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RESEARCH ARTICLE

Fabrication and characterization of silanized echinoidea fillers and kenaf fibre-reinforced Azadirachta-indica blended epoxy multi-hybrid biocomposite

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Abstract
In this research, mechanical, thermal, and water uptake behaviour of surface-modified sea urchin spike biofiller and kenaf woven fibre mat-reinforced neem oil blended epoxy resin composite has been studied. The principal aim of this research was fabrication of eco-friendly hybrid composite and explicitness of the importance of surface modification on reinforcements. Neem oil was blended with epoxy resin to reduce extreme brittleness of epoxy, making the composite as an eco-friendly one. Sea urchin biofiller was prepared using high energy ball mill. Both filler and fibre were surface-treated by amino silane. The results revealed that additions of surface-treated sea urchin particle and kenaf fibre increased the mechanical properties of composite. Similarly thermal results exposed that addition of sea urchin bioceramic filler greatly increased the thermal stability of neem-epoxy biocomposite. SEM fractographs showed uniform dispersion of sea urchin filler and improved adhesion of kenaf fibre with epoxy matrix.

Keywords PMC · Neem oil · Sea urchin fillers/kenaf fibre · Silane treatment

Introduction

Natural filler and fibre-reinforced polymer matrix composites are having attractive applications in automobile, construction and aerospace industries due to their eco-friendly nature, light weight, durability and economical process methodologies [1]. Developing eco-friendly composites with natural reinforcements has huge demand in current engineering applications. Generally in composites, the matrix phase possesses large volume than reinforcement phase; hence, matrix modification as a bioform will render more effective eco-friendly applications [2]. Blending of low-cost edible or non-edible natural oils with epoxy resin, the material cost could be reduced, converting the thermosetting resin as a biocompactable one. Blending of natural seed oils with thermosetting plastics may reduce the extreme brittleness of matrix phase; hence, the final composite product could be a high toughness material [3]. Neem seed oil (Azardica indica) could be a bioblender to epoxy resin, since it could be mixed with resin with more homogenous manner. The low-cost, high-availability and insect-repellent nature of this biooil is an additional advantage among other biovariants. Reduction of green house gases followed by forestation will be a remarkable benefit by planting more neem trees for oil extraction. In spite of many advantages, blending of natural seed oils may lead poor performance in mechanical, thermal and also insulation properties. To overcome this issue, natural fibre and filler could be used as reinforcements in neem oil blended epoxy resin. Many researches tried to develop new eco-friendly biofillers for improving the properties of matrix phase from domestic and sea waste materials. Parivendhan et al. [4] have reported the utilization of egg shell natural filler in epoxy resin. They confirmed that the addition of egg shell fillers increased the thermal behaviour of base matrix. Similarly Praharaj et al. [5] have utilized chitosan bioceramic filler from sea waste as a thermal stability booster in BisGMA-PVP blend. They concluded that the addition of chitosan along with MWCNT increased the mechanical and thermal properties. A novel sea urchin spike

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bioparticle from sea waste could be used as bioceramic filler since it contains rich quantity of calcite and $MgCO_3$. These species could available in plenty, and they may wash ashore via fish catching with nets as sea waste. The spikes of sea urchin will be in the length of 5–6 cm and in the form of reddish grey cone shape. The fine nano-dimensioned sea urchin fillers could be developed by planetary ball mill for several time limits [6]. Calcination could be done after ball milling for conversion of $CaCO_3$ and $MgCO_3$ phases as CaO and MgO since oxide phases are good enough in thermal related properties than carbonate phase [7]. Kenaf natural woven mat fibre could be used as fibre reinforcement for fetching better mechanical properties for neem blended epoxy resin composite. Surface modification of filler and fibre could be done by amino silanes via aqueous solution method for effective dispersion of filler and better adhesion of fibre with matrix. The fabrication of hybrid composites with natural filler and fibre could be done by hand layup method. The characterization of fabricated composites could be done by ASTM standards. These eco-friendly novel material-reinforced composites could be used to make useful products in both domestic and industrial sectors.

Experimental procedure

Materials

The epoxy resin used for this study was liquid diglycidyl ether of Bisphenol-A type having equivalent weight per epoxide group of 195 g/mol, density of 1.2 g/cm^3 with kinematic viscosity of 12,000 cps (Huntsman India Ltd. Mumbai). Triethylenetetramine a low viscous (20 cps) aliphatic hardener was used as curing agent with density of 0.98 g/cm^3 (Huntsman India Ltd. Mumbai). Neem seed oil of density 0.9 g/cm^3 was used as bioblender for epoxy resin. 3-Aminopropyletrimethoxylane (APTMS) a bi-functional coupling agent was purchased from Sigma-Aldrich, USA. Sea urchin spikes were procured from southern coastal regions of India. The kenaf fibre used for this present study was having density of 1.8 g/cm^3 and purchased from National Fibre Traders Pvt. Ltd, Madras, India.

Sample preparation

Preparation of sea urchin filler

The fine CaO ceramic particle from sea urchin was prepared by the following steps. Initially the washed ashore died sea urchin species where collected and the spikes were removed carefully from the scalp of species. Each spike was having length of 5 to 6 cm and in taper cylindrical shape. The separated spikes from the species were dried in sun light for 48 h to remove moisture. The dried spikes were crushed to a fine form and dried off in sun light again for 48 h to remove the inbound moisture and ready for ball mill. Figure 1 shows the basic steps involved in bioceramic sea urchin filler preparation.

