Original Article

Impact of nanoclay on mechanical and structural properties of treated Coccinia indica fibre reinforced epoxy composites

Bhuvaneshwaran Mylsamy\textsuperscript{a}, Sathish Kumar Palaniappan\textsuperscript{b,\textcopyright}, Sampath Pavayee Subramani\textsuperscript{c}, Samir Kumar Pal\textsuperscript{b}, Karthik Aruchamy\textsuperscript{d}

\textsuperscript{a} Department of Mechanical Engineering, K.S.R. College of Engineering, Tiruchengode, Tamil Nadu 637 215, India
\textsuperscript{b} Department of Mining Engineering, Indian Institute of Technology, Kharagpur, West Bengal, 721 302, India
\textsuperscript{c} Department of Mechanical Engineering, K.S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu 637 215, India
\textsuperscript{d} Department of Mechanical Engineering, SSM College of Engineering, Komarapalayam, Tamil Nadu 638 183, India

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\textbf{A B S T R A C T}

Natural fibre composite materials are one such capable material which replaces the conventional and synthetic materials for the practical applications where we require less weight and energy conservation. The present paper emphasizes the effect of Cloisite 30B on the newly identified Coccinia Indica fibre, which is extracted from a medicinal plant (i.e., Cucurbitaceae) by manual process. The chemically treated Coccinia Indica fibre reinforced composite is prepared by using the epoxy resin and the detailed preparation methodology is presented. In this paper, the mechanical properties and morphological characterizations of nanoclay filled chemically treated Coccinia Indica fibre reinforced epoxy composites were compared with the unfilled composite. The experimental evidence shows that the increase in weight percentage of nanoclay enhances the tensile, flexural, impact, compression properties of the treated Coccinia Indica fibre reinforced epoxy composites. These results were also confirmed by the Scanning Electron Microscopy observations of composites and Fourier Transform Infrared Spectroscopy analysis of the chemical structure. Fibre pull-outs on the fractured specimen during physical testing of the composites were also investigated. As a result, the presence of 3 wt.% nanoclay provides better interfacial adhesion between fibres and matrix, which gives the best results compare to others.

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1. Introduction

Global market is promptly moving towards the energy conservation and energy reduction process. Natural fibres are booming in today’s composite world and mostly used in engineering applications because of their specific characteristics
compared to the traditional fibres. Recently, the development of natural fiber composite instead of synthetics fiber has lead to eco-friendly product manufacturing to meet various applications in the field of automotive, construction and manufacturing. In recent times, the development of composite materials is based on renewable or natural sources rising rapidly for numerous reasons [1]. Attention towards plant fibre reinforced polymer composites in different applications increases because of its various desirable properties. Traditional fibre reinforced polymer composites including carbon, aramid fibre and glass fibre are substituted by plant fibres because of its environmental friendly features [2]. But, it also has some disadvantages like heat, poor adhesion to polymers, poor transverse strength and water sensitivity. Several studies were carried out to improve the interfacial strength by chemically treating it with the likes of alkali, anhydrides and silanes etc., which results in improved interfacial bonding between matrix and fibre [3]. Alkali treatment in concentrations of 5%, 10% and 15% were performed on borassus fruit fibre, of these 5% of alkali treatment shows a better mechanical property [4]. Fibre surface was damaged when the alkali concentration is increased in the solution, which relates to decrease in the mechanical properties of the composites [5].

Hussain Barbhuiya et al. reported that the property of natural fibre composite strongly depends on optimum fibre length and weight percentage of fibre [6]. Nowadays, attention on polymer nanoclay composites increased due to their excellent characteristics [7]. The mechanical properties of polymer composites were enhanced by the addition of small concentration of nanoclay, which was clearly reported in the review on polymer clay hybrid nano composites [8]. Research on polymer nanoclay composites in which polymer is used as a matrix material and nanoclay as the reinforcement particle filler were carried out. The mechanical, thermal and physical properties of polymeric matrix improved due to addition of nanoclay were reported [9]. Interstitial voids that were created between the surface modified natural fibre and polymer matrix results in the premature breakage in composites. Inorganic fillers such as nanoclay [10], silica nanoparticle [11] and carbon nanotube [12] were used to enhance stress transfer between filler and the matrix due to its higher aspect ratio, low cost and miscibility with matrix. Montmorillonite (MMT) mineral serves as good nanoclay filler because of its dispersibility in the matrix. A small amount of nanoclay (5 wt.% or less) possesses superior specific strength and stiffness, good fire retardant and enhanced barrier properties when compared to conventional filled polymer with micron sized particle [9].

