

# Mercerization Effect on Bio-waste Eggshell Reinforced Polymer Composite for Energy Saving Application

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**Abstract.** Polymer composite from biowaste material have gained enough interest by its unique light weight, high strength, high corrosion resistance, affordability, pollution free, renewability and ecofriendly natures. These important factors are relevant to form an energy efficient domain which will boost the fuel economy in many engineering and industrial sectors. In present study, composite material has developed from waste chicken eggshells (CES). Existing hydrophilic semipermeable membrane in eggshell create trouble during the development of composite with hydrophobic matrix. So (CES)/matrix interface was modified by treating CES with sodium hydroxide chemical which better known as “Mercerization”. Structural, morphological, vibrational and mechanical properties were investigated both for untreated and treated CES particle as well as composites. Structural result showed an increase in crystallite size of ESP which indicated the additional crystal growth in crystalline region. A smooth surface with porous membrane were spotted from morphological study. Combinely, porous membrane and crystallite size increment facilitated the interfacial bonding between ESP/matrix which may cause the improvement in mechanical properties of composites.

## INTRODUCTION

In the contemptuous world, many effort have been made to make composite materials from agro wastes which set a new bench mark for creating a greener composite world. Recently, composite reinforced with Chicken Egg shell (CES) filler type material has gained an extensive research interest as it reduce matrix ductility nature, thus increase the modulus of materials. Incorporation of CES into polymer matrix offer an opportunity to recycle for beneficial purposes. Low hardness of eggshell bio filler reduce the abrasion of processing products. Calcium (90-94%) rich eggshell derive composite products offer high compressive strength, stiffness, good corrosion resistance and are biodegradable, environment friendly absorb CO<sub>2</sub> emission. So all these properties may be useful to develop lightweight materials for different energy saving applications[1][2]. Using heavy strength materials to fabricate various structural parts consumes a vast amount of energy [3]. Vehicle, turbine blades, solar panel’s structural parts, aircraft segments designed with lightweight composite material can able to improve safety, enhance the performance, lower the cost, maximize the fuel economy benefits of accomplished product and create clear energy sources for solar and wind energy to generate power and electricity[4][5]. But major issue involve with eggshell is the existing semipermeable membrane which allow air and moistures to pass through its pores. The hydrophobic polymer matrix and hydrophilic eggshell make poor adhesion at interface of filler/matrix thus deteriorate the properties of end use products. Various author reported many pretreatment techniques to modify the surface of CES to make a good adhesion between filler/matrix interfaces[6][7][8]. Disposal of eggshells together with membrane to the landfills attract vermin which cause harm and annoyance. So it is primarily necessary to remove the membranes out from shells. Present investigation is mainly dealing with effect of Sodium Hydroxide (NaOH) treatment on the crystalline as well as mechanical property of the eggshell reinforced composite. NaOH acts as a coupling agent which make a strong bridge between filler/matrix, affect chemical composition of filler, hence make a good adhesion for developing strong, stiff composites.

## MATERIALS AND METHODS

CES were collected from kitchens of National Institute of Technology Rourkela. Thermosetting Epoxy (L-12) and Hardener (K-6) were purchased from Himedia Laboratories Private Limited, India. For treatment of CES surface, Sodium Hydroxide (NaOH) was supplied by Merck Life Science Pvt. Ltd, Mumbai, India.

## Experimental Procedure/Model and Characterization Techniques

Initially CES membranes were separated from shell by soaking them in water for about 48 hours. The floated membranes were observed over water with placing the heavier shells in the bottom. The shells were then rinsed with deionized (DI) water various times and dried for 24 hours at room temperature and named as “Untreated CES (UCES)”. For treatment, UCES were soaked in NaOH concentrations (5, 10 and 15%) for 24 hours at room temperature and rinsed with DI water. The shells were dried in an air circulated oven to remove moisture and chemicals. Treated CES were crushed mechanically and sieved to the particle size up to 150 μm. The treated CES were collected and named as 5NCES, 10NCES and 15NCES where ‘N’ denoted as NaOH treated CES. X-Ray spectral patterns of both untreated and treated CES powder were recorded by CuK radiation by Ultima IV- Rigaku, Japan diffractometer. Data were taken at 2θ range from 10°- 50° and scanning rate of 3°/min with step size 0.01. Functional groups were investigated by FTIR PerkinElmer Spectrum with averaged over 8 scans using a nominal resolution of 4 cm<sup>-1</sup>. The surface morphology of CES powder were carried out by using (Nova Nanosem 450, Japan) FESEM at 10KV accelerating voltage. The CES reinforced composite were fabricated using Hand lay-out technique. CES powder and epoxy resin were mixed initially and placed it under an ultrasonicator probe to make the solution slurry. Hardener was mixed aftermath and stirred well together to avoid bubbles. A mould of dimension (100 × 70 × 5) mm<sup>3</sup> was prepared. All specimens were cured at room temperature for 24 hours. Four sets of samples were cut according to the ASTM standard for flexural measurement. Flexural strength was measured using 3 point bending test by Universal Testing Machine (Instron-5967, UK) with Environmental Chamber. Specimens were cut with (90×13×5) mm<sup>3</sup> dimension according to ASTM-D7254 at a loading rate of 5mm/min. The flexural strength of the composite were determined using the following equation-(2).