Ball milling the crushed sea urchin biowaste up to 16 h gives significant outcomes. The ball milling process was carried out in a planetary ball mill having 10 g loading capacity (RETSCH PM 100, Germany). In this process, the ball material used was tungsten carbide and ball-to-powder ratio was maintained as 10.5:1. The average ball weight measures 7.6 g and total ball weight used was 53 g. The diameter of each ball measures 10 mm. The milling speed was maintained at 300 rpm throughout the process [8]. The average size of the particle in different milling time was investigated using a particle size analyser (HORIBA, SZ 100, Japan). Ball-milled powder samples were dispersed in distilled water of refractive index 1.33 and ultrasonically stirred for 10 min before testing. Figure 2 shows the graph of particle size to milling time. It is clear that the particle dimension get reduced rapidly up to 2 h after that no significant reduction was observed. This is because of in first 2 h the chances of hitting ball and powder was maximum thus leads deformation of particle as rapid. But 2 to 16 h milling, the chances of collision between powder and particle was less and also they tend to sticking with neighbouring particle. This phenomenon gives unaltered dimensions of particle after 2 h of milling.

The ball-milled sea urchin bioceramic particle then subjected for calcination to convert calcium carbonate phase ($CaCO_3$) to calcium oxide (CaO). The working temperature for this process was calculated by performing thermogravimetric analysis on sea urchin particle. Figure 3 shows the TGA graph of raw sea urchin particle. The TGA test was carried out by using a thermogravimetric analyser (NETZSCH STA Jupitar 409 PL Luxx, Germany). The graph explicated that maximum conversion of $CaCO_3$ phase to CaO phase occurs in the temperature between 500 and 650 °C. From this study, the calcination temperature for sea urchin particles was set up as 700 °C. The calcination process was carried out in a box furnace at air atmosphere with operating temperature as 700 °C and soaking period of 2 h. After the soaking period, the particles were cooled within the furnace chamber for uniform cooling. Figure 4 shows the XRD plots of before and after calcinated sea urchin samples. The x-ray diffraction was performed using a powder X-ray diffractor (Match phase analyser, Germany).

A strong peak at 29° (2θ) confirms the $CaCO_3$ state (trigonal) in un-calcinated sea urchin particle. Other weak peaks were observed at 36°, 40°, 44°, 48°, 58° and 61° 2θ. The after calcination particle shows both $Ca(OH)_2$ and CaO phase. This is because of unstable phase of CaO in atmosphere quickly reacting with moisture and forms $Ca(OH)_2$.