Natural fiber-reinforced composites are now used to replace the conventional materials for light-weight application [13]. Most of the previous literatures [14,15] presented the significance of newly developed fibres that have used to prepare the composites and also optimized the fibre length, volume and weight fractions. In this paper, one such natural fibre is extracted from a medicinal plant and treated with alkali. The main objective of this work is to interface nanoclay into the alkali treated Coccinia Indica fibre (CIF) reinforced epoxy composites and study the mechanical properties of the same with nanoclay. The significance of this work is that the infusion of nanoclay has further increased the adhesive, mechanical and morphological properties of the composites. Hybrid composite method using nanoclay in addition to a matrix is available in this work [16]. Fibre is the primary load bearing element in the composite. It is interesting to enhance the property of natural fibre reinforced composites by nanoclay infusion in fibre and matrix. The chemical treatments were performed on CIFs to eliminate the unwanted amorphous, hemicellulose and lignin phase of the fibre. The enhancement in concentration of in-house cellulosic phase increases the cellulosic phase content [4]. This study is to find the possibility of using nanoclay as filler in Coccinia Indica (CI) fibre as reinforcement in structural polymer composite materials because of its lightweight and eco-friendly nature. To overcome the disadvantages of natural fibre, NaOH treatment were performed on the prepared CI fibre. The mechanical properties of prepared reinforced polymer composites were enhanced by the addition of small concentration of nanoclay onto it. The introduction of nanoclay into the novel natural reinforcing material is the innovation and novel aspect of this research. This finds potential application as reinforcing material in composite materials manufacturing. In this present work, the mechanical properties and morphological changes on the effect of nanoclay inclusion for alkali treated CIFs-reinforced epoxy composites were discussed in detail.

2. Materials and preparation

CIFs were extracted from the medicinal plant which comes from the family of Cucurbitaceae [17], which are available at Kanuvukkarai Village, Coimbatore District, Tamil Nadu State, Southern part of the India. Fibres were separated from the CI plant stem and dipped in water for 3 weeks to allow for microbial degradation. The soaked stems were cleaned with fresh water and dried at normal atmospheric temperature for a week. Finally, the fibres were extracted from the dried stems by combing process with the help of metal teeth brush. The extracted fibres were dried in sunlight for 8 h to remove the excess water content of the fibres. CIF bundles were soaked in a stainless steel vessel containing 5% NaOH solution at room temperature for 1 h. Fibres were taken out and thoroughly washed with distilled water to remove the excess acid present in the fibres. Final washing was done with water containing 1% acetic acid, and these treated fibres were dried in sunlight for 5 days. Those fibres were cut into 30 mm (approx.) and used to prepare the NaOH treated CIFs-reinforced epoxy composite.

