose (I) and cellulose (II). The LC fibers are reported earlier to contain 60% cellulose, 30% hemi cellulose and 10% lignin[1].

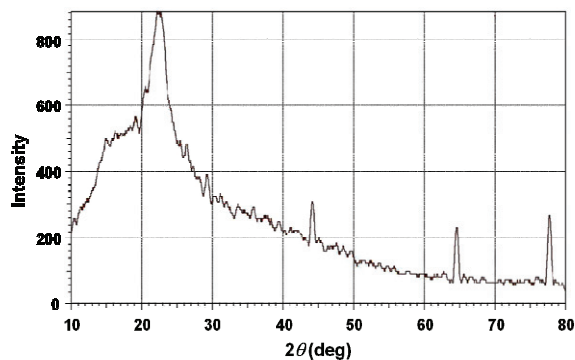


Fig. 3. X ray diffraction pattern of B1 (composite of LC fiber modified with calcium carbonate and resin in equal weight

The crystallite size of composites determined from XRD analysis using Debye-Scherrer Formula [8] is given by

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where  $D$  = crystallite size,  $K$  = shape factor = 0.9,  $\lambda$  = Wavelength of Cu  $K_{\alpha}$  1.5496 Å,  $\beta$  = FWHM (full width at half maximum) and  $\theta$  = Bragg's diffraction angle. Crystallite size of calcium phosphate based composites (B3 and B4) was found to be lying within 20 nm to 50 nm, whereas for calcite based composites (B1 and B2) the crystallite size was lying between 70 to 90 nm. With increase in weight of fibers in the composite, crystallite size was found to be decreased. Also the broad peaks and higher values of FWHM in the XRD patterns of all the samples indicate low crystallinity nature of the composites.

### 3.4. Thermo gravimetric analysis (TGA)

The LC fibers contain 60% of cellulose along with 30% hemicellulose. Cellulose is a linear macromolecule consisting of D-anhydroglucose repeating units. Each repeating unit contains three hydroxyl (-OH) groups in its structure[9]. The hydroxyl groups in the main backbone chain of resorcinol-formaldehyde resin provide sites for hydrogen bonding to the surface of LC fibers which also contains many hydroxyl groups. These hydroxyl groups in both resin and fiber and their ability to form hydrogen bonds play a major role in deciding thermal stability of the composites. Thermogravimetry analysis (TGA) of all the samples was carried out in nitrogen atmosphere.

Table 1. Mass loss of the composite during thermo gravimetry in % with temperature

Sample	200 °C	400 °C	600 °C	800 °C
B1	13.07%	41.28%	63.75%	82.82%
B2	11.57%	44.68%	80.47%	96.32%
B3	12.10%	36.18%	61.60%	84.93%
B4	11.48%	38.03%	62.30%	82.67%

B1: calcium carbonate modified luffa-resorcinol nanocomposite (1:1)  
 B2: calcium carbonate modified luffa-resorcinol nanocomposite (2:1)  
 B3: calcium phosphate modified luffa-resorcinol nanocomposite (1:1)  
 B4: calcium phosphate modified luffa-resorcinol nanocomposite (2:1)

The TGA curves of sample B3 are shown in Figure 4. The results given in Table 1 shows the loss of mass of the composite in various temperature ranges and Table 2 shows peak positions of rate of change of mass of the composite with temperature. The initial loss of mass, till the first peak (37 °C) is probably due to presence of moisture in the composite. The second peak obtained between 341.91 °C and 350 °C may be due to degradation of cellulose present in the LC fibers. The third peak obtained around 570 °C and 580 °C may be due to degradation of lignin. The results of Table 1 and 2 indicate that all the composites decompose within temperature range of 250 - 600 °C. It was further observed that incorporation of more fiber in to the resin decreases the thermal stability indicating that chemical bonding between the resin and the LC fiber is relatively stronger when the weight of fiber is less in the composite.

