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Mechanical Characterization of Bio-epoxy Green Composites Derived from Sodium Bicarbonate Treated Punica Granatum Short Fiber Agro-waste

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Abstract

Investigations into green materials owing to the growing environmental concerns have become one of the hot topics for the scientific community. The present work aims to fabricate and investigate the mechanical and physical properties of short Punica granatum fiber (SPGF) reinforced bio epoxy (BE) biocomposites. The bio epoxy has been derived from cashew-nut shell oil. The composites are fabricated using different wt% of SPGF (10%, 20%, 30%, and 40%) that are chemically treated using 10 wt% sodium bicarbonate solution for different treatment duration i.e., 1 day, 5 days and 10 days. It has been revealed through the chemical characterization approach of X-ray diffraction (XRD) methodology that the aforementioned eco-friendly chemical treatment process doesn't promote the transformation of the treated SPGFs to cellulose II from cellulose I. Thermogravimetric (TGA) analysis reveals degradation of hemicellulose as well as the pectin content of the SPGFs. The effect of the chemical treatment with varied treatment duration on the mechanical properties as such tensile, flexural, and impact properties of fabricated green composites are investigated. The physical properties such, water absorption, moisture content, and thickness swelling are also investigated. The mechanical properties of the fabricated composites weren't affected by the alkaline treatment. However, better physical properties and mechanical properties were revealed for the composites fabricated using 5 days treated Punica granatum short fibers in comparison to other dissolution conditions. The alkaline treatment, therefore, proves to be effective in enhancing the properties of the composite specimen. The treatment process takes care of the environmental concerns as it is benign to the environment when disposed of in comparison to the strong alkaline treatment solutions. Moreover, the developed green composites promote sustainable and cleaner processing in the world of composites.

Keywords Green production · Green composites · *Punica granatum* fiber · Eco-friendly chemical treatment · XRD · TGA · Tensile properties · Flexural properties · Impact properties

Introduction

Over the last decade, natural fibers have occupied the center stage of the research community owing to the growing environmental concerns. Natural fibers possess the following advantages: better properties specific properties, cheaper, lower density, recyclability, and biodegradability. Moreover, they are CO_2 neutral and are renewable in comparison to their synthetic counterpart. Therefore, a wide variety of natural fibers have been explored as a potential reinforcement for composite materials.

The most common natural fibers that have been explored for their applicability includes hemp, kenaf, sisal, flax, banana [1], jute [2], sugarcane [3], oil palm fruit [4], etc. There have been researched investigations into lesser commonly known natural fibers as such olive tree leaf [5], sansevieria [6], Cordenka rayon [7], ferula [8], Arundo [8–10], peach palm trees [11], Aristida adscensionis (AA) plants [12], okra [13], isora [14], buriti [15], etc.

Pomegranate has its roots in the Punicaceae family. Its availability can be traced from Iran to the Himalayas in Northern India. In India, the area of cultivation for Pomegranate accrues to more than one lakh hectares. Pomegranate

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cultivation is one of the major sources of employment for the people in the agricultural domain. Pomegranate has medicinal benefits as such in curing microbial infections, respiratory problems, stomach related diseases etc.

Although pomegranate is well known for its medicinal benefits, it presents a challenging problem of its waste management since the produced waste cannot be used to feed the cattle nor it can be stored. The major source of wastes is from the extraction of the plant, its juice, and peel.

An effective waste management approach can help in solving the associated environmental problems. Therefore in the present study, short Punica granatum fibers (SPGF) obtained as a result of waste from the cultivation of the pomegranate have been explored as a potential reinforcing agent in green polymeric composites.

The matrix is one of the important constituents of fiber-reinforced polymeric composites as it acts as a barrier against the adverse environmental conditions and protects the fibers from the effect of mechanical abrasion. Matrix also aids in transferring the load to the fibers. Thermoplastics as well thermosets have been employed widely as the matrix, however, thermosets yield better mechanical properties in comparison to the thermoplastics. However, the employability of matrices that have been derived from petroleum resources posses environmental concerns and therefore reduces the overall applicability of the natural fiber-reinforced composites. These matrices present challenges from various perspectives i.e., carbon footprint, environmental toxicity as well as toxicity to human health. Some of the epoxy resins as such the diglycidyl ether of bisphenol A are endocrine disruptors and possess a great danger to the aquatic life. Owing to the environmental concerns sustainable alternatives have been developed [16–19].

Owing to the contradictory nature of the natural fibers and matrix, poor adhesion between the fiber and the matrix occurs and hence low load transfer between the fibers and the matrix. This cumulative effect results in poor mechanical properties of the resulting composites [20]. The interfacial fiber-matrix bonding strength depends on the surface topology of the fibers [21, 22] and therefore needs to be modified to achieve better interfacial strength and hence the mechanical properties. There are physical as well as chemical methods to alter the surface topography of the fibers [23–29]. It is the need of the hour to exploit cost-effective chemical treatment processes that are less detrimental to the environment and also to the inherent properties of the fibers. However, the aforementioned chemical treatments are expensive as well as harmful to the environment when disposed of [30]. Moreover, the aforementioned chemical treatment procedures enhances the fiber-matrix adhesion, but at the expense of tensile properties associated with the fibers. The primary reason for degraded tensile properties is the excessive degradation of the cellulosic chain and delignification

[25]. Owing to the aforementioned concerns, the employability of the cost-effective and eco-friendly chemical treatment processes in the form of sodium bicarbonate has been reported by Fiore et al. [30]. Okra and coir fibers were treated chemically using combinatorial sodium bicarbonate solution and chromium sulfate solution [31, 32]. The influence of biological pre-treatment of wheat straw fibers on the final properties of the epoxy composites has been reported by Maria et al. [33].