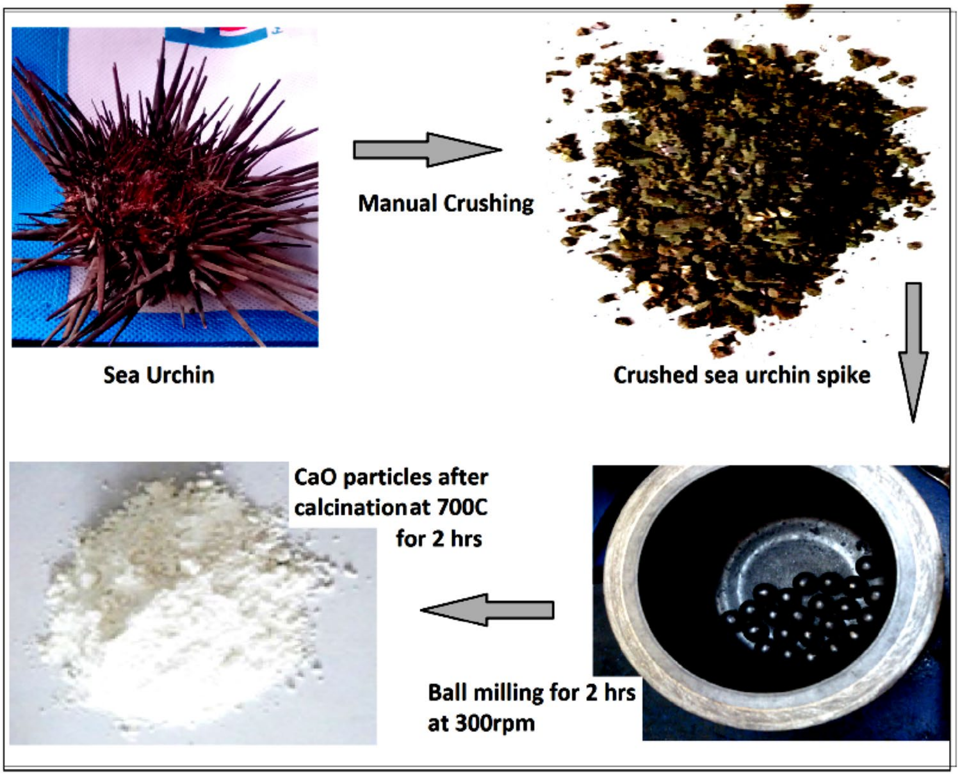

Fig. 1 Steps involved in CaO particle production from sea urchin spikes

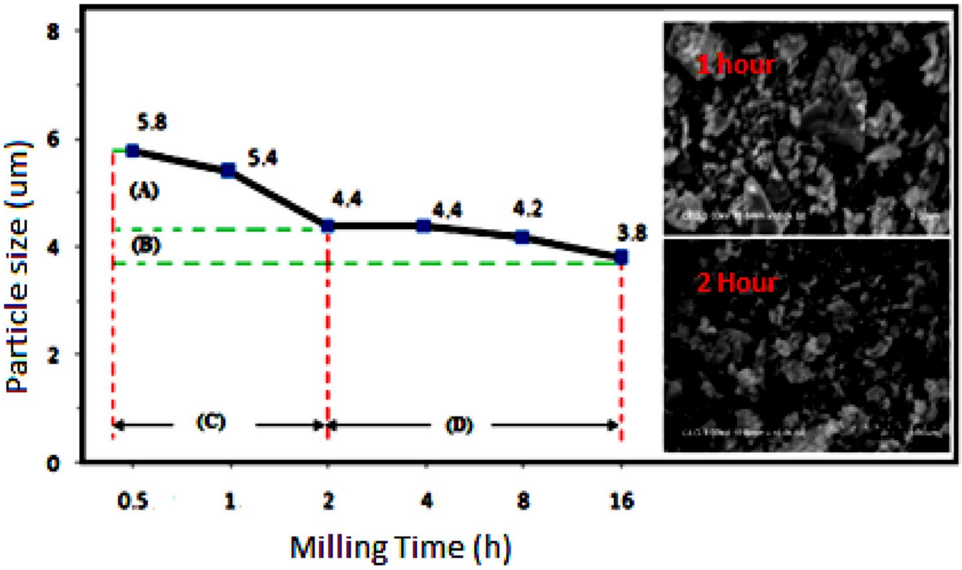

Fig. 2 PSA graph, particle size versus milling time and morphology

Anyway percentage of CaO is more in calcinated sample. The peaks at 44°, 55° and 63° 2θ confirm the presence of CaO phase with cubic crystal structure [9].

Surface modification of sea urchin filler and kenaf natural fibre

The sea urchin biofiller and kenaf natural fibre were surface-treated using an amino silane by acid hydrolysis method. Generally acetic acid of 4N concentration was used to adjust the pH of aqueous solution in the range 4.5 to 5.5, which may enforce the hydrolysis of silane. Formally 2 wt% of silane coupling agent was added with aqueous solution drop by drop to form homogeneous mixture. The hydrolysis was done in the silane by cleavage of methoxy groups from silane substance and created Si–OH structure. In this reaction, the methyl alcohol (CH_3OH) is a leaving group. The sea urchin filler and kenaf natural fibre were immersed in

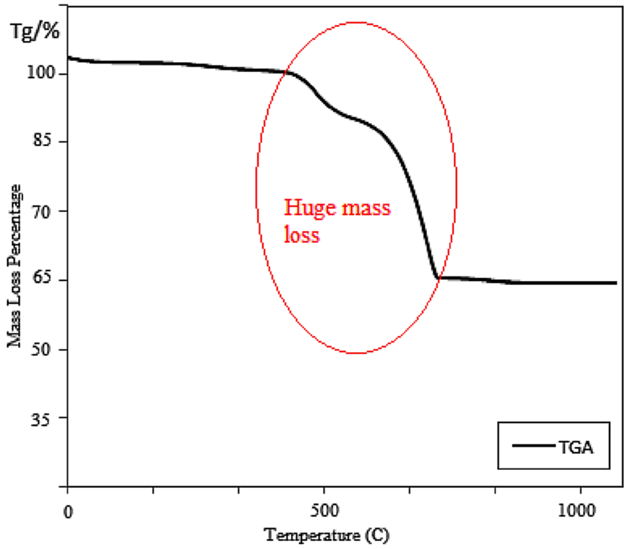

Fig. 3 TGA graph of sea urchin particle

silane solution for 10 min. The rinsed particle and fibre were evacuated from the silane solution and dried in a hot oven at 110 °C to form Si–O–Si structure [10].

Figure 5 shows the FT-IR spectral graph of silane-treated sea urchin and kenaf fibre. The absorbance spectral analysis was conducted using Bruker alpha ATR mode (Germany). The peak 3185 cm^{-1} indicates the presence of amine group (NH_2) N–H stretch on sea urchin and kenaf fibre surface, which is from silane. The peak at 2925 cm^{-1} indicates the presence of propyl group (C–H stretch) on second-phase surface. The peak at 1410 cm^{-1} indicates the presence of C–H bend, which is from NH_2 attached propyl group. The peak 1028 cm^{-1} reveals the presence of Si–O–Si structure on second-phase surfaces [11]. Thus, the FT-IR spectral result revealed that the surface modification process persuaded NH_2 functional group on second-phase surface, which may ensure good dispersion and better adhesion of reinforcement on epoxy matrix.

Composite preparation

(a) Making of epoxy-neem oil bioblend.

A fixed quantity of epoxy resin was mixed with variable quantities of neem oil (Azadirachta-indica) in a beaker at 80 °C with constant stirring. The stirring process continued until a homogeneous solution of epoxy-neem oil was formed. The resulted solution was then cooled to room temperature for making of composites. Figure 6 shows the FT-IR spectra of epoxy-neem oil blend. A peak at 1736 cm^{-1} confirms the presence of C=O stretch from eliminated acetic acid by the reaction between acetoxy group in neem and hydroxyl group in epoxy resin. Similarly peaks of 2966 cm^{-1}, 1507 cm^{-1} and 1295 cm^{-1} indicate the presence of O–H, C–H and C–O bonds from eliminated acetic acid. Thus, the temperature rise up to 80 °C improves kinetic energy of molecules, which enforces the acetic group elimination from epoxy-neem oil blend and the formation of flexible ether groups [12].

(b) Making of kenaf fibre-reinforced sea urchin particle added epoxy-neem biocomposite.