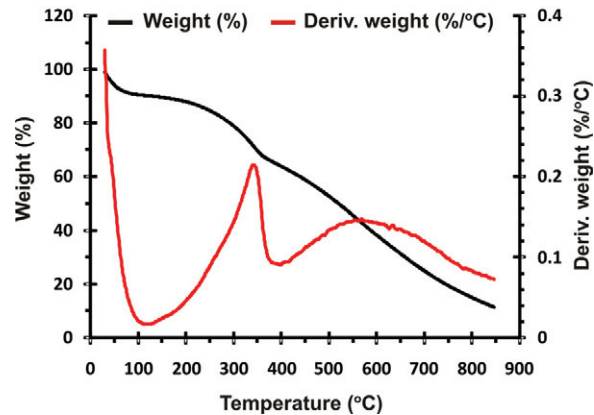


Fig. 4. TGA/DTG curve of B3 (composite of LC fiber modified with calcium phosphate and resin in equal weight proportion)

Table 2. Peak Positions of derivative curve of thermo gravimetry analysis

Sample	Peak I	Peak II	Peak III
B1	44.4	342.47	553.61
B2	36.35	338.69	583.14
B3	37.43	341.93	579.92
B4	48.15	332	571.34

### 3.5. Mechanical properties

Testing of sample for compressive strength, tensile strength and flexural strength was done in Universal testing machine. The tensile strength measurement was performed in accordance with ASTM D 638 method. Compressive strength was measured using ASTM D 682 method and flexural strength was measured using ASTM D 790 method. All the results are given in Table 3-5.

Table 3. Values of ultimate tensile stress, yield strength, breaking stress and tensile modulus of B1 and B2 composite

Sample	Ultimate tensile stress (MPa)	Yield strength (MPa)	Breaking stress (MPa)	Tensile modulus (MPa)
B1	14.88	12.7	13.5	680
B2	9.7	7.59	9	387

Table 4. Values of ultimate compressive stress, yield strength, breaking stress and compressive modulus of B1 and B2 composite

Sample	Ultimate compressive stress (MPa)	Yield strength (MPa)	Breaking stress (MPa)	Compressive modulus (MPa)
B1	70.28	59.5	66	2687
B2	62.64	52	58.8	1483

The tensile, compressive and flexural properties are found to be maximum in B1 sample where LC fibers and the resin are in equal weight proportion. With the increase in weight of fibers in the composite

all the mechanical parameters are decreased. It shows that the mechanical properties depend on the fiber matrix interaction. When the amount of fiber is more, the resin is insufficient to completely wet the fiber. Probably due to incomplete impregnation of the fiber within the resin the mechanical parameters decrease in the sample B2.

Table 5. Values of ultimate flexural stress, yield strength, breaking stress and flexural modulus of B1 and B2 composite

Sample	Ultimate Flexural stress (MPa)	Yield strength (MPa)	Breaking stress (MPa)	Flexural modulus (MPa)
B1	80.67	72.8	76	3338
B2	70.64	59	63	2260

#### 4. Conclusion

All the composites are found to be less crystalline. The crystallinity and crystallite size of the composites decrease with increase in weight of fiber in the resin as evident from XRD patterns. These low crystallinities of composites are the features of good bone implant and bone bonding. As a result calcium phosphate and calcium carbonate based composites may provide the proper bony substrate when used with LC fiber framework. The thermal study reveals that the composites are more thermo setting than thermo plastic in nature. Secondly, these composites can sustain decomposition to maximum range of 800 °C. Mechanical properties are found to depend on adhesion between fibers and resin as well as fiber loading which requires more resin to wet the fiber in order to have effective mechanical properties. In this investigation LC fibers modified with calcium carbonate and calcium phosphate shows potential alternatives as reinforcing materials for polymer based composites. Their biodegradable nature can also contribute to a compatible ecosystem and the possibilities of using these composites for biomedical application can be extended by further trials.

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