With the motivation to promote sustainability and eco-friendly production practices in the world of composite manufacturing, the present work investigates the processing and fabrication of green materials that are less detrimental to the environment. As such the present work investigates the mechanical, as well as the physical properties of short Punica granatum fiber (SPGF), reinforced bio epoxy (BE) composites. The SPGFs are obtained as agricultural waste from pomegranate cultivation and bio epoxy is derived from cashew nut shell oil. The SPGFs are treated chemically using eco-friendly and cost-effective sodium bicarbonate solution for different treatment duration and have been chemically characterized by employing the following methodologies: X-ray diffraction (XRD) and Thermogravimetric (TGA) analyses. The bio-epoxy resin has been derived using the cashew-nut shell oil. The cashew nut shell liquid has the following characteristics properties [34]: pH 5.79, Specific gravity: 0.95 gm/cm^3, viscosity: 58.9 poise, refractive index: 1.48, total dissolved solids: 1.53 g and molecular weight: 5030.74. The presence of anacardic acid (carbopenta-dicadienyl-phenol) makes cashew nut shell liquid acidic in nature. The green composite test specimens are fabricated with different wt% of SPGFs i.e., 10%, 20%, 30%, and 40%, and analyzed for variation in physical and mechanical properties. Figure 1 describes an overview of the present research work.

Materials and Methods

Materials

The composites were processed from two components i.e., Punica granatum straw collected after the cultivation of pomegranate plant of variety Muskat from Maharashtra, India, and the bio-based epoxy resin that was sourced from Cardolite India Pvt. Ltd. (Bangalore, India).

Preparation of Short Punica granatum Fibers

The short Punica granatum fibers (SPGFs) are obtained through the following procedural steps:
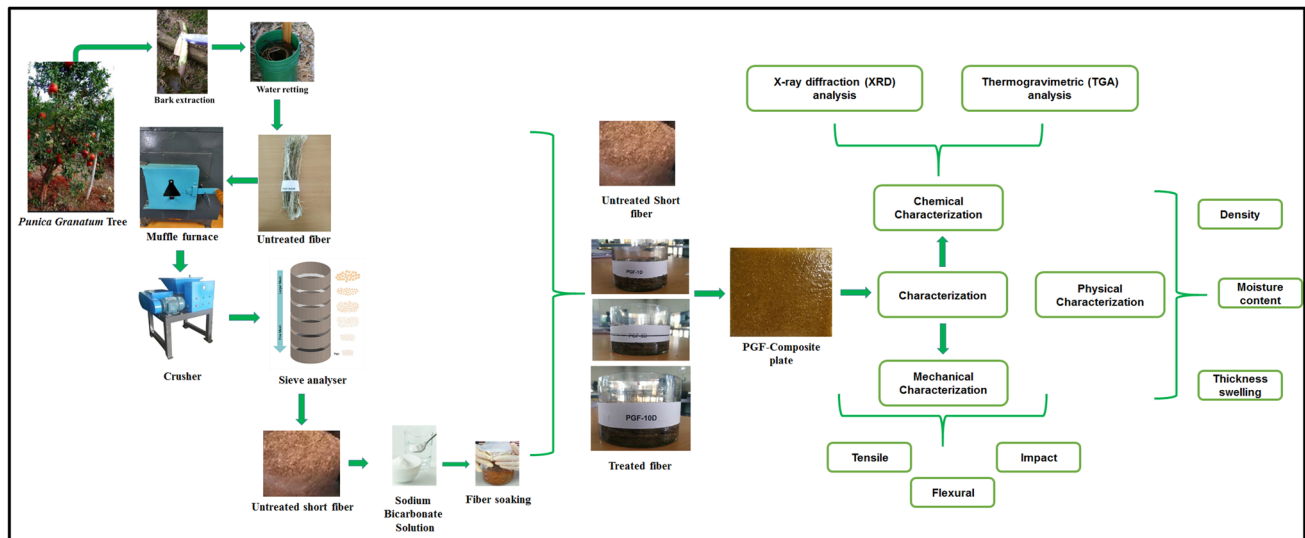
Fig. 1 Overview of the present research work

(1) The Punica granatum straws are immersed in water to facilitate the procurement of fiber strips through microbial degradation. The obtained fiber strips are washed thoroughly under the stream of running water. This ensures the removal of foreign impurities. Then the washed fiber strips are heated in a muffle furnace to remove excess moisture.

(2) The thoroughly washed and oven-dried Punica granatum fiber strips are segmented in a crushing machine and small fragments of the strips are obtained.

(3) The segmented and crushed fiber strips are then allowed to go into another cutting process wherein these are cut to fit the sieve analysis machine.

(4) The obtained SPGFs are soaked in 10 wt% sodium bicarbonate aqueous solution for different time durations i.e., 1 day, 5 days, and 10 days at room temperature. The longer treatment duration is owing to the mild alkaline nature of sodium bicarbonate solution in comparison to sodium hydroxide solution. The SPGFs soaked in aqueous sodium bicarbonate solution were then gently washed using distilled water and then dried in a muffle furnace for 24 h at 45 °C.

Fabrication of Composite

The biocomposites are fabricated through the Hand lay-up process. This was followed by cold uniaxial pressing. The aluminum sheet measuring 300 mm×300 mm was placed onto the metallic mold. A releasing agent was applied onto the aluminum sheet. The short Punica granatum fibers (SPGFs) were distributed randomly by the required wt% onto the greased aluminum sheet that has been placed on the metallic mold. The polymeric matrix is prepared by mixing of bio epoxy resin and hardener in 10:3 ratio by weight and the prepared mixture is degasified in desiccator which is maintained at a vacuum pressure of 0.1 Torr. The degasified mixture is spread over the randomly distributed SPGFs and a hand roller was used to remove the trapped air. The upper mold of another aluminum sheet, applied with releasing agent, is then placed on the top and a pressurized for a duration 12 h at room temperature. After the composite plate within the mold has been cured for the said time, the composite specimen is removed from the mold and then sealed in a plastic bag to prevent the absorption of moisture. The prepared composite plate is cut following the ASTM standard as required by the respective tests. Table 1 depicts the abbreviations for the samples obtained with the different wt% and chemical treatment duration of fiber treatment.

Characterization of Short Punica granatum Fibers (SPGFs)

The polymorphic transformation that takes place in the structure of SPGFs owing to the chemical treatment process has been well identified with the X-ray diffraction (XRD) analysis. The chemically-treated SPGFs are scanned through X-Ray diffractometer and the deflected intensities are recorded for 2θ varying from 5° to 90° with an increment of 1°/min. The wavelength of the incident CuKα radiation used is 1.54 nm and is operated at 45 kV and 40 mA.

