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ORIGINAL ARTICLE

Mechanical, wear, fatigue, and water absorption behavior of epoxy biocomposite toughened using marine waste *Sepioteuthis sepioidea* pen chitosan biopolymer and pineapple plain-weaved fiber

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Abstract
This study investigates the characteristics of epoxy biocomposites strengthened using *Sepioteuthis sepioidea* chitosan biopolymer and reinforced using plain-weaved pineapple fiber mats. Fabricated through the hand layup method, these composites underwent systematic characterization, evaluating their mechanical, wear, fatigue, and water absorption behaviors in compliance with ASTM standards. Among the various composite designs, EP3 (chitosan of 3 vol.%), comprising 30 vol.% pineapple fiber and 2 vol.% chitosan particles, demonstrated superior mechanical strength and fatigue resistance. In terms of mechanical properties, EP3 exhibited a tensile strength of 132 MPa, flexural strength of 191 MPa, compressive strength of 171 MPa, impact energy of 4.27 J, V-notch rail shear of 24 MPa, and plane shear of 81 MPa. Additionally, composite EP3 demonstrated improved fatigue life counts with the applied stress level of 18.4 MPa for 1×10^6 life counts. This indicates that the composites are suitable for repeated load-bearing applications. The incorporation of *Sepioteuthis sepioidea* chitosan biopolymer as a toughening agent in the epoxy matrix enhanced the overall mechanical and fatigue performance, while the pineapple plain-weaved fiber mats acted as reinforcing elements, strengthening structural integrity and strength. Furthermore, a higher chitosan concentration led to improved wear resistance, as evidenced by EP4's (chitosan of 5 vol.%) reduced specific wear rate of 0.009 mm^3/Nm and coefficient of friction of 0.22. However, the larger chitosan content also resulted in increased water absorption, with EP4 (chitosan of 3 vol.%) reaching a water absorption percentage of 0.36%. These findings provide valuable insights into the collaborative impact of *Sepioteuthis sepioidea* chitosan biopolymer and pineapple fiber reinforcement on the mechanical, wear, fatigue, and water absorption properties of epoxy biocomposites. These properties improved composites that could be used in making car door inner panels, modular kitchen slabs, temporary partitions, and thermal insulated food storage tanks.

Keywords Composites · Fiber · Biopolymer · Mechanical properties · Wear · Fatigue

1 Introduction

The use of biocomposite materials in various engineering applications is more significant when compared to synthetic composite materials, mainly due to its renewable, less expensive, biodegradability, less dense, and higher strength and stiffness [1]. These biocomposite materials comprise a combination of organic and inorganic elements, encompassing natural and synthetic polymers, polysaccharides, proteins, ceramics, metals, and nanocarbons. Based on the matrix which is used for reinforcement, the composite is classified into polymer matrix, metal matrix, ceramics matrix, carbon matrix, etc. Among the polymer matrices are most commonly used across many industries due to their low specific weight, high material stability against corrosion, good

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electrical and thermal insulation, ease of shaping, and mass production, etc. [2, 3]. Besides these advantages, the growing attention on climate change mitigation against environmental pollution makes the nations around the world utilize eco-friendly, biodegradable components. As a consequence, biosynthesized polymers are utilized in the biocomposite material. Biopolymers are molecular chains composed of repetitive chemical units derived from sustainable sources, and they possess the ability to undergo degradation in the environment [4]. The distinctive qualities of non-toxicity and biodegradability associated with biopolymers enhance their suitability for various applications, including but not limited to automotive, aviation, electronics, medical devices, energy, and food packaging [5, 6].

Chitosan stands out as a biopolymer polysaccharide, resulting from the deacetylation process of chitin molecules. This linear chain polysaccharide, chitosan, comprised ß-(1–4)-linked D-glucosamine and *N*-acetyl-D-glucosamine units distributed randomly. The existence of free amine groups along the chitosan chains facilitates the formation of crosslinked polymeric networks when combined with dicarboxylic acids, contributing to the enhancement of chitosan's mechanical properties [7, 8]. These chitosan molecules are obtained from the outer skeleton of shellfish and crustaceans, including crab, squid (*Sepioteuthis sepioidea*), lobsters, shrimps, and sea urchins. Among those varieties, *Sepioteuthis sepioidea* is considered as a sea floor-dwelling invertebrate belonging to the phylum Echinodermata, having high nutritional content such as vitamins, proteins, minerals, fatty acids, and polysaccharides, and it also possesses certain medicinal properties such as anticancer, antithrombotic, antimicrobial, and antioxidant [9]. Most of the center bone pen waste from this *Sepioteuthis sepioidea* is considered as waste and remains unused, which might create pollution because of dumping that waste in open space. But it is a rich source of chitin as well as chitosan. So, in order to use their waste in an economically beneficial way, it is used for extraction of chitosan biopolymer from it, and there were various research studies done on chitosan contained sea-based species under different applications [10].

In the investigation conducted by Arun Prakash et al. [11], the focus was on characterizing silanized Echinoidea fillers and kenaf fiber-reinforced *Azadirachta indica*-blended epoxy multi-hybrid biocomposite. The study's findings led to the conclusion that the incorporation of surface-modified sea urchin biofiller and kenaf fiber resulted in an enhancement of both mechanical and thermal properties. Additionally, the adhesion of the composite material was notably improved as a result of these modifications. Similarly, Arociam et al. [12] investigated on mechanical and thermal characterization of additive manufactured fish scale powder reinforced PLA composite. The author reported that the addition of 20% fish scale powder increased the tensile strength and flexural strength of the 3D printed PLA composite in the range of 15% and 39.78% respectively. Similarly, Rumengan et al. [13] conducted a study on the characterization of chitin extracted from fish scales of marine fish species like *Chlorurus soridus* and *Lutjanus argentimaculatus* by analyzing through FTIR under infrared spectroscopy. The author reported that both contained chitin of 45% and 33% and also resulted that this chitin-extracted fish species has also contained the hydroxyl amine band spectra of up to 3500 cm^{-1}. Moreover from this chitin, easily the chitosan bio-polymer could be derived as post-process. Similarly, there were many studies done under sea urchins on biofilm, packaging, and biomedical application [14, 15]. Like this, there were very minimal studies done on syntheses of chitosan from sea-based species as well as *Sepioteuthis sepioidea.*

In addition to these advantageous features in the chitosan, the inclusion of natural fiber into composite material further enhances the strength, stiffness, and properties of the composite materials. Further, the natural fiber reinforcement provides less density, high specific strength, and better thermal insulation, chemical resistance, and biodegradability properties when compared to artificial synthetic fibers [16]. Moreover, these natural fibers can be obtained from various stem, flower, root, leaf, and fruit parts of different plant species. For instance, the root part of *Solanum tuberosum*, the leaf part of pineapple, the fruit part of coir, the flower part of banana, the stem, the bast part of kenaf, etc. Extracting natural leaf fibers, like those from pineapple plants, is particularly straightforward due to an easy retting process facilitated by the high cellulose content in the leaves. These leaf fibers offer notable strengths and stiffness, consume less energy during extraction, are environmentally friendly, and provide superior insulation properties compared to synthetic fiber-based composites [17]. Pineapple leaf fibers are widely acknowledged for their exceptional characteristics, including low machining wear, cost-effectiveness, and excellent performance in various engineering applications. These attributes position them as superior reinforcing materials when compared to other plant fibers. Typically comprising 70–82% cellulose, 5–12% lignin, and 1.1% ash content, pineapple leaf fibers boast a high cellulose content, which significantly contributes to heightened tensile and flexural strength in composite materials [18].