$$\text{Flexural Strength} = \frac{3FL}{2BD^2} \dots\dots\dots (2)$$

Where F= force at the fracture point, L= length of the support span, b & d= width and diameter of specimen

## RESULTS AND DISCUSSION

Fig.1 a) showed the XRD spectral lines for both treated and untreated CES powder. All the untreated and treated CES showed an equivalent diffractogram patterns. Main characteristics peaks were appeared at the Bragg’s angle of 23.1°, 29.4°, 36.0°, 39.5°, 43.2°, 47.6°, 48.6° corresponding to miller indices [012], [104], [110], [113], [202], [018] and [116] respectively. XRD analysis confirmed the presence of calcite mineral in CES which is pure and stable form of CaCO<sub>3</sub> and matched with (JCPDS-72-1651) file. The most prominent intense peak appeared at the angle of 29.4°, which clearly defined that calcite is purely crystalline in nature and rhombohedral in structure.

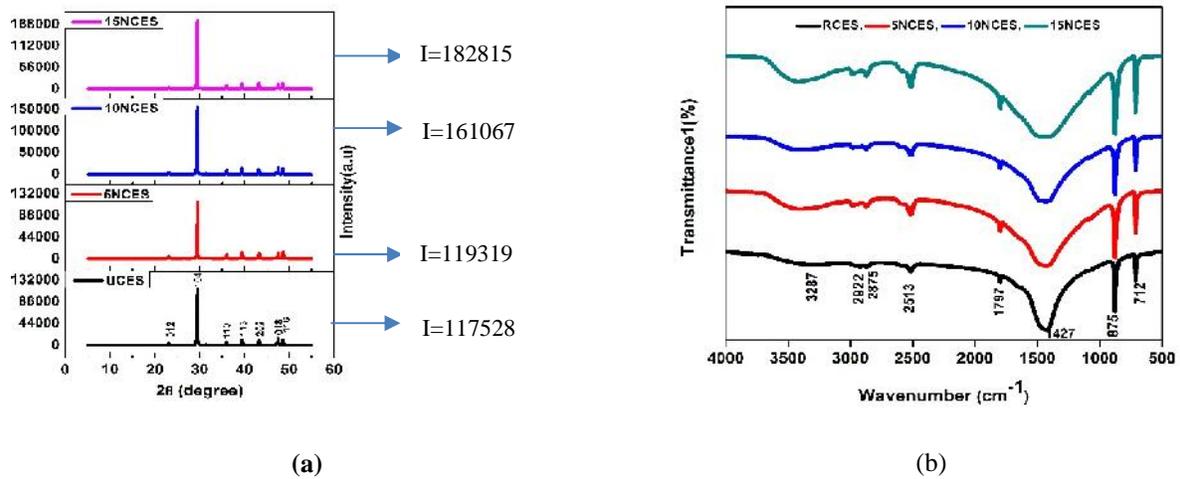
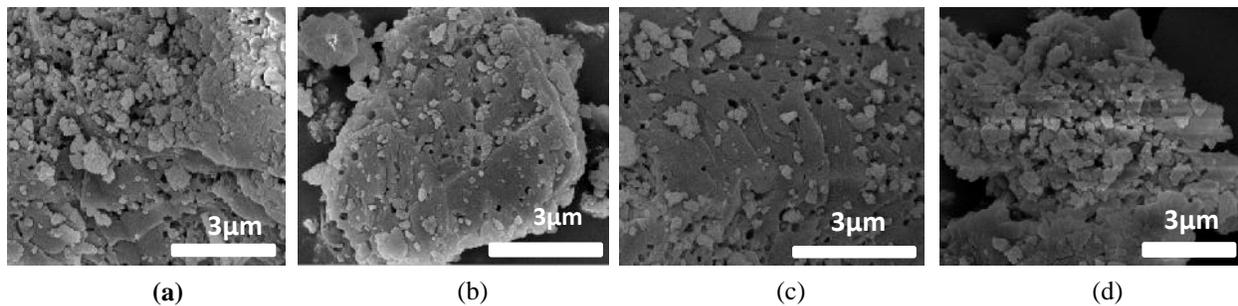


FIGURE 1. a) XRD b) FTIR spectral pattern of untreated and treated CES powder

It is clearly observed that with increase of NaOH concentrations, the intensity values are gradually increasing which explains the increase in crystalline size of CES particles. The reason might be due to the additional crystal growth in the crystalline region due to the ionic interaction among NaOH chemical, calcite mineral and thermosetting epoxy resin where they stick together to form a large crystal structure. Increase of intensity with treatment also indicate the more arrangement and ordered polymer chains within crystalline region. Due to the crystal growth, there might may be less chance for crystal to cause defects which in turn result an increase of crystallite size.