The composites were prepared using a silica rubber mould. First a liberal coat of wax was applied for easy removal of composites. The surface-modified sea urchin particle dispersed epoxy solution was then poured into the mould and allowed to fill completely. Three layers of surface-modified kenaf fibre were then laid one by one. The entrapped air bubbles were removed using a cotton roller. The composites

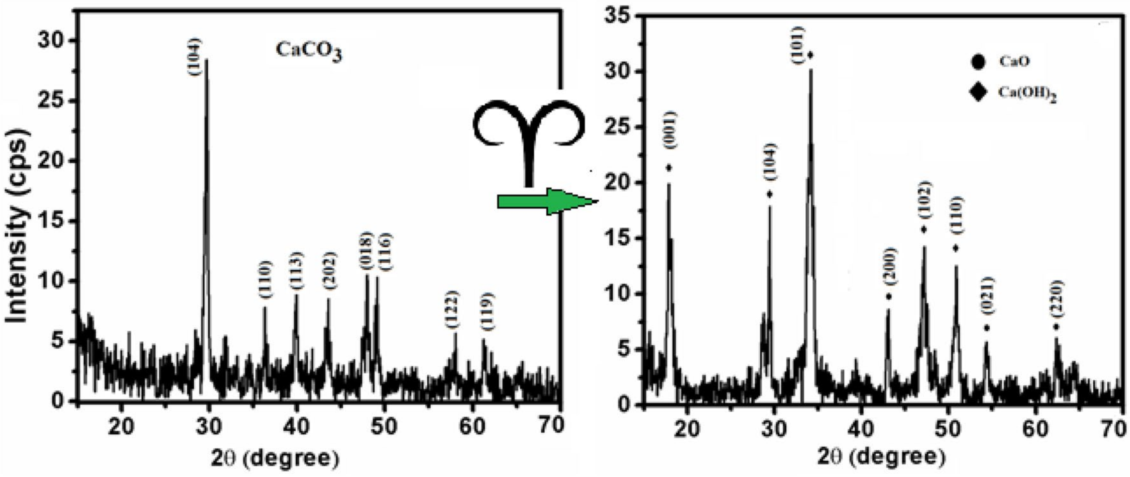

Fig. 4 XRD graphs of sea urchin particle before and after calcination

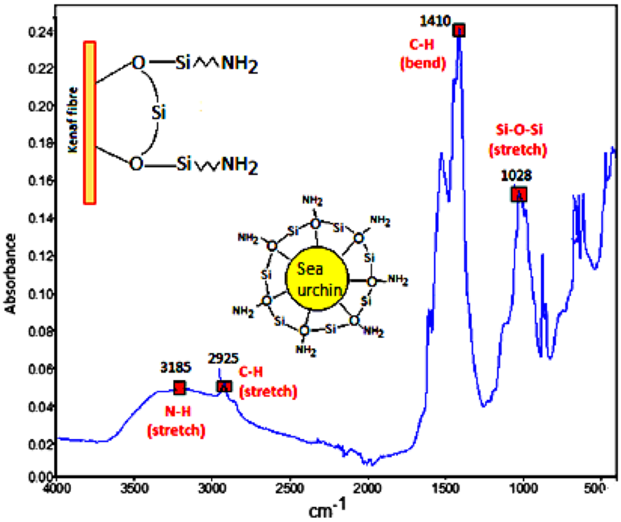

Fig. 5 FT-IR spectra of silane-treated sea urchin and kenaf fibre

were cured at room temperature for 24 h and post-cured at 48 h. Table 1 shows the designation and composition of composites fabricated.

Test specimen preparation

The fabricated multi-hybrid biocomposites are checked for visual defects. Test samples with suitable dimensions based on ASTM standards were cut by using an abrasive water jet machine (Maxiem water jets 1515, KENT, USA) with garnet size of 80 mesh; abrasive flow rate of 0.30 kg/min, maximum pressure of 220 MPa and nozzle diameter of 1.1 mm were maintained.

Results and discussion

Mechanical properties

Tables 2 and 3 show the mechanical behaviour of as-received and surface-modified kenaf fibre-reinforced sea urchin particle added epoxy-neem oil multi-hybrid biocomposite.

(a) Effect of neem oil addition into epoxy resin.

The tensile strength of pure epoxy measures 70 MPa. Addition of neem oil into epoxy resin decreased its tensile strength. The decreased tensile strength of 11%, 23% and 31% was observed for composite designations EN_1, EN_2 and EN_3, respectively. This decrement in tensile strength is because of the formation of IPN structure and ether group formation [13]. The flexural strength also found to be decreasing 20%, 27% and 35% for composite designations EN_1, EN_2 and EN_3, respectively. Similarly the reduced impact toughness of 14%, 20% and 31% was observed for composite designations EN_1, EN_2 and EN_3, respectively. The flexible ether group formation is the cause for decreased impact toughness [14]. The hardness values of neem oil blended epoxy composite show decreased values. The decrement in hardness of 3.5%, 6% and 9.5% was observed for composite designations EN_1, EN_2 and EN_3, respectively. The