In a study conducted by Praveena et al. [19], the mechanical properties and water absorption behavior of polymer composites reinforced with pineapple leaf fibers were investigated. The research reported that an increase in fiber addition led to improvements in tensile strength, flexural strength, Young's modulus, impact strength, and water absorption behavior of the composite material. Similarly, Saha et al. [20] conducted an analysis on the mechanical properties of polymeric composites reinforced with pineapple leaf particulates. The study revealed that the addition of

pineapple leaf fibers resulted in enhanced interfacial adhesion, improved Young's modulus in both longitudinal and transverse directions, and improved shear modulus in both in-plane and out-plane orientations of the composite material. Furthermore, Kohphaisansombat et al. [21] studied the performance of mycelium-based composites derived from spent coffee grounds with pineapple fiber reinforcement. The result revealed that the addition of 10 wt.% of pineapple fiber shows maximum compressive strength, and the addition of 30wt.% of pineapple fiber represents enhanced bending strength and water absorption behavior of the composite material. Because of their specific features and improved mechanical and thermal properties of the material, it has been studied many researches under various applications [22].

Thus, the current development in composite fields attributes new innovations in material science. Especially, biopolymer chitosan reinforcement enhances the mechanical, wear, and water absorption behavior of the composite material. But there were no such studies done on the extraction of chitosan from *Sepioteuthis Sepioidea*. Moreover, there is no research study to the best of our knowledge conducted on the biocomposite comprising chitosan derived from *Sepioteuthis sepioidea* and pineapple leaf fiber mat with epoxy resin. Therefore, the present study aims to investigate the mechanical, wear, fatigue, and water absorption behavior of the chitosan biopolymer and natural pineapple leaf fiber-reinforced epoxy biocomposite. Thus, this study makes an opportunity for academicians and researchers to study more about this biopolymer and natural fiber-reinforced composite. Thus, this biocomposite could be applied in wide sectors such as automation, aviation, military, biomedical, and pharmaceutical industries.

2 Experimental procedure

2.1 Materials

In this study, the epoxy resin employed was a liquid DGEBA (LY566) characterized by an average molecular weight of 190 g/mol and a kinematic viscosity of 12,000 cps. The curing agent used was triethylenetetramine (TETA) HY951, recognized for its low viscosity aliphatic amine properties, boasting a viscosity of 20 cps and a density of 0.98 g/cm^3. Both the epoxy and the curing agent are sourced from Huntsman India Ltd., Mumbai, India. The *Sepioteuthis Sepioidea* needed for chitosan production was obtained from fishermen in the southern coastal regions of India. The reinforcing material, a plain weaved woven mat of pineapple fibers (250 GSM) with a thickness of 0.63 mm and a density of 1.4 g/cm^3, was procured from Metro Composites, Chennai, India.

2.2 Preparation of chitosan biopolymer

The production of chitosan involves various chemical processes, including decalcification, deproteinization, decolorization, and deacetylation. The demineralization of *Sepioteuthis sepioidea* pen is commonly done using mild HCl solutions at room temperature, although other acids such as HNO_3, H_2SO_4, and CH_3COOH may also be employed. The concentration of acid and the treatment duration depends on the chitin source. Pen deproteinization is carried out using diluted NaOH solutions at temperatures ranging from 65 to 100 °C for 72 h. To convert chitin into chitosan, deacetylation is typically achieved through the hydrolysis of acetamide groups using concentrated NaOH or KOH (40–50%) at temperatures exceeding 100 °C. The resulting chitosan particles are further subjected to ball milling process to reduce the particle size. A planetary ball mill was used to reduce the particle size further. About 50 g of chitosan particle is taken in the ball mill jar and rotated at the RPM of 300 for 2 h. The powder-to-ball ratio used was 1:15, and the ball material used here was tungsten carbide (WC). There are a total of 10 balls with a diameter of 10 mm used [23].

Figure 1 represents the chitosan preparation from *Sepioteuthis sepioidea*. Figure 2a–c shows the SEM, XRD, and PSA histogram patterns of *Sepioteuthis sepioidea* pen-derived chitosan. In Fig. 2a, the SEM micrograph shows the chitosan microparticles produced from the waste *Sepioteuthis sepioidea* pen. Based on the scale, it is clear that the average size of chitosan powder prepared is about 1–3 µm. Similarly, the particle size histogram shows the particle size ranging between 1 and 3 µm. Moreover, an amorphous diffraction pattern may be seen in the XRD of chitosan powder. Rather than the characteristic acute peaks at $2\theta = 9.6°$ and 28.61° reported in the diffractogram of chitosan powder, the films display a broad maximum of about 19.84°. Similarly, Fig. 3 shows the FTIR spectra of chitosan biopolymer prepared. The functional peak at 3473.33 cm^{-1} indicates the N–H stretch from the chitosan biopolymer which is responsible for making tough bonds with resin. Similarly, other functional peaks 2916.37, 1643.35, 1427.32, 1157.29, and 894.97 cm^{-1} indicate the C-H stretch, C-O stretch, C-H stretch, C-O bend, and C–O–C rock confirm the other secondary functional peaks of chitosan prepared. This confirms that the particles formed are chitosan.

2.3 Preparation of composites

In this study, the hand layup process is employed in the preparation of composites, starting with the cleaning of the lay-up surface. Following the cleaning, wax is applied to facilitate the easy removal of the composite laminate and achieve a smooth surface finish. A silicon rubber is utilized to make the required size of the mold cavity, and the edges were adhesively bonded.