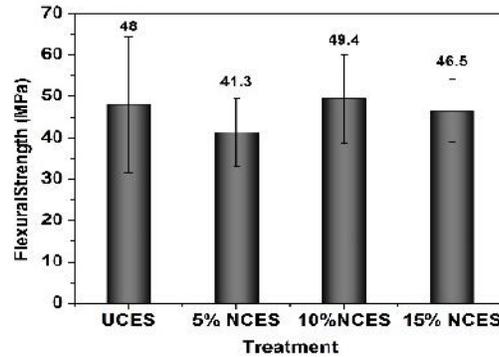
Fig.1 b) showed the FTIR pattern for untreated and treated powdered CES. The spectra for RCES as well as 5NCES, 10NCES and 15NCES exhibit nearly equivalent patterns. The broad absorption band appeared at  $3428\text{cm}^{-1}$  is mainly attributed  $\text{OH}^-$  functional group which explains the presence of residual water present in egg shell. Two smaller vibration band have appeared at  $2513\text{cm}^{-1}$  and  $2875\text{cm}^{-1}$  which are due to presence of  $\text{CO}_3^{2-}$ . Besides that there are two sharp peaks of band have appeared at  $712\text{cm}^{-1}$  and  $875\text{cm}^{-1}$  along with a broad peak at  $1427\text{cm}^{-1}$  which indicates the presence of carbonate  $\text{CO}_3^{2-}$  molecular ion in CES powder. Since all spectrum bands (untreated/treated) exhibit similar nature, it concluded that NaOH treatment did not change the chemical composition of material. FTIR confirmed the well confirmation of calcite phase and unaltered chemical composition of CES particle even after treatment.



**FIGURE 2.** FESEM images of (a) UCES (b) 5NCES (c) 10NCES (d) 15NCES

Fig.2 showed FESEM images of the both untreated and treated CES particle. In fig.4 (a), the holes present in shells are not clearly visible because of membranes deposition. A clean and smooth shell surface were observed in fig4 (b) and (c) due to the treatment with 5% and 10% NaOH solution which may dissolved the membranes and exposed porous areas towards the penetration of chemicals inside the shells. But 10% NaOH treatment greatly washed the shell surface of shell, removed impurities, more pores were uncovered and surface area of pores were increased. So combinely, the expose of more pores and increased surface areas of pores facilitated a better interfacial adhesion between filler and matrix for composite production. Treatment with higher concentration of NaOH (15%) degraded the CES surface as shown in fig4 (d). Due to large amount of penetration of chemical, the particles were agglomeratedly placed together by swelling of surface and the thin eggshell membrane were not visible within the powdered sample. So the degraded surface of CES resulted to a poor interfacial bonding between filler/matrix.

In Fig. 3, flexural strength was observed to be higher for 10% NCES reinforced composite. The failure of flexural strength was occurred at 5%NCES and 15% NCES composite. Increase in crystalline size of particles and more expose of porous surface with increased surface area directly regulate the mechanical strength of composite. FESEM image showed that treatment with 10% NaOH solution exposed eggshell pores towards the penetration of chemicals. NaOH treatment helped to remove surface impurities from CES particles and acted like a bridge by making crosslink between the functional groups of filler and matrix. When loading was performed by the load cell on specimen during test, there was a better and homogeneous stress transfer from matrix to reinforcement and also a proper mixing of CES particle within NaOH solution in case of 10NCES reinforced composite which managed to have a better mechanical and chemical interlocking at the interface. The failure of flexural strength in case of 15% NCES was attributed to low degree of polymerization in the polymer. Treatment of CES with high NaOH concentration although increased the crystalline size of particle but high ion exchange among NaOH, Calcite mineral and epoxy resin lowered the crosslinking process which may led to decrease of degree of polymerization.



**FIGURE 3.** Effect of NaOH treatment on the flexural strength of untreated and treated CES

## CONCLUSION

In the present investigation, the CES filler surface was modified with NaOH with varying concentration. Based on the above study, the following conclusions were drawn. X-ray diffraction and FTIR study confirmed the presence of pure calcite phase in CES particles. Increase in intensity values showed the increase in crystalline size of filler particles. Treatment did not alter the chemical composition of CES filler particles. FESEM images of untreated and treated CES showed 10% NaOH treatment greatly cleaned the shell surface lead to expose more pores towards the penetration of chemicals and increased the surface area of the pores which facilitated the interfacial adhesion between filler/matrix. The flexural strength was found to be enhanced for 10NCES composite due to sufficient blending between filler/matrix with homogeneous stress transfer during loading and increase in crystalline size of CES particles.

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