Thermogravimetric (TGA) analysis was carried out to investigate the thermal stability of the chemically treated SPGFs to the untreated SPGFs. TGA analysis was carried out in a NETZSCH STA 449 F3 Jupiter thermal analyzer. The investigation was carried out under a nitrogen gas flow rate of 50 ml/min. The chemically-treated SPGFs are heated

**Table 1** Sample code and compositions of the various studied composite systems

Sample code	BE (%)	Treatment duration (Days)	PGF (%)
SPGF-RAW-40	60	0	40
SPGF-1D-40	60	1	40
SPGF-5D-40	60	5	40
SPGF-10D-40	60	10	40
SPGF-RAW-30	70	0	30
SPGF-1D-30	70	1	30
SPGF-5D-30	70	5	30
SPGF-10D-30	70	10	30
SPGF-RAW-20	80	0	20
SPGF-1D-20	80	1	20
SPGF-5D-20	80	5	20
SPGF-10D-20	80	10	20
SPGF-RAW-10	90	0	10
SPGF-1D-10	90	1	10
SPGF-5D-10	90	5	10
SPGF-10D-10	90	10	10
Neat (Bio-epoxy)	100	0	0

to 800 °C from room temperature at a heating rate of 10 °C/min. The samples weighing between 3 and 3.8 mg are placed in an alumina pan.

The fabricated composite specimens are characterized mechanically as well as physically. The mechanical analysis of the fabricated composites was carried through tensile, flexural, and impact tests. The short fiber Punica granatum reinforced composite test specimens were fabricated following the respective ASTM test standards. The tensile and flexural tests were carried on the universal testing machine of make and model Instron, UK; 8801 equipped with 100 kN load cell. The cross-head speed during the tensile and flexural tests was kept at 1 mm/min. Charpy Impact Tester was employed to investigate the impact properties of the fabricated composites. Five composite specimens were prepared for each of the tests and the results were obtained by averaging over the five test samples for each of the treatment conditions.

Physical characterization of the fabricated composite specimens has been carried out through the measurements of density, water absorption, and thickness swelling. The test specimens for density measurement were fabricated with dimensions 20 mm × 10 mm × 2 mm and are tested at room temperature. The density measurements are made by employing the scaling machine of make and model Mettler Toledo and analytical balance.

The water absorption test is carried out for different durations of water absorption: 200 h, 400 h, 600 h, 800 h, 1000 h, 1200 h, 1400 h, 1600 h, 1800 h, and 2000 h. The fabricated
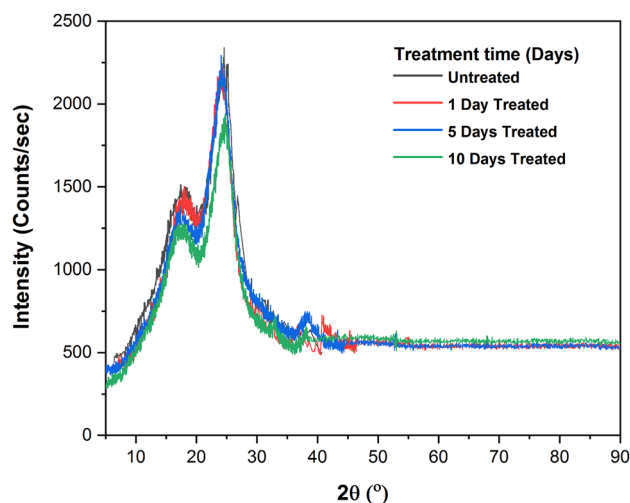
Fig. 2 X-ray diffraction pattern of untreated and treated short punica garnatum fibers

test specimen was dried for 24 h in the oven. The weights of the test specimens were measured before immersing in the distilled water and after the immersion in distilled water. The employed distilled water was kept at room temperature. Water absorption has been obtained using Eq. (1):

$$W_a = \frac{W_i - W_0}{W_0} \times 100 \qquad (1)$$

where W_i denotes the weight of the specimens after immersion in water and W_0 is the weight of the composite specimen before immersion in distilled water.

Digital vernier caliper is used to investigate the thickness swelling of the test specimens. The test specimens with dimensions 20 mm × 10 mm × 2 mm have been used to conduct the thickness swelling test. Specimens were immersed for 100 h duration because immersion of the test specimens for a short duration may not aid in providing accurate results. Thickness swelling was calculated using Eq. (2):

$$T_S = \frac{T_i - T_0}{T_0} \times 100 \qquad (2)$$

where T_s is the selling thickness, T_i is the thickness after immersion, and T_0 is the thickness before immersion.

Results and Discussions

Characterization Results of Short Punica granatum Fibers (SPGFs)

Figure 2 delineates the X-ray diffractograms of SPGFs for different duration of chemical treatment. As observed in

Fig. 2, similar diffraction patterns associated with cellulose-I are revealed to be exhibited by untreated as well as treated SPGFs. In the case of cellulose-I, the major intensity peaks within the X-ray diffractograms are located at 2θ = 17°, 24°, and 36° and are associated respectively with the following crystallographic planes: (10 1),(0 0 2) and (0 4 0) [34, 35]. On the contrary, the intensity peaks associated with the cellulose-II are located at 2θ = 11°, 20°, 22°, and 37° and are revealed to be absent in the diffractograms depicted in Fig. 2 [35, 36]. The reduction in intensity peaks has been revealed only when the duration of chemical treatment reaches 240 h indicating the elimination of hemicellulose and lignin from the SPGFs. The reduced intensity peaks signify a higher crystallinity index. The thermodynamic favourability of polymorphic transition to cellulose-II from cellulose-I depends upon two major factors: concentration of the solution and temperature of chemical treatment [37]. No transformation of the polymeric structure to cellulose-II from cellulose-I has been revealed in the represented diffractograms indicating a mild condition for the chemical treatment of SPGFs with 10 wt% sodium bicarbonate solution.

The TG and differential DTG curves have been depicted in Fig. 3 for raw and treated SPGFs. Three distinct peaks characterize the decomposition profiles. The water evaporation is characterized by the first peak and ranges from room temperature to 100 °C. There occurs an increase in the moisture absorption of the fibers that have been treated with the aqueous sodium bicarbonate solution. This moisture absorption ranges 31.79%, 86.68%, and 28.36% respectively for 1 day, 5 days and 10 days treated SPGFs. The moisture absorption results are indicative of the increased interaction between the SPGFs and the water molecules after the chemical treatment process. The

results obtained show a similar trend to that obtained for the coir fibers treated with sodium hydroxide solution [37].