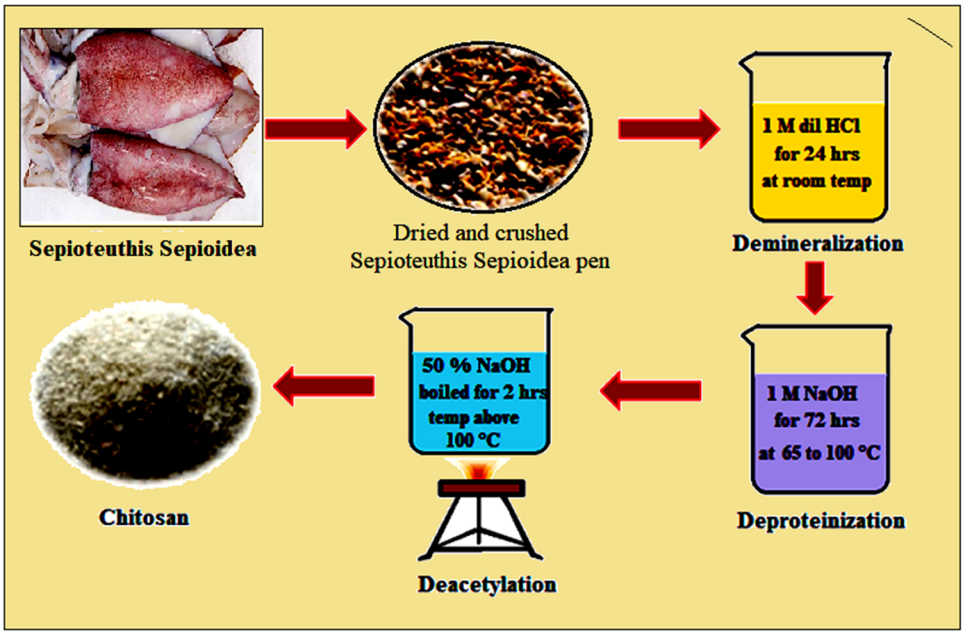

Fig. 1 Chitosan preparation from Sepioteuthis sepioidea pen

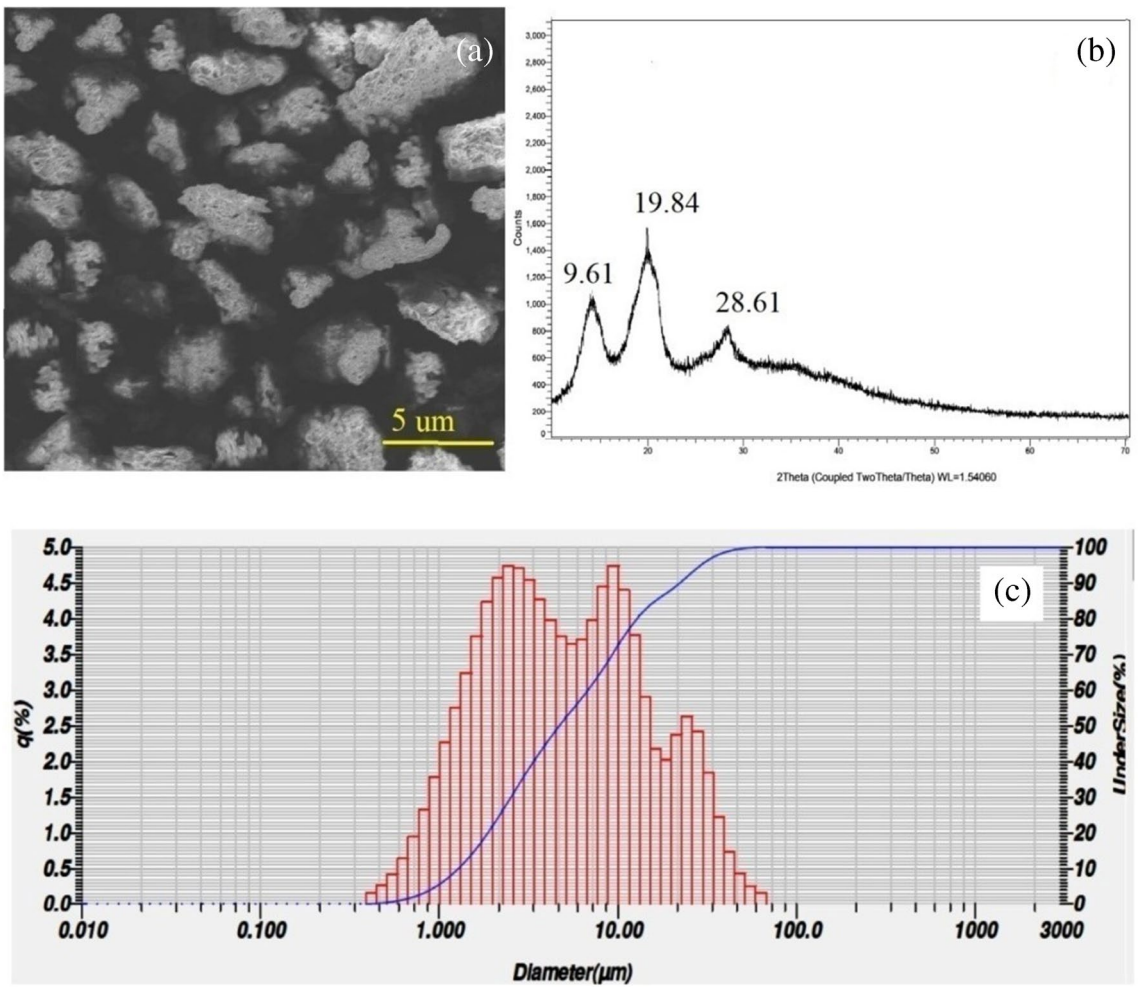

Fig. 2 SEM, XRD, and particle size histogram patterns of Sepioteuthis sepioidea pen-derived chitosan

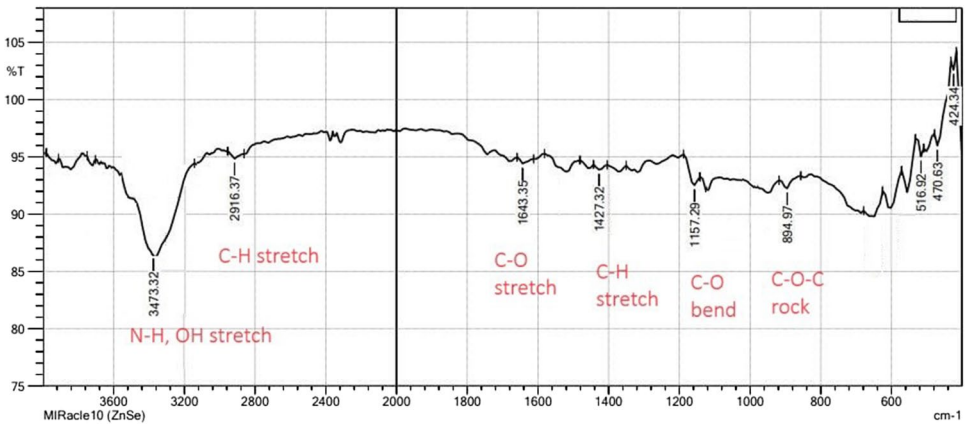

Fig. 3 FTIR spectra of synthesized chitosan from Sepioteuthis sepioidea pen

Table 1 Composite designation with different combinations

Composite designation	Epoxy (vol. %)	Pineapple plain fiber mat (vol. %)	Chitosan (vol. %)
EP	100	–	–
EP1	70	30	–
EP2	69	30	1
EP3	67	30	3
EP4	65	30	5

The epoxy resin is collected in a cleaned glass beaker, which is then filled with chitosan particles of the required volume. The volume is calculated from the true density of chitosan and fiber. It is measured using a pycnometer via the equation $\rho = [(M2-M1)/(((M3-M1)))/((M4-M2))] \times \rho t$, where the mass of the pycnometer and pycnometer filled with fiber or particle was represented by M1 and M2. The mass of the pycnometer with toluene and the mass of the pycnometer with toluene and fiber were represented by M3 and M4, respectively. $\rho t = 0.87$ g/ml is the density of toluene. Thus, from the above equation, the true density is calculated, and from that, the true volume of chitosan and fiber is calculated. Stirring is continued using an ultrasonicator for 20 min to get a homogeneous admixture of resin-chitosan free of particle lumps. Next, the hardener, constituting up to 10% of the total weight of resin, is added to the admixture and stirred gently until the complete hardener is mixed with the resin-chitosan mix. In total, three woven mat fiber layers were laid one by one to make the composite along with resin-chitosan admixture. The curing process takes place for 24 h at room temperature and further post-cured at 120 °C for 48 h in a hot air oven [24]. Table 1 presents the composite designations with different combinations of fiber and chitosan particles. Similarly, Fig. 4 shows the photographic view of the EP2 composite prepared.