A simple hand lay-up method followed by compression moulding process was adopted to prepare the neat and chemically treated unfilled and filled CIFs-reinforced epoxy composites. Commercially available nanoclay (Cloisite 30B, particle size of <13 nm) was purchased from Southern Clay Products Inc., USA. The process began by mixing the filler material thoroughly with industrial grade acetone using a mechanical stirrer for 30 min. The nanoparticles were dispersed in acetone during this process. Then, the required quantity of standard Bisphenol A (LY 556) was taken as epoxy resin (Epoxy Equivalent Weight of 180&190 g/eq.) and mixed with parent solution of nanoclay-acetone mixture solution to prepare CIFs-reinforced epoxy composites. It was preheated up to 80 °C to obtain better wetting of nanoparticles to minimize the viscosity, where the acetone
solutions were evaporated. The mixing process was continued until a homogenous mixture was obtained using mechanical ultrasonicator. Finally, hardener Triethylenetetramine (HY951, supplied by Covai Seenu & Company, Coimbatore District, India) was mixed with epoxy nano mixture (10 wt.% of epoxy:1 wt.% of hardener) for a period of 5 min. A steel die was used to mould the composites and a layer of release agent was coated on the dies for easy removal of composite. To fabricate the composite laminates, treated CIFs and the prepared nano mixture were spread up to the required thickness uniformly. After this process, the closed mould containing treated CIFs-reinforced nano-mixture was kept in a hydraulic press and a compressive pressure of 1500 psi was applied for 3h at a temperature of 80 °C. The obtained epoxy composites were allowed to cool down until it attained room temperature, which reduces the thermal residual stresses [18]. To determine the effect of nano clay, different weight ratios (0, 1, 2, 3 and 4 wt.%) of nano clay was added onto the prepared composites. Formation of specimens remained same for all the experimental conditions.

3. Experiments

The tensile (ASTM D3039), three-point flexural (ASTM D790) and compression (ASTM D3410) testing of CIFs-reinforced epoxy composites with and without nano clay particles were carried out in KALPAK Universal Testing Machine. The samples were aligned carefully in the longitudinal axis of the machine or load cell and the load is applied with a cross head speed of 2 mm/min. The specimens were cut into rectangle strips using a circular saw. During testing, the specimens were broken in between the rectangular strips of the specimen. The images of some specimens before and after tests are shown in Fig. 1. The specimens were placed in the testing machine and compress until it fractures. Deflection of the specimen was measured using strain gauge with computer interface and the flexural strength was evaluated. The compress force was recorded as a function of displacement and the compressive strength of the specimen was determined. Impact testing (ASTM D256) was conducted using Pendulum Impact Tester (Izod Impact Test) and measures the impact energy with the resolution of 0.5J. Five specimens were used for each testing to avoid instrumentation error and the average values of results were reported. The tests were conducted in a controlled atmosphere at an ambient temperature of 24 °C and a relative humidity of 65%.

The FTIR spectra of prepared composites were recorded in the range of 4000–500 cm⁻¹ at a resolution of 2 cm⁻¹ with 32 scans using a Perkin Elmer Spectrum RXI FTIR Spectrometer in KBr matrix. The FTIR spectrum was used to collect and understand the functional groups present in the composite materials. The micro-structural failures of the tensile and flexural fracture of CIFs-reinforced epoxy composites with and without nano clay were studied and analyzed using a SEM VEGA TESCAN 3 with a field emission gun (tungsten filament) and an accelerating voltage of 5 kV to collect images of the surface of composites. In addition, the crack propagation of fracture and toughness of the specimen were also determined. The test specimens were sliced and mounted on aluminium stubs with double sided adhesive tape and sputter coated with thin layer of gold to make the sample conductive. TEM imaging was performed using a HR-TEM model FEI-TECNAI T20 G2 to evaluate the microstructure and dispersion of nanoclay within the CIFs-reinforced epoxy composites.

4. Results and discussions

4.1. Tensile properties of the epoxy composites

The tensile strength of CIFs-reinforced epoxy composites with (1, 2, 3 and 4 wt.%) and without (0 wt.%) nano clay were presented. Fig. 2 depicts the tensile strength bar chart of the CIFs-reinforced epoxy composites with different percentages of nano clay addition. During tensile testing of the epoxy composites, the tensile stress is carried by the fibres and the matrix
is acting as a load transfer medium between the fibres. The NaOH has not removed the moisture content from the fibres during NaOH treatment. This leads to lowest tensile strength of the epoxy composites. The tensile strength of the treated CIFs-reinforced epoxy composites are 33.79, 34.59, 36.91, 38.29 and 35.01 N/mm$^2$ for 0, 1, 2, 3 and 4 wt.% addition of Cloisite 30B onto it. Compared to NaOH treated CIFs-reinforced epoxy composites without nanoclay, the addition of nanoclay had higher stress transfer that is due to better adhesion between the fibres/matrix. This may be due to the removal of certain amount of low strength phases such as hemicellulose, lignin, wax content and other plant (non-cellulosic) impurities present on the fibre surface. A strong cross-linking interaction between fibre and matrix with nanoclay was formed. The percentage variation between the maximum strength of composites (3 wt.%) to other materials are 11.75 (0 wt.%), 9.67 (1 wt.%), 3.60 (2 wt.%) and 8.57 (4 wt.%), respectively.