In the case of the raw SPGFs, the second shoulder of mass loss can be seen to be centered on 313 °C within the DTG curve. This is suggestive of the degradation of the hemicellulosic content [30]. However, the shoulder is found to be absent for the case of the chemically treated SPGFs which indicates that the chemical treatment through the sodium bicarbonate solution was efficient in removing the maximum proportion of the hemicellulosic content of the SPGFs. The results are in close agreement with the X-ray diffractograms depicted in Fig. 2. The maximum mass loss for the raw SPGFs has been revealed to occur in the range 325–380 °C. This is significant for the thermal degradation of the cellulosic content [22, 38]. The maximum temperature of degradation for the raw SPGFs has been observed to be i.e., 347 °C. Whereas in the case of the treated SPGFs, this decreases to 308 °C. This implies an increase in thermal stability with the chemical treatment process. Similar trends have been reported in past research studies [30, 39].

The thermally associated events that occur beyond 380 °C can be because of the lignin degradation that initiates at room temperature and continues beyond 700 °C and above [30, 38, 40]. This can also be linked to the aromatization phenomenon that entails the dehydrogenation reactions [41].

Physical Properties on Fabricated Composites

To justify the applicability of the short Punica granatum fibers (SPGFs) reinforced polymeric composites, tests revealing the physical properties have been carried out.
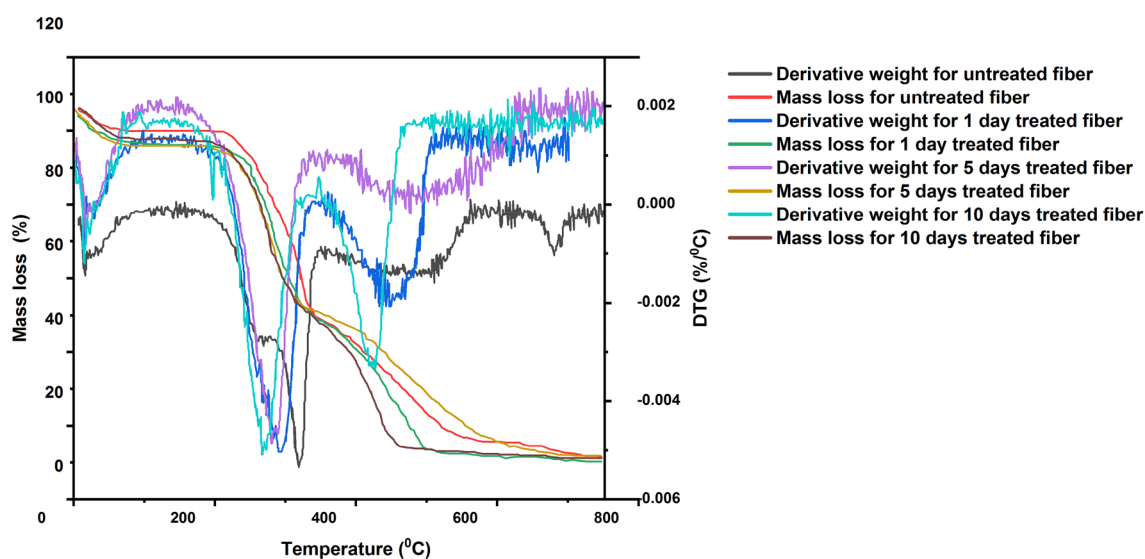

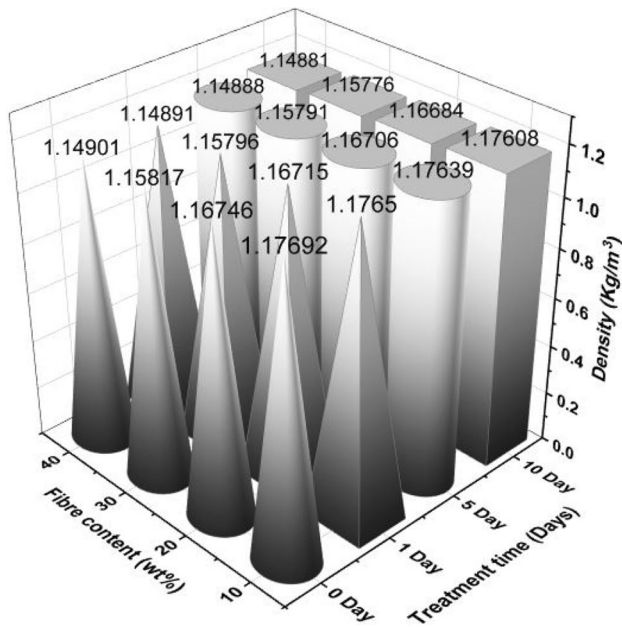**Fig. 3** TGA and DTG curves of untreated and treated short punica garnatum fibers

Fig. 4 Density of short punica granatum reinforced bio-epoxy green composites

Density

Figure 4 displays the values of density, as well as the weight of the SPGFs, reinforced bio-epoxy composite material. One of the major advantages of natural fibers over their inorganic part is the lower density of the former and is one of the favorable properties [42]. The density value ranges 1.14881–1.17692 (Kg/m^3) and it can be observed that there is a reduction in the density with the addition of SPGFs. Few studies have also reported a decrease in the overall density of the composite with the increase in the fiber content [43, 44]. Green composites with lower density are one of the preferred properties because the process of material handling becomes easier. Moreover, the transportation cost associated with green composites possessing lower density is also low [45]. Reduction in density can be attributed to the fibrous structure of the SPGFs with the chemical treatment process.

With the increasing duration of the chemical treatment, the density of the SPGFs also decreases owing to the removal of certain fiber content. The loss in weight and the volume will result in a reduction in density for the natural fiber under investigation [46]. The decrease in the density for the fabricated composite is revealed with the fiber content and is, therefore, one of the favorable physical properties for the fabricated composites to be employed for weight constrained engineering applications [44]. Although, some other studies have reported an increased density of the composites with the increasing fiber content. The increased density has been attributed to the close fiber packing within the natural fiber-reinforced composite material.