Fig. 4 Photographic view of EP1 composite prepared using pineapple fiber and chitosan biopolymer

3 Characterizations

To find any noticeable surface faults, the epoxy-based *Sepioteuthis sepioidea* chitosan dispersed with pineapple fiber mat composite is visually inspected. According to the ASTM standards and specifications test, specimens were cut out of the laminates using an abrasive jet machine (Maxiem water jets, 1515 KENT). The machine runs with a maximum 220 psi jet pressure, 0.3 g/s abrasive flow rate, 1.1 mm nozzle diameter, and 3 mm SOD throughout the processes. Table 2 presents the mechanical, fatigue, wear, and water absorption testing process parameters and its testing machinery details. Figure 5 represents the test specimens which have been cut according to the ASTM standards.

Table 2 Process parameter and testing machinery details

Tests performed	ASTM standards	Machines used
Tensile	D-3039	Universal testing machine (INSTRON 4855, UK) Traverse speed of 1.5 mm/min. The gripper used here was a hydraulic gripper and 5 times each test was repeated
Flexural	D-790	
V notch shear	D-7078	
In-plane shear	D-3518	
Compression	D-695	
Impact	D-256	A mini Izod impact testing machine (Krystal Equipment Ltd., India) with a maximum load capacity of 20 J was used to assess the energy absorbed
Hardness	D-2240	Shore durometer (Bluesteel, India). The indentation is taken at least 5 times in each specimen to compute the average
Fatigue	D-3479	A tension-tension fatigue test machine (MTS Landmark 370 load frame, USA) with force control mode. Modulus of 6 GPa, applied stress of 50% UTS, stress ratio of − 1, and frequency of 5 Hz were selected as process variables
Wear	G-99	Pin-on-disc (Contech Micro Systems, India) with a 10 N of applied load, 1000 m of track running distance, and 500 of disc rotational speed
Water absorption	D-570	For the water absorption test, the specimens are dried in an oven for a specified time and temperature and then placed in a desiccator to cool. Immediately upon cooling, the specimens are weighed. The material is then emerged in water at agreed-upon conditions, often 23 °C for 24 h. Specimens are removed, patted dry with a lint-free cloth, and weighed

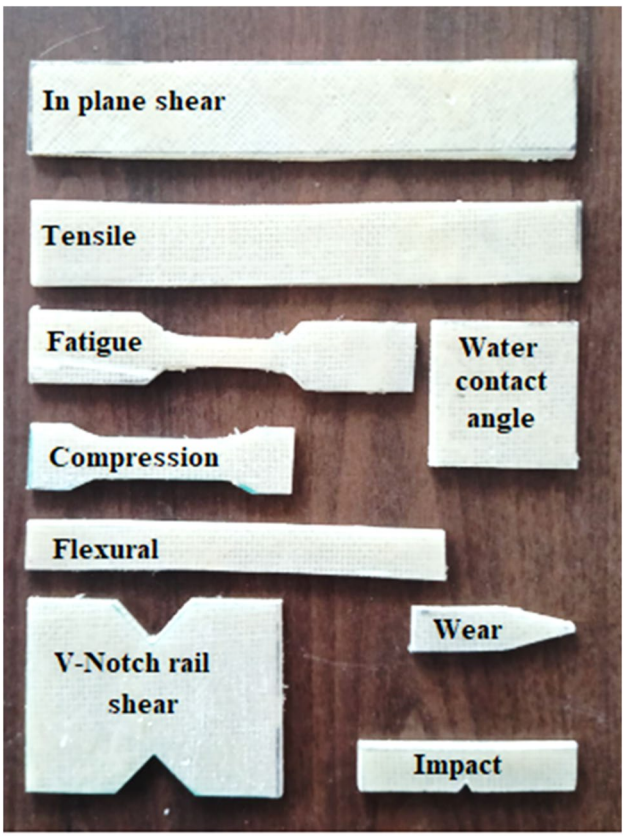

Fig. 5 Test specimens of EP4 as per ASTM standards

4 Results and discussions

4.1 Mechanical characteristics

4.1.1 Tensile strength

Figures 6a and 7a illustrate the tensile strength and stress–strain graphs of various composite designations, including EP, EP1, EP2, EP3, and EP4. The plain epoxy composite, EP, demonstrates a tensile strength of 63 MPa, which is relatively lower compared to other composite designations. This diminished value can be attributed to the absence of reinforcement in the matrix. However, the introduction of pineapple fiber at 30 vol.% significantly enhances the tensile strength, resulting in a 61.9 % improvement for EP1. The incorporation of pineapple fibers reinforces the matrix, providing better load-bearing capacity and consequently improving tensile strength [25]. Furthermore, the additional inclusion of chitosan filler particles at 1, 3, and 5 vol.% contributes to a further enhancement in tensile strength for EP2, EP3, and EP4. Notably, EP3 exhibits a high tensile strength of 132 MPa. The presence of chitosan in the matrix improves toughness and stiffness, filling microvoid spaces and enhancing the overall structural integrity of the matrix [26]. However, at higher volumes of chitosan, there is a slight reduction in tensile strength. Consequently, EP4 delivers a tensile strength of 124 MPa, which is 6.06% lower than the EP2 composite designation. This observed decrease may be attributed to agglomeration or over-rigidity in the matrix resulting from the higher volume of chitosan particles.

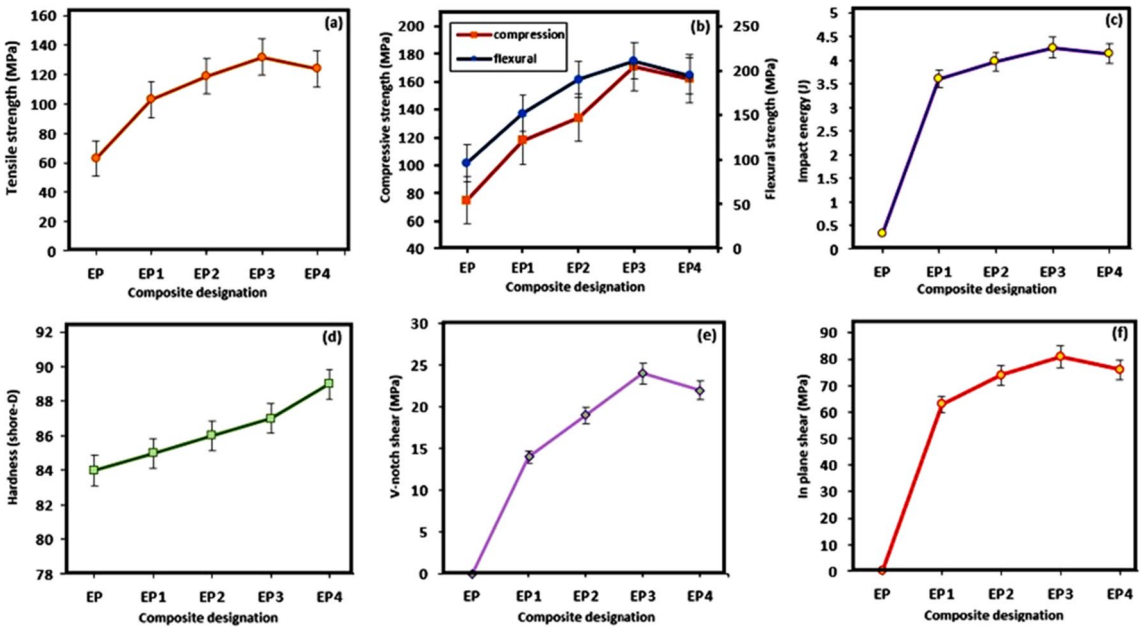

Fig. 6 Mechanical characteristics including a tensile strength, b flexural and compressive strength, c impact energy, d hardness, e V-notch rail shear, and f plane shear, for various composite designations