### 4.2. Flexural properties of the epoxy composites

The flexural strength is an important property for structural materials. The beam or plate is subjected to withstand perpendicular load in structural applications. The flexural strength of treated CIFs-reinforced epoxy composites with and without nanoclay is shown in Fig. 3. Five specimens of each composition were tested and the average value of flexural strength was reported. The flexural strengths are different for various compositions. The NaOH treated fibre composites show higher value of flexural strength due to elimination of certain amount of lignocelluloses binder from the fibre that leads to better adhesion in the matrix. The flexural strength of the treated CIFs-reinforced epoxy composites are 79.86, 81.44, 85.69, 92.77 and 90.26 MPa for 0, 1, 2, 3 and 4 wt.% addition of Cloisite 30B onto it. The maximum increment obtained for 3 wt.% nanoclay addition compared to neat sample is due to filling of maximum voids present in the matrix by the fillers which leads to saturation value of flexural properties.

Even though, the flexural strength of NaOH treated CIFs reinforced unfilled epoxy composite was lower compared to nanoclay filled epoxy composites. This may be due to poor adhesion between the fibre/matrix and presents of more lignin, wax and moisture content in the fibre. More crack paths have formed and propagated very shortly, which breaks the material. This leads to lower flexural strength for unfilled composite compared to filled epoxy composites. The higher flexural strength was found for 3 wt.% addition of Cloisite 30B onto the epoxy composites.

The percentage variation between the maximum flexural strength of composites (3 wt.%) to other materials are 13.92 (0 wt.%), 12.21 (1 wt.%), 7.63 (2 wt.%) and 2.71 (4 wt.%), respectively. Higher addition (4 wt.%) of nanoclay onto the treated CIFs-reinforced epoxy composite led to decrease in the flexural strength to 90.26 MPa, which was due to the presence of excess intercalated aggregate. It is important to note that the same results were obtained for the increase of nanoclay filler reinforcement in the epoxy composites. Therefore, the NaOH treated CIFs-reinforced epoxy composite with 3 wt.% nanoclay addition is a good competitor and has potential to replace the existing structural materials.

### 4.3. Impact properties of the epoxy composites

The impact resistance is an important property for all materials, which have to absorb energy under sudden impact load. In other words, impact strength is the ability of the materials to resist the fracture under the applied stress at higher velocity (speed). The material shows higher impact resistance when the load is evenly distributed throughout the material. When certain materials have been widely used for structural application under impact loading conditions where they act as damping materials. The impact strength of the unfilled epoxy composite is compared with nanoclay filled composites. Fig. 4 shows the impact strength of the treated CIFs-reinforced epoxy composites with and without nanoclay.
The impact strength is measured in kJ/m² from the standard Izod impact strength apparatus at room temperature. For each case, five specimens were tested and an average value of impact strength was reported. Impact strength of unfilled treated CIFs-reinforced epoxy composite is 58.01 kJ/m². It was increased up to 67.25 kJ/m² for 3 wt.% of nanoclay addition, which was observed to be the best possible improvement in impact strength of nano composites. This is due to better adhesion between the fibre and matrix, and the presence of natural fibre in polymer composites leads to more crack path at interface and absorbs more energy. The percentage variations between the highest impact resistance to all other compositions are 13.74 (0 wt.%), 8.46 (1 wt.%), 4.27 (2 wt.%) and 3.11 (4 wt.%), respectively. The impact strength was found decreased in its value to 65.16 kJ/m² for 4 wt.% of nanoclay reinforcement, which the composite becomes more brittle [19].