Water Absorption Test Analysis

The tendency of the developed composite to absorb water was adjudged through the water absorption test which was performed gradually through 0.5 h to 2000 h. The test aided in determining the behavior of fabricated composite in the water and thereby revealing information about the sensitivity of the bio-composite material towards their exposure to water. Results have been depicted in Fig. 5. The enhanced absorption in water may be attributed to the poor interfacial adhesion between the matrix and the incorporated fibers. This is due to the affinity of the hydrogen bonds between the water and the cellulosic content of the natural fiber [47]. An increasing fiber content has resulted in decreasing water absorption and this could be attributed to the hydrophobic nature of the SPGFs and greater affinity of the matrix towards water [48]. Moreover, the increase in fiber content results in a significant hindrance to diffusion of water in the fabricated composites. The physical properties of the SPGFs reinforced bio-epoxy composites are improved with the incorporation of the SPGFs. There is a decrease in water absorption, solubility, and water content with the incorporation of SPGFs [49]. The water absorption in the composites fabricated using treated SPGFs has been revealed to be lower in comparison to that fabricated using raw SPGFs. This may be attributed to the loss of unstable compounds during the delignification process.
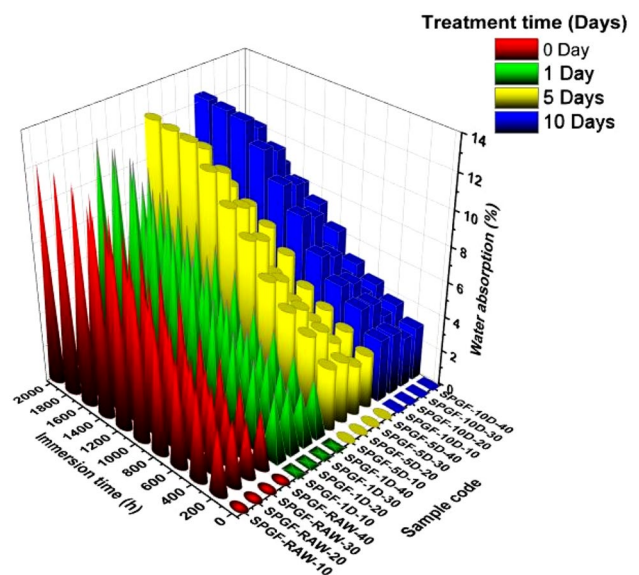

Fig. 5 Water absorption of short punica granatum reinforced bio-epoxy green composites
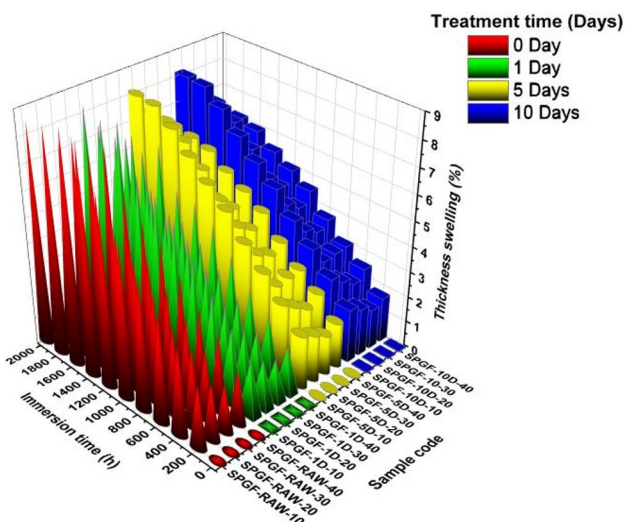
Fig. 6 Thickness swelling of short punica granatum reinforced bio-epoxy green composites

Thickness Swelling Test

The results associated with thickness swelling have been depicted in Fig. 6. A low thickness swelling of the fabricated bio-composites is revealed when immersed in distilled water for 0 h to 2000 h. Hence a greater resistance of the composites to swelling has been revealed. The hydrophobic nature of the fiber is the determinant factor for the thickness swelling. There occurs a change in the dimension of the natural fiber with the moisture content. Water intake within the fiber takes place due to the capillary action and hydrophobic properties of the natural fiber. As a result of the water intake by the fiber, the dimensions associated with the natural fiber-reinforced composite also exhibits an increasing trend [50]. The presence of polar groups within the fiber results in their poor resistance to the water intake. The polar groups in the fiber allure the water molecules through the hydrogen bonding. As a result, the build-up of the moisture takes place within the cellular walls of the fiber and hence the interface between the matrix. In totality, there occurs a change in the dimensions i.e., linear dimensions of the natural fiber-reinforced composites [51]. The dimensional stability of the fabricated composites enhanced with the addition of SPGFs. Moreover, the dimensional stability of the composites fabricated using treated SPGFs has been revealed to be higher in comparison to that fabricated using the raw SPGFs. The reason may be attributed to the removal of unstable compounds during the chemical treatment process that otherwise would have increased water intake by the SPGFs.