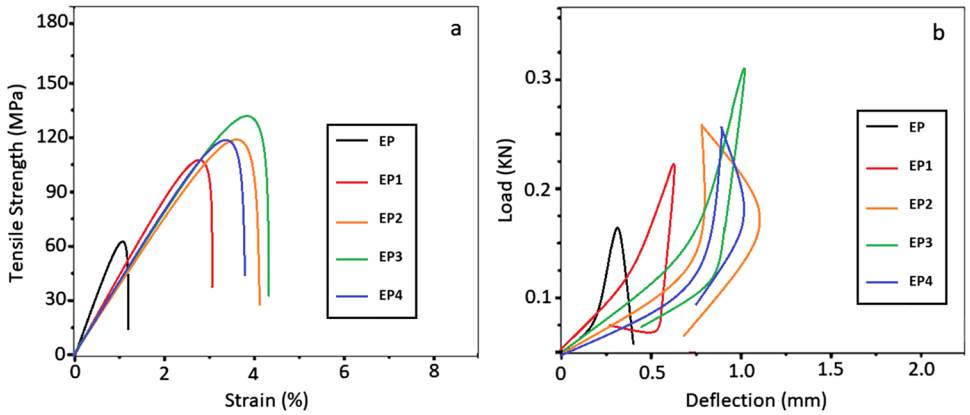

Fig. 7 Graphs of a stress–strain and b load–deflection of plain resin and composites

4.1.2 Flexural strength

Figures 6b and 7b display the flexural strength values exhibited by various composite designations, namely EP, EP1, EP2, EP3, and EP4. The initial composite, EP, demonstrates a flexural strength of 102 MPa. The inherent brittleness and lack of filler or fiber content contribute to the lower flexural strength in EP composite designations [27]. However, the introduction of pineapple fiber into the matrix improves flexural strength. These fibers, present in the matrix, absorb and distribute applied stress throughout the structure, resisting the load and enhancing bending strength. Consequently, EP1, with 30 vol.% of pineapple fiber, exhibits a flexural strength of 138 MPa. Moreover, the inclusion of filler content further enhances flexural strength. EP2, EP3, and EP4, with chitosan filler content, exhibit flexural strengths of 161 MPa, 177 MPa, and 162 MPa, respectively. Notably, EP2 delivers superior flexural strength among the composite designations. Chitosan in the matrix acts as reinforcement, improving the interaction between the matrix and pineapple fibers [28]. This enhanced adhesion and compatibility at the interface reduce the likelihood of fiber-matrix separation, contributing to better load transfer and increased flexural strength. Therefore, cluster particle formation at higher volumes caused a reduction in flexural strength which was observed in EP4.

4.1.3 Compression strength

In Fig. 6b, the compression strength values of various composite designations, including EP, EP1, EP2, EP3, and EP4, are presented. The baseline composite, EP, demonstrates

compression strength of 75 MPa. The pure epoxy matrix has limited energy absorption capacity, which not effectively absorbs and dissipates the applied energy, leading to the relatively modest compression strength observed in EP. However, with the introduction of pineapple fiber (at 30 vol.%) into the matrix, there is a noticeable enhancement in compression strength. The inclusion of pineapple fibers in the matrix improves load distribution within the material. As the fibers bear the compressive load, they help spread the stress more evenly across the composite. This even distribution minimizes stress concentration points and enhances the material's ability to withstand compression. Consequently, EP1, with a composition of 30 vol.% pineapple fiber, showcases a substantial increase in compression strength, reaching 118 MPa. Furthermore, the incorporation of chitosan filler content serves to further augment compression strength. EP2, EP3, and EP4, each featuring varying levels of chitosan, exhibit compression strengths of 125 MPa, 171 MPa, and 162 MPa, respectively. Notably, EP3 stands out with the highest compression strength in this set. The chitosan in the matrix enhances the overall strength of the composite. The toughening effect of chitosan helps resist compressive forces and prevents the initiation and propagation of cracks, leading to improved compression strength. It is important to highlight that the observed decrease in compression strength in EP4 may be attributed to the formation of cluster particles at higher chitosan volumes, introducing a distinct influence on the overall compressive performance [29].

4.1.4 Impact toughness

The impact energy of different composite designations is shown in Fig. 6c. The initial composite designation EP designation exhibits a low impact energy of 0.35 J. This lower impact energy is attributed by the presence of microvoids presence in the matrix. When impact force is applied, stress is concentrated around these voids, and fractures initiate from these points. Fracture initiation often leads to crack propagation, which further diminishes the material's resistance to impact. However, impact resistance improved with the addition of 30 vol.% of pineapple fiber in the matrix; thus, EP1 delivers an impact energy of 3.61 J. This is because of pineapple fibers in the matrix, which provide flexibility to the composite, allowing it to deform under impact without fracturing. This flexibility helps absorb and distribute the impact energy, reducing the severity of the damage. Further addition of chitosan further improves the impact resistance. Thus, EP2, EP3, and EP4 are observed with impact energy of 4.02 J, 4.27 J, and 4.14 J. Thus, chitosan, along with pineapple fibers, contributes to reducing the formation and propagation of microcracks within the composite. By reinforcing the matrix and preventing or mitigating microcracking, chitosan and pineapple fibers collectively improve impact resistance. However, agglomeration of chitosan results in reduced impact energy which is observed in EP4.

4.2 Hardness

In Fig. 6d, the Shore-D hardness values of different composite designations, namely EP, EP1, EP2, EP3, and EP4, are depicted. The initial epoxy matrix, EP, exhibits a hardness of 84. The introduction of pineapple fibers in EP1 leads to a slight increase in hardness to 85. The subsequent addition of chitosan further elevates the hardness levels in EP2, EP3, and EP4, reaching values of 86, 87, and 89, respectively. The observed enhancement in hardness is attributed to the combined reinforcing effects of chitosan and pineapple fibers within the composite matrix. Pineapple fibers contribute inherent strength and stiffness, while chitosan brings toughening properties to the material [30]. This collaborative action creates a synergistic effect, significantly improving the material's ability to resist deformation and, consequently, elevating its overall hardness. Moreover, the inclusion of pineapple fibers not only reinforces the matrix but also contributes to the effective load transfer mechanism within the composite. This efficient load transfer minimizes stress concentrations, resulting in increased hardness. Additionally, the compatibility of chitosan and pineapple fibers with the matrix material enhances the overall cohesion, providing a strong bond at the fiber-matrix interface that contributes to the improved hardness of the composite.