Fig. 6 FT-IR spectra of acetic acid in epoxy-neem oil blend

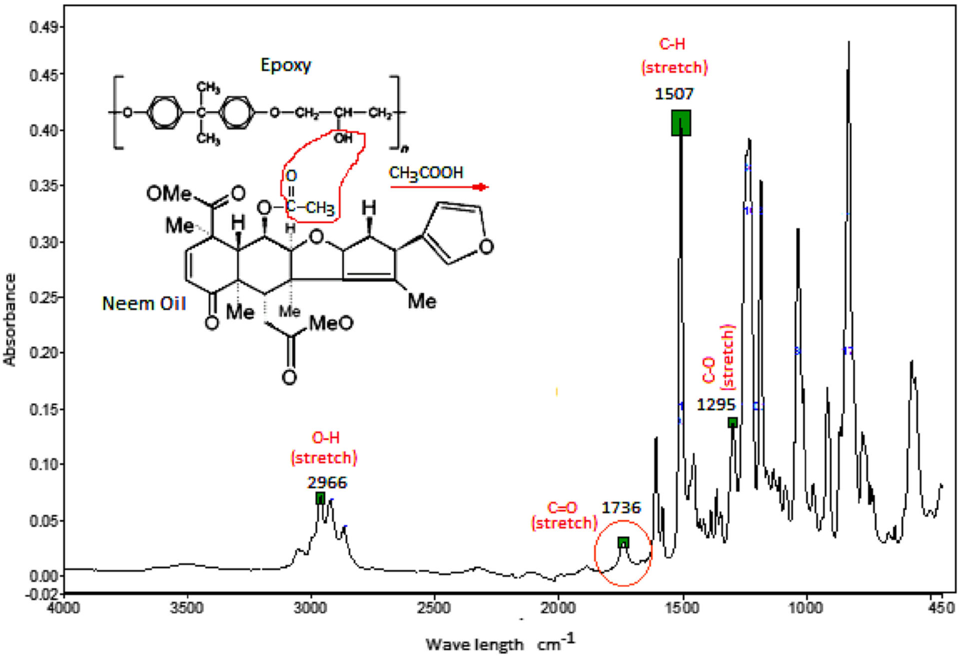

Table 1 Composition and designation of composites

Composite designation	Epoxy (vol%)	Neem Oil (vol%)	Kenaf fibre (vol%)	Sea urchin particle (vol%)
E	100	0	0	0
EN_1	85	15	0	0
EN_2	70	30	0	0
EN_3	55	45	0	0
ENF	35	25	40	0
$ENFS_1$	34	25	40	1
$ENFS_2$	33	25	40	2

E epoxy, *N* neem oil, *F* fibre, *S* sea urchin particle

inter-penetrating polymer networks are the cause of lower hardness value. The specific wear rate and coefficient of friction of neem oil blended epoxy composites shown increased values. The wear test was conducted with applied load of 5N, sliding distance of 400 m and sliding speed of 800 rpm. The increment in specific wear rate and COF of 65%, 84% and 86% and 15%, 23% and 29% is observed for composite designations EN_1, EN_2 and EN_3, respectively. This is because of the addition of soft neem oil molecules, which forms IPN structure while blending. These IPN structure is poor in wear resistance; thus, larger wear rate is observed. Hence, the addition of neem oil into epoxy resin decreased the mechanical properties of epoxy resin due to IPN structure and ether group formation.

(b) Effect of kenaf fibre into neem-epoxy composite.

Additions of kenaf fibre of 40 vol% into epoxy resin increased the tensile, flexural and impact properties. The as-received kenaf fibre of 40 vol% into epoxy resin increased the tensile, flexural and impact strength as 33%, 34% and 83% for composite designation ENF, whereas the surface-modified kenaf fibre of 40 vol% into epoxy resin increased the tensile, flexural and impact strength as 41%, 38% and 85% for composite designation ENF. This improvement is because of addition of kenaf fibre, which receives the load and transfer to matrix thereby improving mechanical properties. The surface-modified kenaf fibre into epoxy resin gives improved results than as-received kenaf fibre-reinforced epoxy-neem composite. This improvement is because of improved adhesion of kenaf fibre with epoxy resin due to the reaction of NH_2 functional group [15]. Figure 7 shows the fractograph of as-received and surface-modified kenaf fibre-reinforced epoxy-neem biocomposite. The SEM fractograph was performed using a scanning electron microscope

Table 2 Mechanical properties of as-received kenaf fibre/sea urchin multi-hybrid biocomposites

Material designation	Tensile strength (MPa)	Flexural strength (MPa)	Izod Impact (J)	I.L shear strength (MPa)	Hardness (Shore-D)	Sp. Wear rate (mm^3/Nm)	COF
E	70	110	0.65	0	85	0.012	0.6
EN_1	62	88	0.56	0	82	0.034	0.71
EN_2	54	80	0.52	0	80	0.076	0.78
EN_3	48	72	0.45	0	77	0.088	0.84
ENF	105	165	3.85	25	78	0.054	0.75
$ENFS_1$	94	152	3.52	23	81	0.042	0.68
$ENFS_2$	90	145	3.38	20	84	0.022	0.65

E epoxy, *N* neem oil, *F* fibre, *S* sea urchin particle

Table 3 Mechanical properties of surface-treated kenaf fibre/sea urchin multi-hybrid biocomposites

Material designation	Tensile strength (MPa)	Flexural strength (MPa)	Izod Impact (J)	I.L shear strength (MPa)	Hardness Sp. (Shore-D)	Wear rate (mm^3/Nm)	COF
E	70	110	0.65	0	85	0.012	0.6
EN_1	62	88	0.56	0	82	0.034	0.71
EN_2	54	80	0.52	0	80	0.076	0.78
EN_3	48	72	0.45	0	77	0.088	0.84
ENF	118	178	4.23	28	78	0.050	0.71
$ENFS_1$	126	185	4.40	27	83	0.036	0.63
$ENFS_2$	135	193	4.75	27	86	0.015	0.61