Mechanical Properties of the Fabricated Composites

Tensile Properties of the Fabricated Composites

The variation of tensile properties: tensile strength and tensile modulus with fiber content and treatment of chemical duration have been depicted in Fig. 7a and b respectively. The value of tensile strength and tensile modulus ranges respectively 17.48–29.93 MPa and 1.93–3.2 GPa. The results depict that with the incorporation of the SPGFs there is an increase in the tensile strength of the fabricated composites for a given duration of chemical treatment. The maximum tensile strength occurs at 30 wt% of SPGF loading. The tensile strength decreases beyond 30 wt% of SPGF loading and hence no investigation has been carried
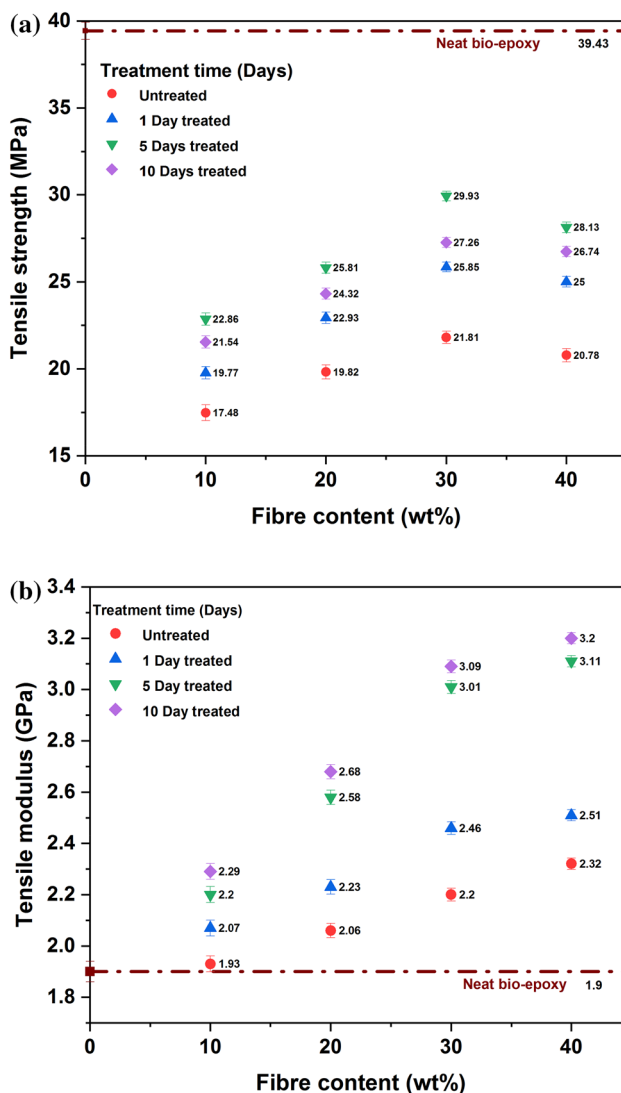

Fig. 7 a Tensile strength (MPa) of short punica granatum reinforced bio-epoxy green composites b Tensile modulus (GPa) of short punica granatum reinforced bio-composites
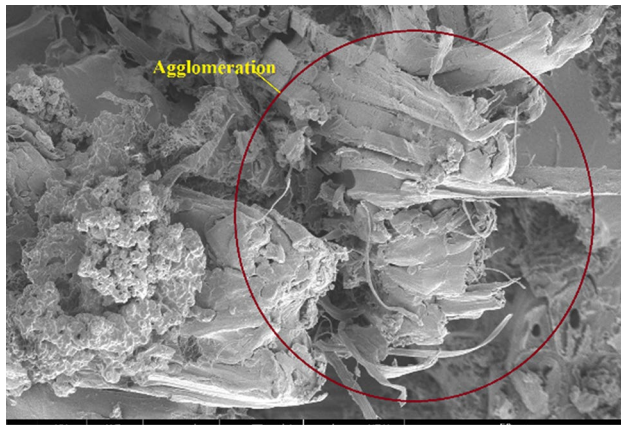
Fig. 8 Agglomeration at higher fiber loading for short punica granatum fiber reinforced bio-epoxy green composites

out beyond 40 wt% of SPGFs loading. This may be attributed to the agglomeration phenomenon and is evidenced in the depicted SEM image in Fig. 8. However, the maximum obtained tensile strength is lower in comparison to the neat bio-epoxy matrix in a pristine state. Poor adhesion between the SPGFs and the bio-epoxy resin may be another reason for the poor strength of the fabricated composites [52]. Moreover, the short length and randomness of the incorporated SPGFs hinder the distribution of load and only the SPGFs that are oriented along the direction of the load are proactive as reinforcement. On the other hand, the SPGFs that are aligned transversely results in stress concentration and hence reduced tensile strength for the fabricated composite structure [30, 36, 53]. The transversely oriented short fibers act to restrict the stress distribution homogeneously and the resulted high concentration zones will promote the fracture of the composite specimens at very low load levels and hence reduces the tensile strength associated with the fabricated composites [53, 54].

On the other hand, the tensile modulus of the fabricated composites is always higher than that of the bio-epoxy matrix in its pristine condition. This is true irrespective of the fiber treatment condition and the fiber content. The enhanced tensile modulus of the composites may be attributed to the higher stiffness of the SPGFs in comparison to the bio-epoxy matrix. The composites fabricated using treated SPGFs have higher tensile properties in comparison to that fabricated using raw SPGF. The SPGFs become stiffer with the increased duration of chemical treatment owing to the removal of surface impurities which otherwise would have resulted in stress concentration [55, 56]. The removal of hemicellulose due to the chemical treatment leads to the formation of novel hydrogen bonds between the chains of the cellulosic content in the fibrils and hence a closer fiber packing [56, 57].

Flexural Properties of the Fabricated Composites

The variation of flexural properties: flexural strength and flexural modulus with the fiber content and chemical treatment duration have been depicted in Fig. 9a and b. The flexural strength and flexural modulus values have been revealed to range 36.23–54.86 MPa and 2.3368–4.4667 GPa respectively. The addition of SPGFs to the bio-epoxy resin results in lower flexural strength of the fabricated composite structure in comparison to the flexural strength of the resin itself in its pristine state. Weak adhesion between the SPGFs and the matrix is one of the primary reasons for the reduced flexural strength of the fabricated composites [35]. Poor compatibility between the hydrophilic SPGF and the hydrophobic
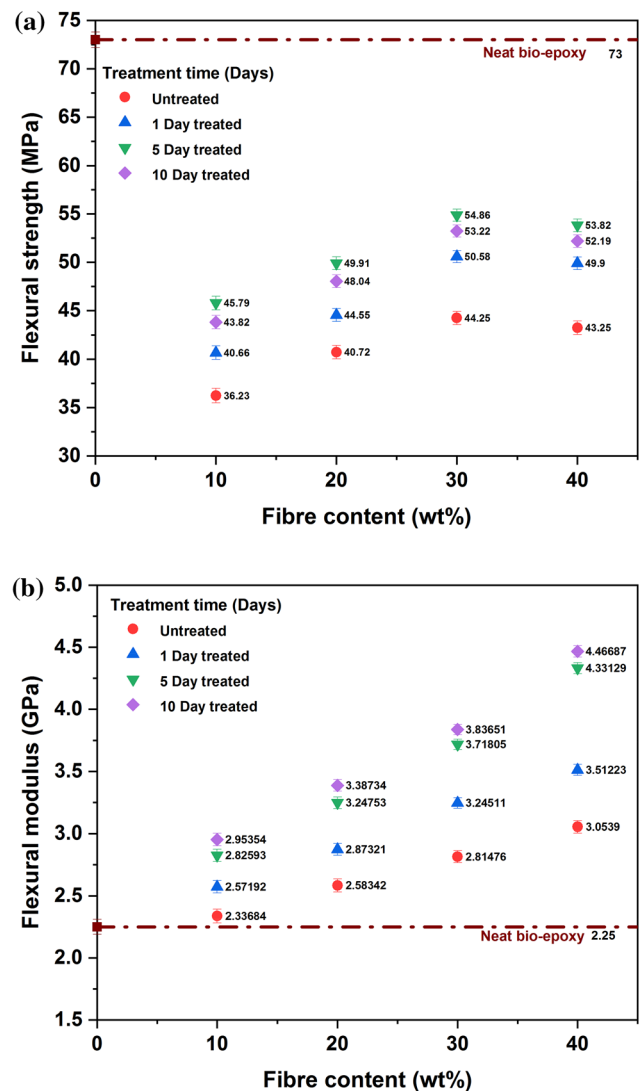