4.2.1 V-notch shear

In Fig. 6e, the V-notch shear strength values of different composite designations are depicted. Notably, EP1 exhibits a significant shear strength of 14 MPa, a performance attributed to the inclusion of pineapple fibers. The inherent strength and stiffness of these fibers play a crucial role in reinforcing the matrix against shear forces [31], contributing to the observed increase in shear strength by preventing or delaying material failure. Upon further enhancement with chitosan filler content, the V-notch shear strength in EP2, EP3, and EP4 continues to improve. Specifically, EP3 stands out with a notable shear strength of 24 MPa. The addition of chitosan introduces toughness to the composite matrix, complementing the reinforcing effects of pineapple fibers. This collaborative action between chitosan and pineapple fibers enables the absorption of energy during shear loading, mitigating the risk of sudden failure. The toughening effect further facilitates material deformation under shear forces, thereby contributing to the overall improvement in V-notch shear strength. However, it is noteworthy that EP4 demonstrates a reduction in shear strength. This decrease can

be attributed to stress points formed by the higher volume of chitosan particles in the composite. The agglomeration or over-rigidity of chitosan particles may lead to localized stress concentrations, potentially diminishing the material's shear strength.

4.2.2 In-plane shear strength

In Fig. 6f, the exhibited in-plane shear strength values for EP1, EP2, EP3, and EP4 composite designations are presented. EP1 demonstrates a notable shear strength of 63 MPa, primarily attributed to the presence of pineapple fibers in the matrix. During in-plane shear loading, the strategic alignment of pineapple fibers plays a crucial role in redistributing and dispersing applied loads. This even distribution of stress helps mitigate the risk of localized stress concentrations, ultimately enhancing the overall shear strength of the composite. Furthermore, the incorporation of chitosan further enhances the in-plane shear strength for EP2, EP3, and EP4 composite designations. Notably, EP3 stands out with a high shear strength of 81 MPa. The synergistic effect of pineapple fibers and chitosan proves instrumental in inhibiting crack initiation and propagation within the material. Pineapple fibers act as reinforcements, fortifying the matrix, while chitosan, with its toughening properties, actively prevents the formation and spread of cracks. This proactive inhibition of crack development is critical for preserving the material's integrity and contributing to the improvement in in-plane shear strength. However, it is noteworthy that EP4 experiences a reduction in shear strength (76 MPa). This decline can be attributed to stress concentration points formed by clusters of a high volume of chitosan particles in the composite. The agglomeration or over-rigidity of these particles may lead to localized stress concentrations, potentially diminishing the material's in-plane shear strength.

Figure 8 shows the SEM tensile fractograph of composite designations EP1, EP2, EP3, and EP4. It is noted that the addition of fiber improved the toughness of the matrix that could be seen in the form of a wavy fracture. The addition of fiber reduces the brittle fracture phenomenon by sharing the load across the matrix uniformly. Similarly, the addition of chitosan additionally into the resin further improved the toughness. The addition of chitosan bio-polymer firmly

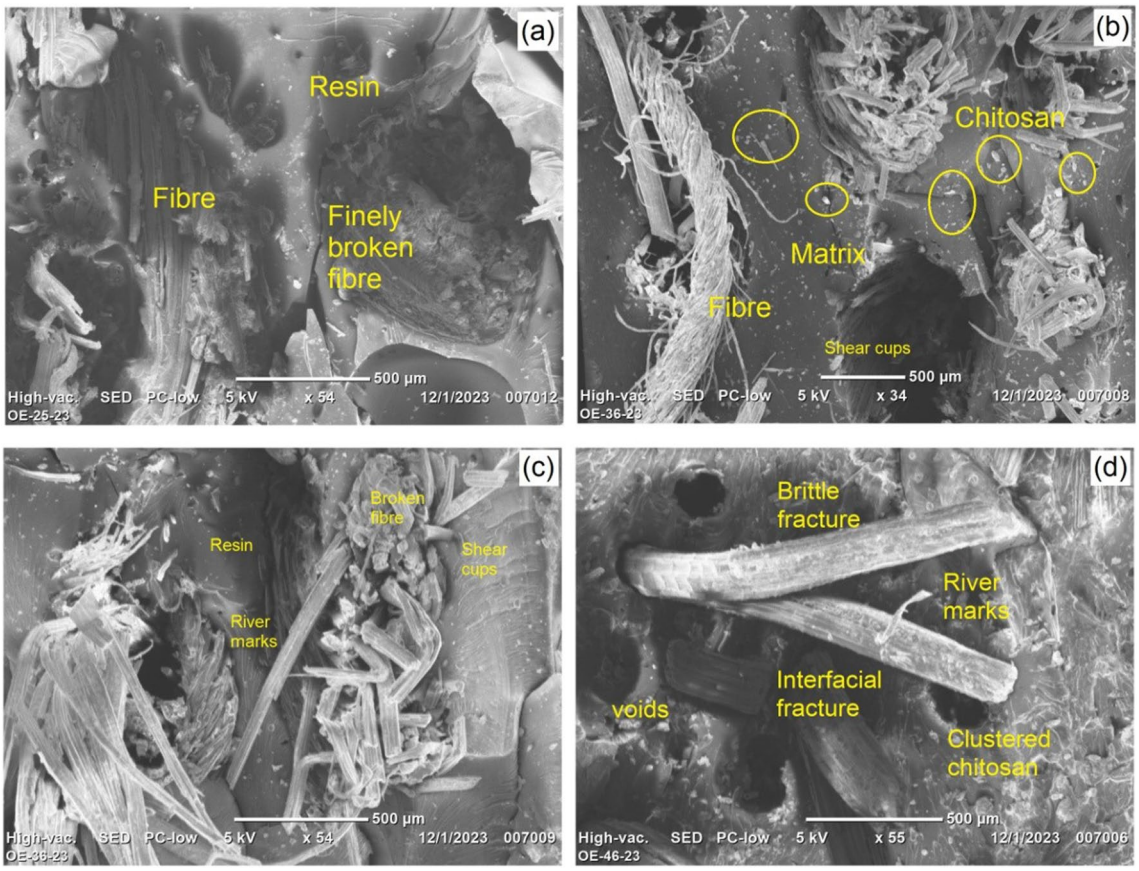

Fig. 8 SEM tensile fractograph of a EP1 after tensile test, b EP2 after tensile test, c fiber and filler interaction in EP3, and d EP4 after tensile fracture

improved the cross-linking density via the NH functional group reaction. The fewer amount of chitosan effectively dispersed both in the EP2 and EP4. The presence of shear cups in the matrix is the trace of improved toughness. However, the large dose of chitosan addition into the resin formed a cluster in the matrix and hindered the uniform load transfer. The larger cross-linking density via larger chitosan reduced the toughness and made the matrix brittle [32]. Thus, river marks are spotted across the matrix indicating the increased brittleness in the matrix. The increased brittleness also produced more residual stress along the fiber-matrix interface thereby producing fiber-matrix de-lamination. Overall, the addition of chitosan bio-polymer improved the toughness of the composite along with cellulosic pineapple fiber.