E epoxy, *N* neem oil, *F* fibre, *S* sea urchin particle

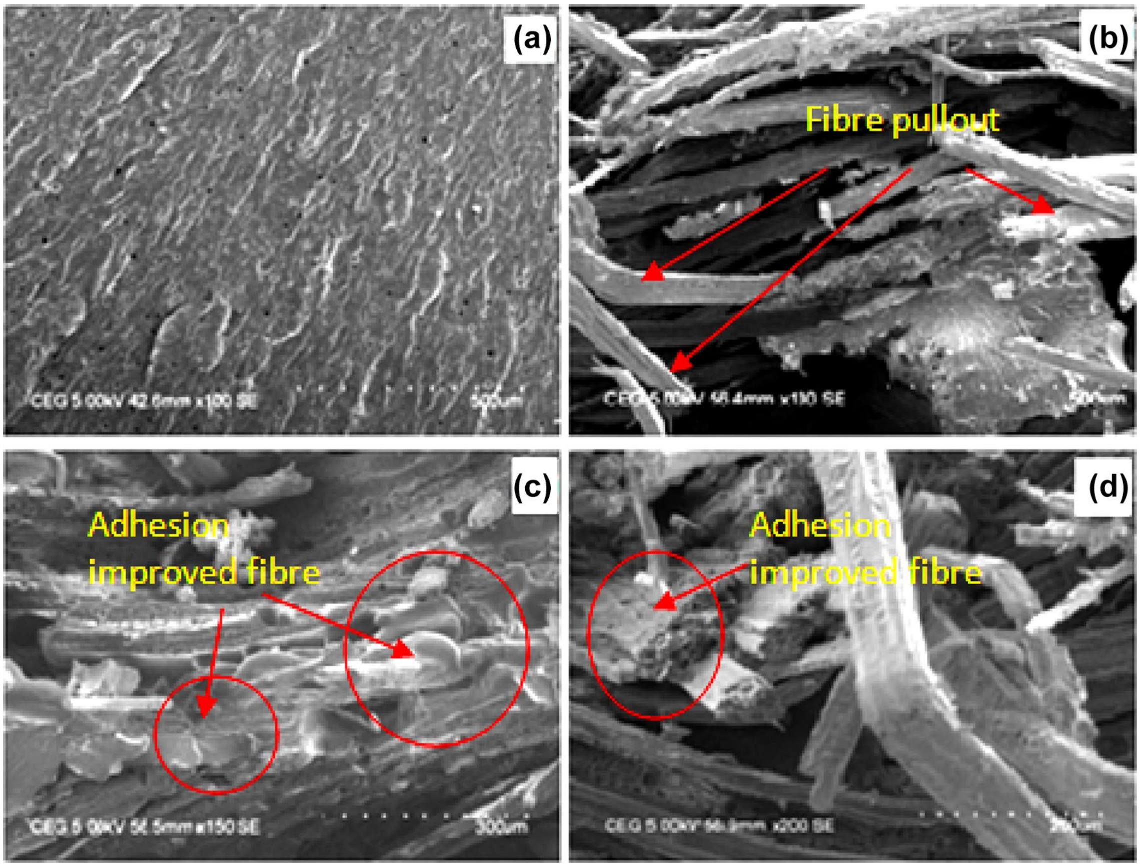

Fig. 7 Fractograph of **a** fractured surface of epoxy-neem composite, **b** as-received fibre showing fibre pullout under tensile loading, **c** adhesion improved fibre showing good bonding of fibre with matrix and **d** adhesion improved fibre explicit debris of matrix

HITACHI, S-1500, Japan. Figure 7a shows the fractured surface of epoxy-neem oil composite, which shows homogeneous mixture of epoxy and neem oil. Figure 7b shows the fractograph of as-received kenaf fibre in epoxy-neem oil biocomposite. From fractograph, it is observed that the fibre to resin bonding is significantly low, which gives fibre pull out while tensile loading, whereas Fig. 7c shows improved adhesion of surface-modified kenaf with epoxy matrix, which shows finely broken fibre parts. Figure 7d shows the adhesion improved fibre, which having the debris and same colour of matrix.

It is observed that the interlaminar shear strength of surface-modified kenaf fibre-reinforced epoxy-neem oil biocomposite is higher than the as-received fibre-reinforced composite. The ILSS of 25 and 28 MPa was observed for composite designation ENF in as-received and surface-modified form, respectively. This improvement in ILSS was attributed to the improved adhesion of kenaf fibre with matrix, which can share the shear load throughout the composite. Thus, higher ILSS was observed. The hardness value of kenaf fibre-reinforced epoxy-neem biocomposite gives decreased value of 78 (Shore-D). This is near 8% decrement on comparing with epoxy resin. This reduction in hardness is the cause of addition of neem oil into epoxy resin and forming flexible IPN structure [16]. It is observed that the specific wear rate and COF of kenaf fibre-reinforced epoxy-neem biocomposite showed increased specific wear rate and COF. The increment of 78%, 20% and 76%, 15% was observed in specific wear rate and COF of as-received and surface-modified composite designation ENF, respectively. This poor wear resistance of epoxy resin is attributed to the addition of neem into epoxy resin. Further addition of kenaf fibre marginally improved wear resistance. On comparing epoxy-neem composite, the kenaf fibre-reinforced epoxy-neem oil composite gives improved wear resistance and COF. This improvement is due to the addition of fibre into epoxy-neem matrix, which reduces the contact area of matrix phase to expose on the rubbing disc, thereby improving the wear resistance [17].

(c) Effect of sea urchin particle addition into kenaf fibre-reinforced neem-epoxy composite.