4.4. Compressive properties of the epoxy composites

The unfilled treated CIFs-reinforced epoxy composites exhibited compressive strength value of 51.38 N/mm², whereas the strength values of nanoclay filled treated CIFs-reinforced epoxy composites are 55.90, 57.16, 64.84 and 61.47 N/mm² for 1, 2, 3 and 4 wt.% addition of Cloisite 30B onto it. This great increase in the compressive strength value at 3 wt.% nanoclay loading is primarily attributed to reinforcing effect imparted by the fibres, which allow a uniform stress sharing from continuos polymer matrix to dispersed fibre phase. The percentage variations between the highest compressive resistance to all other compositions are 20.76 (0 wt.%), 13.79 (1 wt.%), 11.84 (2 wt.%) and 5.20 (4 wt.%), respectively. The sudden decrease at higher loading (4 wt.%) implied poor adhesion which promoted micro-crack formation at the interface as well as non-uniform stress transfer due to agglomeration within the matrix (Fig. 5).

4.5. FTIR analysis

The treated CIFs-reinforced epoxy composites with and without nanoclay were characterized by FTIR spectroscopy to confirm the chemical reactions within the lignocelluloses elements of the fibres. It serves as a direct means for the identification of the polymer compositions and organic functional groups on the surface of the sorbent. FTIR spectra of treated, untreated and nanoclay filled CIFs-reinforced epoxy composites in the region 4000 to 500 cm⁻¹ wave numbers were presented in Fig. 6. Plants comprise up to 80% of their dry weight of carbohydrates, with the most important including cellulose, starches, pectin and sugars, such as glucose and sucrose. The mid-infrared assignments of common plant carbohydrates are cellulose at 1170-1150, 1050, 1030 cm⁻¹, lignin at 1590, 1510 cm⁻¹, hemicellulose at 1732, 1240 cm⁻¹, pectin at 1680-1600, 1260, 955 cm⁻¹ and β-D-cellulose at 916, 908 cm⁻¹. The infrared analysis of plant materials has traditionally relied upon the use of harsh chemicals and modification of the intractable cell walls.

The sharp peaks observed in untreated composites at 2928 cm⁻¹ and 2871 cm⁻¹ is due to vibrations of asymmetric and symmetric CH2 and CH3 functional groups respectively. The peaks at 1243 cm⁻¹ and 918 cm⁻¹ show stretching absorption of C=O in the epoxide ring. Similarly, the peaks at 1607 cm⁻¹ and 1508 cm⁻¹ reveal C=C stretching vibrations of benzene present in the epoxy. In NaOH treated CIFs-reinforced epoxy composites, the peaks at 3336 cm⁻¹, 2912 cm⁻¹, 1426 cm⁻¹ corresponding to OH, CH, and CH2 stretching vibrations of cellulose molecule of Coccinia grand present in the composites. In chemical treatment, the hydrogen of hydroxyl group was substituted by acetyl groups, resulting in lower hydroxyl groups able to carry through hydrogen bonds. After chemical treatment, there was a decrease in OH band and its displacement from 3400 to 3700 cm⁻¹. The treatment had removed most of the lignin and hemicellulose.
component and the treatment had changed the hydrophilic of the fibres to hydrophobic nature. The wide band between 3400 and 3200 cm\(^{-1}\) were due to OH stretching vibrations of alcohols, attributed to hydroxyl (OH) groups among the fibres. After nanoclay addition, the axial deformation of the OH group occurred at the peak of 3336 cm\(^{-1}\). The peak at 1426 cm\(^{-1}\) was characteristics of CH\(_2\) stretching vibrations of cellulose molecule. The bands at 915 cm\(^{-1}\), 792 cm\(^{-1}\) and 624 cm\(^{-1}\) represent Al-AO vibrations of nanoclay.