4.3 Wear behavior

The wear characteristics depicted in Fig. 9 for composite designations EP, EP1, EP2, EP3, and EP4 underscore a significant enhancement in wear resistance facilitated by the inclusion of chitosan particles. The observation strongly indicates that an increased content of chitosan further augments wear resistance. Specifically, the chitosan-inclusive composite designations EP2, EP3, and EP4 exhibit specific wear rates of 0.024 mm^3/Nm, 0.018 mm^3/Nm, and 0.009 mm^3/Nm, respectively. The coefficients of friction for these composites are measured at 0.41, 0.34, and 0.22. This noteworthy improvement in wear resistance is attributed to the reinforcing nature of chitosan, which not only toughens the matrix but also acts as a self-lubricating agent [33], effectively reducing both friction and wear rates. Furthermore, the combination of pineapple and chitosan in the composite forms a densely packed structure with improved bonding, contributing

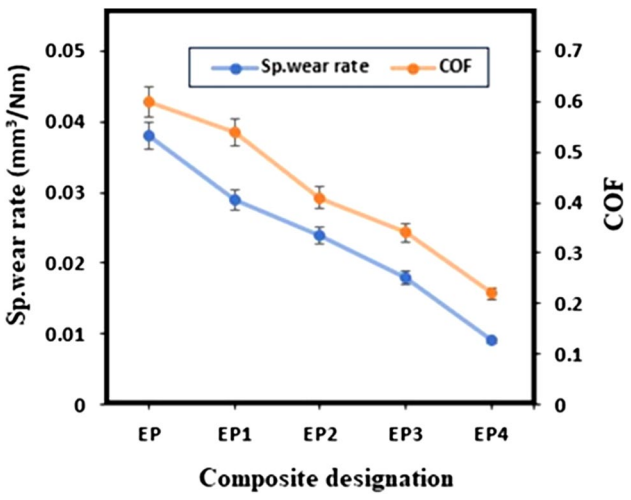

Fig. 9 Wear characteristics (Sp. wear rate and coefficient of frictions) for different composite designations

to a well-structured and integrity-enhanced composite material. This enhanced bonding plays a crucial role in preventing the separation of the matrix and filler, thereby significantly enhancing the material's resistance to wear. In comparison with the plain epoxy matrix, the high wear resistance composite EP4 demonstrates remarkable performance, featuring a 76% reduction in specific wear rate and a 63% reduction in the coefficient of friction compared to the EP composite designation. The inferior wear resistance observed in the EP composite is attributed to the soft and brittle nature inherent in the EP matrix, compounded by the absence of reinforcing particles.

Figure 10 shows the SEM worn surface of the plain resin and *Sepioteuthis sepioidea* chitosan biopolymer dispersed pineapple fiber epoxy composites. It is noted that the plain resin (Fig. 10a) gives an almost flat worn surface, indicating a high three-body abrasion happened surface. Since the plain resin is brittle, it easily breaks when the shear force is applied. This removed particles stuck between the abrasion disc and sample material thereby improving the three-body abrasion wear loss with the fully grained surface. However, Fig. 10b shows a slight wavy surface indicating high adhesion between the material and abrasion disc and irregular material removal. The presence of fiber reduced the COF and reduced the frictional force. Thus, lower wear loss is noted. It is further noted that Fig. 10c, d shows the worn surfaces of the composite containing 1 and 5 vol.% of chitosan particles (EP2 and EP4). The surface is wavy in nature indicating the improved adhesion wear loss. However, the total wear loss is less compared with plain resin since the addition of chitosan improved molecular bonding and reduced the free spaces. Thus, more shear force is required to remove the molecules from the sample, and this in turn improved the wear resistance.

4.4 Fatigue characteristics

The S–N curve of various composite designations is illustrated in Fig. 11. Upon observation, the EP composite designation displays comparatively lower fatigue counts. At 28 MPa, it gives 2100 life counts, and once the stress decreases, the counts increased. The plain resin achieved a 1×10^4 life counts at a stress level of 3.8 MPa. This is because of lower applied stress and less residual stress build-up. However, when the pineapple fiber is included in the resin the stress level is increased. The composite designation EP1 withstands a higher stress level of 48 MPa and produces minimum life counts of 8200. This further increased with reduced stress level. The composite designation EP1 attains 1×10^6 life counts at a stress level of 8.2 MPa. This is about an increment of 115.7% compared with plain resin. This improvement is the reason for the effective reinforcement given by the pineapple fiber. The presence of fiber disperses

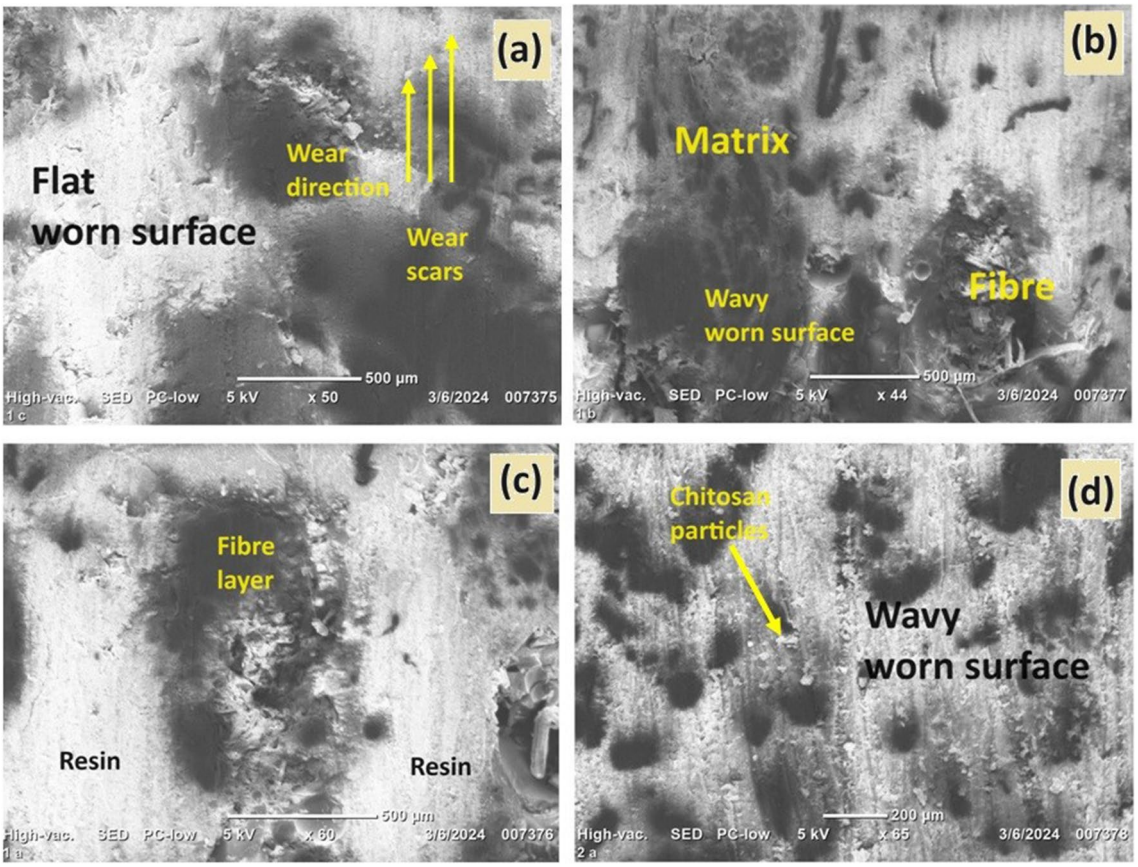

Fig. 10 SEM worn surface morphology of plain resin and composites after wear test