Tables 2 and 3 show the mechanical properties of as-received and surface-modified sea urchin particle added kenaf fibre-reinforced epoxy-neem multi-hybrid composite. The addition of as-received sea urchin particle into kenaf fibre-reinforced epoxy-neem oil biocomposite gives decreased tensile, flexural and impact strength compared to ENF composite designation. The decrement of 10.5% and 14% in tensile strength, 8% and 12% in flexural strength and 8.6% and 12% in impact toughness was observed for as-received composite designation $ENFS_1$ and $ENFS_2$, respectively. Similarly the decreased interlaminar shear strength of 8% and 20% was observed for as-received composite designation $ENFS_1$ and $ENFS_2$, respectively. This decrement is because of cluster formation of as-received sea urchin particle in epoxy-neem oil blended matrix. Since the sea urchin (CaO) particle has tendency to attract moisture and formation of cluster, they denied uniform dispersion on matrix. This phenomenon decreased the load sharing ability of matrix and led the composite to failure [18]. But the addition of surface-modified sea urchin particle into kenaf fibre-reinforced epoxy-neem biocomposite improved the mechanical properties. The improvement of 6% and 13%, 4% and 8% and 4% and 11% was observed in tensile, flexural and impact toughness of composite designation $ENFS_1$ and $ENFS_2$, respectively. This is because of uniform dispersion of sea urchin particle, which absorbs the load and distributes it in uniform direction, thereby improved the tensile, flexural and impact properties. The hardness value of as-received and surface-modified $ENFS_1$ and $ENFS_2$ found to be higher as 4%, 7% and 6%, 9% on comparing with ENF composite designation. This improvement is because of addition of sea urchin particle, which improved cross-linking density of epoxy-neem biocomposite and giving resistance to deform [19]. The interlaminar shear strength of surface-modified sea urchin particle added kenaf fibre-reinforced epoxy-neem biocomposite gives almost same result as ENF designation. This phenomenon is the cause of uniform dispersion of sea urchin particle, which ensures that no particle clusters are present in fibre–polymer interface. This phenomenon enhances the interlaminar shear strength of sea urchin dispersed fibre-reinforced composite.

It is observed that addition of as-received sea urchin particle into kenaf fibre-reinforced epoxy-neem biocomposite gives improved wear resistance. The decreased specific wear rate of 22% and 59% was observed for composite designation $ENFS_1$ and $ENFS_2$ on comparing with ENF designation. This improvement in wear resistance is because of reduced expose area of epoxy resin into the abrasion disc. The dispersed sea urchin particles are in contact with the abrasion wheel and reduce the possibility of epoxy getting abraded by lowering the COF. Thus, improved wear resistance was noted. It is noted that the addition of surface-modified sea urchin particle into kenaf fibre-reinforced epoxy-neem biocomposite gives improved wear resistance than as-received composite designations ($ENFS_1$ and $ENFS_2$). The improvement of 28% and 70% was observed for surface-modified composite designations $ENFS_1$ and $ENFS_2$, respectively. This improvement is because of surface-modified sea urchin particle not produced any cluster and dispersed in matrix more uniform. The uniform dispersion of particle provides maximum resistance to wear by lowering COF and reduced the direct contact of epoxy resin to the abrasion wear disc. It is observed that the 1.0 vol% sea urchin particle added composite ($ENFS_2$) gives improved wear resistance than 0.5 vol% of sea urchin added composite $ENFS_1$. This improvement is because of exposing of more ceramic sea urchin particle into abrasion disc by lowering the COF of 11% and 14%, respectively [20].

Thermal properties

Tables 4 and 5 show the thermal properties of as-received and surface-modified sea urchin particle added kenaf fibre-reinforced epoxy-neem biocomposite.

(a) Effect of adding neem oil into epoxy resin.

It is observed that the addition of neem oil into epoxy resin decreased the glass transition temperature of epoxy resin. The decrement of 19%, 25% and 37% was observed for composite designation EN_1, EN_2 and EN_3, respectively. This is because of the addition of neem oil forms IPN structure and reduces the cross-linking density of epoxy resin. Since the cross-linking density is directly proportional to glass transition, decreased Tg values were observed. When cross-linking density is less, the energy, which is required for activating the secondary molecular chains, is also less. Thus, at lower temperature itself the secondary molecular chains start rotating, thereby showing lower Tg values. It is observed that addition of neem oil into epoxy resin increased the initial, rapid and final

Table 4 Thermal properties of as-received kenaf fibre/sea urchin multi-hybrid biocomposites

Material designation	Tg (°C)	Initial decomposition (°C)	Rapid decomposition (°C)	Final decomposition (°C)
E	63	320	385	550
EN_1	51	285	370	534
EN_2	47	260	364	525
EN_3	40	234	360	480
ENF	45	218	354	465
$ENFS_1$	60	248	372	473
$ENFS_2$	82	270	380	495

E epoxy, *N* neem oil, *F* fibre, *S* sea urchin particle

Table 5 Thermal properties of surface-modified kenaf fibre/sea urchin multi-hybrid biocomposites

Material designation	Tg (°C)	Initial decomposition (°C)	Rapid decomposition (°C)	Final decomposition (°C)
E	63	320	385	550
EN_1	51	285	370	534
EN_2	47	260	364	525
EN_3	40	234	360	480
ENF	63	240	368	492
$ENFS_1$	92	292	382	508
$ENFS_2$	98	315	415	535

E epoxy, *N* neem oil, *F* fibre, *S* sea urchin particle

mass decomposition. The formation of aqua molecules by the reaction of neem and epoxy is the cause of larger mass loss at lower temperature. Similar decrement in thermal stability was observed in rapid and final stage.

(b) Effect of adding kenaf fibre into epoxy-neem bioblend.

It is observed that further addition of as-received kenaf fibre decreased the Tg of fibre-reinforced epoxy-neem biocomposite. This reduction is because the as-received kenaf fibre reacts with free OH groups from epoxy resin and forms aqua molecules. These aqua molecules are getting evaporated in lower temperature itself. Thus, lower Tg is observed, whereas the surface-modified kenaf fibre-reinforced epoxy-neem biocomposite gives improved Tg value on comparing with as-received ENF. This improvement is because in surface-modified ENF designation the direct intimate contact of kenaf fibre with epoxy resin is restricted due to surface modification. Hence, larger temperature is required to break the silane layer on fibre, which increases Tg value of composite [21]. The addition of as-received kenaf fibre into neem-epoxy biocomposite further decreased the initial, rapid and final thermal stability. The direct expose of cellulose in kenaf fibre to epoxy resin creates water molecules and then evaporates in early temperature. Similarly, the low specific heat of cellulose contain kenaf fibre cannot withstand for raise of temperature. When temperature increases, the volatile contents from fibre get evaporated, thereby giving huge mass loss at lower temperature [22]. But by the addition of surface-modified kenaf fibre in epoxy-neem composite, the direct contact of fibre to resin is typically restricted due to the coverage of silane on fibre surface. Hence, aqua formation is hampered and also heat energy required for depleting the silane on fibre surface getting increases. Thus, higher thermal stability is observed. Similar improvements were observed in rapid and final stages of surface-modified ENF designation.