4.6. Transmission electron microscope analysis

Morphology of the 3 wt.% nanoclay loaded NaOH treated CIFs-reinforced epoxy composite were done using TEM analysis, which is depicted in Fig. 7. Dispersion state of nanoclay in epoxy matrix were visualized from the typical image, as shown in Fig. 7a, in which the dark region indicates the filler phase and bright region indicates the matrix phase. Fig. 7b depicts the approximate size of nanoclay as 0.26 nm. Nanocomposites reveal the combination of intercalated and exfoliated nanoclay platelet within the epoxy matrix of uniform dispersion from TEM analysis. It was also observed that nanoclay within the nanocomposites produced a strong adhesion.

4.7. Scanning electron microscope analysis

The fractured specimen from the tests of CIFs-reinforced epoxy composites is considered for analysis using SEM at controlled atmosphere. One half of the fractured specimen is utilized for performing SEM analysis. The SEM micrograph of the fractured specimen with 3 wt.% nanoclay loading is shown in Fig. 8. Interfacial delamination of the interphase is found to be much higher. Tensile strength values have confirmed that the adhesion between the fibre and matrix is good and the fibre pull-out is not so predominant. Strength at the interphase of the fibre and matrix is found to be higher due to the breakage of the individual fibre to the vicinity of the interphase at the loading region. Due to the strong interphase, CIFs have undergone individual fibre breakage appreciably which is displayed in Fig. 8a. At this weight fraction, intra fibre delamination is not as frequent as the fibre breakage which is found to be dominant. Fibre wetting at this weight fraction is higher when compare to the other weight fractions which leads to the fibre breakage and also the intra fibre delamination. Loading region consists of the concentration of the fibres which is dominant for the fibre breakage and it have justified the higher strength values. In the reinforced layer, less agglomeration is seen in the surface for lower concentration of nanoclay. Agglomer-
ation acts like a superior structure and it also serves as a crack initiation site [18]. Altogether, considering all the factors, the optimized strength values of 3 wt.% nanoclay loaded CIFs-reinforced epoxy composites have very good interfacial properties, higher wetting, lesser fibre pull-out and poor intra fibre delamination.

From Fig. 8b, fibre pull-out is clearly visible from the micrograph and in particular, CIFs are found to be more broken in that image. Also, the intra fibre delamination is found to be more predominant in CIFs, hence the scattered nature of the fibre exists through the matrix. Fibre pull-out occurs mainly due to the poor interfacial bonding at the interphase of the fibre and matrix. Interphase specifies the intersectional plane of the fibre and the matrix whose properties are studied by using the SEM micrograph. It is found that the fibres at the vicinity of the loading region are more prone to damage. Strength values of the fibre at this region might have decreased and that leads to the fibre pull-out at this region. Due to the improper interfacial bonding, a smaller amount of the delamination at the interphase is found. It is evident from the micrograph that the adhesion area between the fibre and matrix is reasonably less, so the tensile strength is also less in the unfilled composites.

5. Conclusion

The feasible effects of nanoclay on morphological and mechanical properties of alkali treated CIFs-reinforced epoxy composites were explored in this study. NaOH treated CIFs-reinforced epoxy composites with and without nanoclay particles were prepared and tested. The mechanical properties such as tensile, flexural, impact and compression of prepared composites were superior for 3 wt.% of nanoclay addition. In this work, it is observed that the mechanical properties of composites with organoclay have improved due to intercalation of nanoscale clay particles in the matrix which restricts the mobility of polymer chains under loading. Better interfacial adhesion between fibre and matrix was noticed on 3 wt.% loading of nanoclay onto the prepared epoxy composites. However, decrease in strength values at higher loading (4 wt.%) implied poor adhesion which promoted micro-crack formation at the interface as well as non-uniform stress transfer due to agglomeration within the matrix. The axial deformation of the hydroxyl group and CH$_2$ stretching vibrations of cellulose molecule after nanoclay addition were confirmed through FTIR analysis. Failure features such as fibre breakage and fibre pull-out were noticed from SEM images, which support as the evidences for failure of the unfilled CIFs-reinforced epoxy composites. Nanocomposites reveal the combination of intercalated and exfoliated nanoclay platelet within the epoxy matrix of uniform dispersion from TEM analysis.

Conflicts of interest

The authors declare no conflicts of interest.

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