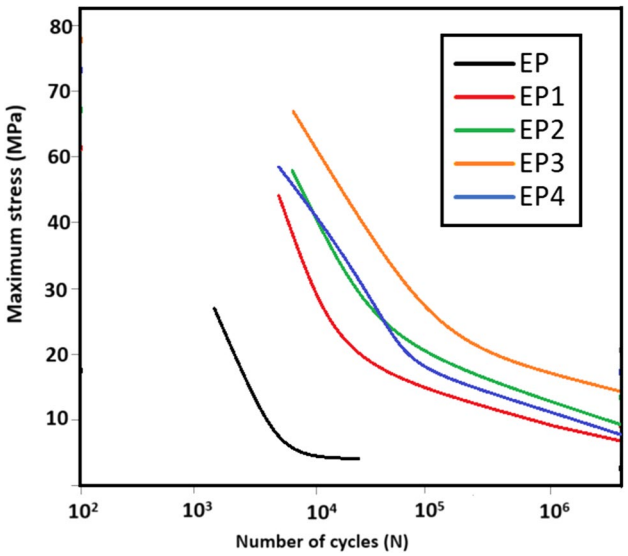

Fig. 11 S–N curves of different composite designations

the applied load uniformly; thus, the stress concentration points in the composite are less. This phenomenon increased fatigue life counts even after the applied stress is higher [34].

It is further noted that the addition of chitosan biopolymer into the resin further improved the fatigue life cycles. At higher stress level, the composite designation EP2 and EP3 gives reasonable fatigue life cycle increment. Compared with the plain resin at 1×10^6 life counts, the stress values are higher for EP2 and EP3. About 12.5 MPa and 18.4 MPa were recorded to achieve a minimum of 1×10^6 life counts. This improvement in fatigue life counts is the reason for the effective polymer toughening using chitosan. When adding the chitosan, the epoxy is toughened and reduces the accumulation of plastic strain. Thus, composites withstand higher fatigue life counts [35, 36].

However, a slight reduction in fatigue counts is observed in the EP4 composite designation compared to EP3. The EP4 exhibits 1×10^6 life counts at a stress level of 11.3 MPa which is about 38.58% of reduction compared with EP3. This reduction is attributed to the agglomerated particles of chitosan, which form stress points in the matrix, initiating cracks during cyclic loading conditions and scored lesser stress levels.

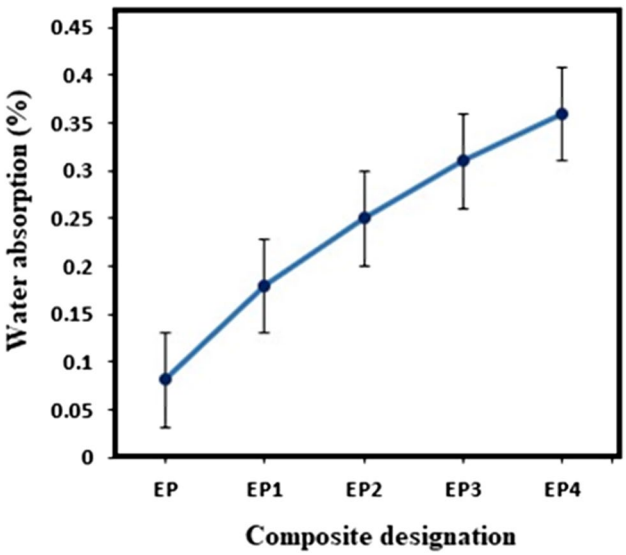

Fig. 12 Water absorption percentage of different composite designations

4.5 Water absorption behavior

The analysis of Fig. 12 indicates that the introduction of both pineapple fiber and chitosan has led to an observable increase in the water absorption percentage within the composite materials. Specifically, EP1, EP2, EP3, and EP4 exhibit water absorption percentages of 0.18, 0.25, 0.31, and 0.36, respectively.

Notably, an increasing trend emerged as the chitosan content rises, correlating with an augmentation in water absorption across the composite variations. This rise in water absorption is attributed to the inherent hydrophilic nature of both pineapple fibers and chitosan filler [37]. Both materials, being naturally hydrophilic, contribute to the increased water absorption observed in the composites. Pineapple fibers, similar to other natural fibers, actively facilitate capillary action within the composite structure. This action creates channels through which water is drawn into the composite material [38]. Moreover, the chitosan particles introduce additional hydrophilic functional groups, including amino and hydroxyl groups [39]. These functional groups play a significant role in enhancing the water absorption capacity of chitosan. The formation of hydrogen bonds between these groups attracts more water via ion charge ($^{+}$ or $^{-}$) attraction and increment in surface energy [40]. This nature significantly increased the water molecule admittance into the composite under immersion.

5 Conclusions

In conclusion, this research elucidates the comprehensive assessment of epoxy biocomposites prepared with *Sepioteuthis sepioidea* pen chitosan biopolymer and pineapple plain-weaved fiber mats. The following are the conducted research findings.

i. The mechanical properties, EP3 composite designation, prepared with 30 vol.% pineapple fiber and 2 vol.% chitosan particles showcasing superior mechanical strength.
ii. A highest tensile strength of 132 MPa, flexural strength of 191 MPa, compressive strength of 171 MPa, impact energy of 4.27 J, V-notch rail shear of 24 MPa, and plane shear of 81 MPa indicate that the composite with 2 vol.% of chitosan performed well in load-bearing effect. However, a larger dose of chitosan (5 vol.%) reduced the uniform load transfer.
iii. Additionally, composite EP3 demonstrated improved fatigue life counts with the applied stress level of 18.4 MPa for 1×10^6 life counts. This indicates that the composites are suitable for repeated load-bearing applications.
iv. However, EP4 composite designation with a higher chitosan content exhibits improved wear resistance, as evidenced by reduced specific wear rates and coefficients of friction of 0.009mm^3/Nm and 0.22. This shows that the composites could be used as human prosthetic joints where high frictional force is prone.
v. The water absorption behavior of composites shows controlled water intake though the hydrophilic chitosan particles are included. This indicates that these composites could be used for automotive outer panels receiving high rainfall hits during monsoons.
vi. These outcomes reveal that the chitosan derived from *Sepioteuthis sepioidea* pen could be a potential reinforcement for polymer composites where a balance in load bearing, fatigue resistance, and hydrophobity is required.
vii. Moreover, there is a new scope of research that could be done by using new marine waste biopolymeric sources for the development of sustainable composite materials for safe environmental uses.

Author contribution VBN and RS: research work and drafting. BSG and PS: testing and drafting supports.

Data availability All data are available in the manuscript.

Declarations

Ethical approval NA

Competing interests The authors declare no competing interests.

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