Fig. 9 a Flexural strength (MPa) of short punica granatum reinforced bio-epoxy green composites **b** Flexural modulus (GPa) of short punica granatum reinforced bio-composites

polymer matrix results in internal strains and hence poor mechanical strength of the fabricated composite structure.

The flexural modulus for the fabricated composite structure is higher in comparison to the neat bio-epoxy resin. The enhanced flexural modulus is owing to the addition of rigid SPGFs into the resin. The dependence of modulus on the interfacial adhesion is low because of the measurements made at small deformations [58].

The flexural properties of the composite structure fabricated using treated SPGFs are higher in comparison to that fabricated using the raw SPGFs. This is due to the removal of amorphous compounds with the chemical treatment process. However, with the chemical treatment duration higher than 5 days the flexural strength decreases due to the deterioration of the SPGFs. On the other hand, the flexural modulus of the composites fabricated using treated SPGFs is always higher than the ones fabricated using raw SPGFs.

Impact Test Results for the Fabricated Composites

Figure 10 delineates the variation of impact test results with the fiber content and the treatment of the chemical duration of the SPGFs. The resistance of the developed green composites towards impact ranges from 6.49 to 8.736 kJ/m^2. The impact resistance of the natural fiber-reinforced composites is significantly affected by the interfacial level of bonding. The energy-absorbing mechanism in the natural fiber-reinforced composite consists of the following: the energy that can aid in debonding the fiber and the matrix and hence to completely pull out the fiber from the matrix and secondly is the usage of weak interfaces between the matrix and the incorporated fiber. The aforementioned twin conditions are however at odds with the ones required for

better strength of the composite structure. The fiber-pull out mechanism reflects most of the energy absorbed during the impact. A very strong interface has an adverse effect on the impact properties of the fabricated composite structure. This is due to the reduction in the fiber pull-out mechanism [54]. The impact strength associated with the developed composite material is lower than the bio-epoxy resin itself. Also, the impact strength of the composite fabricated using raw SPGFs is more than that possessed by the composite structures fabricated using treated SPGFs. This is corroborated by the tensile strength results.

The fracture taking place results from the macro-cracks that form in the matrix. The formed cracks show very little resistance in comparison to the embedded fibers in the matrix. The fibers behind the crack front tend to stretch themselves along the edges of the crack faces. These fibers absorb energy and the absorbed energy is available at the tip of the crack. The fibers also tend to slide along the length wherein the debonding takes place and where the motion is hampered by the frictional force. The presence of frictional force results in thermal energy. The thermal energy generated during the process of sliding motion will be dissipated when the fiber pulls out at increased stress levels. Pull-out can be considered to be the predominant factor behind the energy dissipation process owing to the abundant presence of short fibers within the matrix. Figure 11 depicts the morphology associated with the fiber pull-out mechanism observed in the developed green composite.

Table 2 summarizes the mechanical properties i.e., tensile strength, tensile modulus, flexural strength, flexural modulus, and impact strength of the different composite systems under investigation. A comparative analysis of mechanical properties for different short (natural) fiber-based epoxy composites with the proposed green composites has been delineated in Table3.
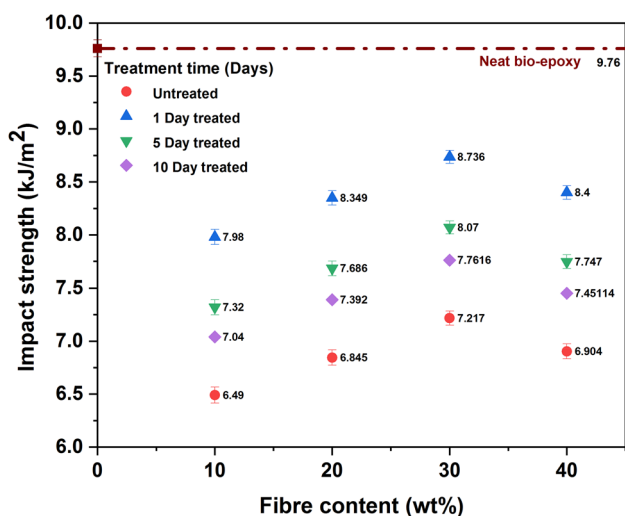

Fig. 10 Impact strength of short punica granatum reinforced bio-epoxy green composites
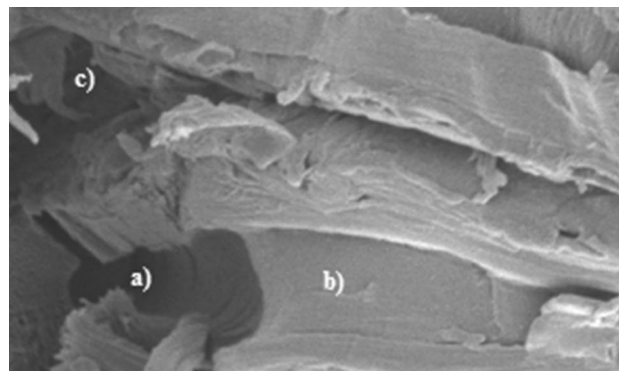