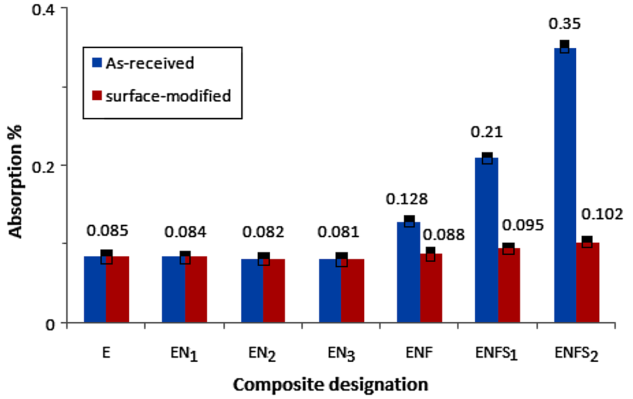

Fig. 8 Water absorption behaviour of biocomposite

(c) Effect of adding sea urchin particle into kenaf fibre-reinforced epoxy-neem biocomposite.

Addition of sea urchin particle into kenaf fibre-reinforced epoxy-neem biocomposite is giving improved thermal stability. The highest glass transition of 82 °C and 98 °C was observed for as-received and surface-modified $ENFS_2$ designation. This improvement is because of high specific heat capacity (50 kJ/mol °K) and density (3.34 g/cm^3) of calcinated sea urchin particle, which increases the heat absorption rate and increases the Tg of composite. Tables 4 and 5 show the initial, rapid and final mass decomposition of as-received and surface-modified $ENFS_1$ and $ENFS_2$ composite designations. The improvement in initial thermal stability of 12% and 19% was observed for as-received $ENFS_1$ and $ENFS_2$ designations on comparing with ENF. But the surface-modified $ENFS_1$ and $ENFS_2$ designations give improvement of 19% and 24%. This is because of surface-modified sea urchin particle dispersed in epoxy-neem bioblend in more uniform manner than as-received particle. The surface-modified particles are covered by silane substance; hence, larger amount of heat energy is required to exhaust the silane coverage. This phenomenon increases the initial thermal stability. Similar improvements were observed in rapid and final decomposition stages.

Water uptake behaviour

Figure 8 shows the water uptake behaviour of as-received and surface-modified kenaf fibre-reinforced sea urchin particle added epoxy-neem biocomposite. The water absorption test was conducted based on ASTM-D 570.

It is observed that by the addition of neem oil into epoxy resin no such difference is found in weight after immersion. The before and after immersion weight shows almost same value. This is because of hydrophobic nature of neem oil, which does not change the supreme water resistance property of epoxy resin [23]. The addition of as-received kenaf fibre into epoxy-neem biocomposite increased the weigh up to 34% after immersion. The bare surface of kenaf fibre absorbs more moisture when the composite is immersed in water. But by the surface-modified kenaf fibre in epoxy-neem composite the weight after immersion is near same to pure epoxy. A marginal increase of 3.4% in weight was observed for surface-modified ENF designation. This water resistance stability is because of reduction in moisture absorption by kenaf fibre due to surface modification. It is observed that the as-received composite designation $ENFS_1$ and $ENFS_2$ is found to be producing increase in weight after immersion. The increase of 60% and 78% was observed for composite designation $ENFS_1$ and $ENFS_2$, respectively. The formation of $Ca(OH)_2$ after reaction with water is the cause of this increase. But the after immersion weight of surface-modified composite designation $ENFS_1$ and $ENFS_2$ is found to be very minimum on comparing with as-received $ENFS_1$ and $ENFS_2$, respectively. This low water absorption behaviour of composites is because of silane covered sea urchin particle, which hindered the formation of hydroxide state; thus water absorption resistance is maintained.

Conclusion

An eco-friendly multi-hybrid neem oil blended epoxy resin (~ 50 vol% neem) with addition of kenaf fibre and sea urchin bioparticle-based biocomposite for sustainable material technology is prepared and characterized. The surface treatment of fibre and particle is successfully done using aqueous solution method. Addition of neem oil into epoxy resin decreased the mechanical and thermal properties but converts the epoxy composite as bioform. Addition of surface-modified kenaf fibre into epoxy-neem bioblend gives improved mechanical properties. The as-received kenaf fibre in matrix forms moisture and gives poor thermal properties. But the surface-modified kenaf fibre-reinforced epoxy composite explicated improved thermal properties. The surface-modified sea urchin particle further improved the mechanical and thermal properties of epoxy-neem biocomposite rather than as-received one. The water absorption results show unaltered nature of surface-modified composite designations after immersion. Thus, in the process of making eco-friendly biocomposite the addition of neem oil decreased the mechanical and thermal properties, whereas adding kenaf fibre greatly improved mechanical properties and sea urchin particle improved the thermal properties. These biocompactable mechanically and thermally strengthened composites are having the properties equal to epoxy resin with eco-friendly nature. These eco-friendly composites are capable to serve in structural, industrial and domestic applications.

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