Fig. 11 Fiber pull-out mechanism **a** Macro-cavity as a result of fiber-pull out **b** Fiber slide along debond length **c** Micro cavity as a result of fiber pull-out

Table 2 Summary of the mechanical properties for various systems under consideration

Sample code	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m^2)
SPGF-RAW-40	20.78	2.32	43.25	3.05	6.91
SPGF-1D-40	25.00	2.51	49.90	3.51	8.40
SPGF-5D-40	28.13	3.11	53.82	4.33	7.74
SPGF-10D-40	26.74	3.20	52.19	4.46	7.45
SPGF-RAW-30	21.81	2.20	44.25	2.81	7.21
SPGF-1D-30	25.85	2.46	50.58	3.24	8.73
SPGF-5D-30	29.93	3.01	54.86	3.71	8.07
SPGF-10D-30	27.26	3.09	53.22	3.83	7.76
SPGF-RAW-20	19.82	2.06	40.72	2.58	6.84
SPGF-1D-20	22.93	2.23	44.55	2.87	8.34
SPGF-5D-20	25.81	2.58	49.91	3.247	7.68
SPGF-10D-20	24.32	2.68	48.04	3.38	7.39
SPGF-RAW-10	17.48	1.93	36.23	2.33	6.49
SPGF-1D-10	19.77	2.07	40.66	2.57	7.96
SPGF-5D-10	22.86	2.20	45.79	2.82	7.32
SPGF-10D-10	21.54	2.29	43.82	2.95	7.04
Neat (Bio-epoxy)	39.43	1.90	73.00	2.25	9.76

Conclusions

The observations of the present work can be summarized as follows:

- The present work proposes green composites from agro-waste reinforced in bio-epoxy resin derived from cashew nut shell oil. The chemical treatment followed with the sodium bicarbonate solution is eco-friendly as well as cost-effective. Composites from agro-waste aids in agricultural waste management and reduces the overall crop burning issues that have adverse effects on the global climatic conditions. The employability of bio-resins aid in eliminating the human as well as environmental toxicity. The eco-friendly and cost-effective chemical treatment process aids in restricting environmental concerns when disposed of.
- No structural transformation to cellulose II from cellulose-I for the sodium bicarbonate treated Punica granatum fibers has been revealed through the X-ray diffractogram analysis.
- The degradation of pectin, as well as hemicellulosic content from the surface of the fiber, has been evidenced in the TGA curves.
- A reduction in tensile strength and an increase in the tensile modulus of the short Punica granatum fiber (SPGFs) reinforced bio-epoxy composites have been revealed. The enhanced stiffness of the chemically treated SPGFs is the reason for the enhanced modulus of the fabricated bio-composites. On the other hand,

the poor fiber-matrix adhesion is the primary reason for the reduced tensile strength of the fabricated bio-composites.
- The tensile and flexural modulus of the fabricated composites enhances with the incorporation of 5 days of chemically treated SPGFs. The interfacial adhesion between the fibers and the matrix doesn't play a prominent role in affecting the aforementioned properties. These are closely associated with the stiffness of the incorporated fibers.
- The resistance of the fabricated composites towards impact is also low in comparison to the bio-epoxy in its pristine state. However, the impact properties improved for the composites fabricated using 5 days treated SPGFs.
- Outstanding physical properties have been revealed of the fabricated composites. Excellent resistance to water as well as thickness swelling has been observed. The fabricated composites have a low weight.

The fabricated composites promote sustainable practices in the production of materials and minimize the disposal of hazardous waste to the surrounding environment. The composites are in real sense green wherein each of its constituent as well as the processing conditions promote sustainable and clean practices in the world of composites. As a part of future research work, the *Punica granatum* short fibers can be hybridized with other inorganic or organic particulates and can be explored for other applications as that carried out by Abu-Dalo et al. [65] for water disinfection.

Table 3 Comparative analysis of mechanical properties for different short fiber epoxy composites with the proposed composite system

Reference	Chemical composition	Tensile strength (MPa)	Tensile Modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact Strength (kJ/m^2) or impact energy (J)	Potential application
Present work	*Punica granatum* (30 wt%)-Epoxy composites (CSNL-Based)	29.93	3.20	54.86	4.46	8.73 (kJ/m^2)	Automotive sector, household products, the casing of electronic equipment
Prakash et al. [59]	Syngonanthus nitens (30 wt%)-Epoxy composites (LY556)	20.80	1.038	59.27	1.583	–	–
Hassan et al. [3]	Sugarcane (20 wt%)-Green epoxy composites	–	–	29.70	–	4.43 (kJ/m^2)	–
	Coconut (20 wt%)-Green epoxy composites			39.90		4.83 (kJ/m^2)	
	Cotton (20 wt%)-Green epoxy composites			81.70		9.73 (kJ/m^2)	
Kumar et al. [60]	Pineapple leaf (2.5 wt%)-Epoxy composites (AW 106)	21.87	0.570	31.00	0.890	–	Household products, the casing of electronic equipment
Kumar et al. [61]	Coir (2.5 wt%)–Epoxy composite (AW 106)	27.58	0.738	33.92	0.994	–	Shoes and sandals
Kumar et al. [62]	Wood (7.5 wt%)-Epoxy composite (AW 106)	23.22	0.708	24.00	0.480	–	Electronic appliances and consumer goods like housewares and luggage
Jayaseelan et al. [1]	Banana (35 wt%)-Epoxy composites (LY556)	35.59	3.64	67.16	1.83	0.32 (J)	–
Kumar et al. [63]	Bamboo (10 wt%) Epoxy composites (AW 106)	21.06	–	43.47	–	–	–
Valasek et al. [64]	Empty fruit bunches-oil palm (2.5 wt%)-Epoxy composites (bisphenol A and F based)	~43.82	~2.21	-	–	–	Simple boards and similar applications
Constante and Pillay [4]	Lyngbya algae (56 wt%)-Epoxy composites (cycloaliphatic amine SC-15)	40.96	4.65	70.50	3.8	–	Automotive sector
Bisaria et al. [2]	Jute- Epoxy composites (AY-105)	42.14	0.059	168.74	14.28	6.61 (kJ/m^2)	–

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