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Chitosan-based green and sustainable hybrid composites

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Research article

Chitosan-based green and sustainable hybrid composites

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Abstract

In recent years, there has been much effort to provide eco-friendly and biodegradable materials for the next-generation composite products owing to global environmental concerns and increased awareness of renewable green resources. In this context, the present study reports the preparation of green composite materials from natural, biocompatible, and biodegradable chitosan films reinforced with seashells and waste glass using a solution-casting method. The surface morphological features and chemical interactions of the composite films were studied using SEM, EDS, FTIR, and XRD techniques. The swelling degree (SD) and hardness properties of composites with various reinforcement weight proportions are compared to those of pure chitosan film. The reinforced materials, especially CSG532 and CSG523 with porous rod-like surface textures, improved the hardness of chitosan by two-fold. The SDs of the hybrid composites were also significantly lower than those of the unmodified chitosan film.

Keywords: Chitosan; seashell; waste glass; polymer composite; sustainability.

1. Introduction

Composite materials have been widely used for various applications for the past several years due to their chemical and corrosion resistance, flexibility in design, durability, and good performance at elevated temperatures. However, conventional composites are derived from non-renewable reinforcements and therefore pose a significant threat to the environment. The majority of these multi-component materials are

made from fossil-derived oil and gas and are segregated as waste when they reach the end of their useful life (i.e., linear economy). Recyclability and environmental safety are therefore significantly essential for a sustainable and better future (i.e., a circular economy) [1]. With mounting concerns, the linear economy that prioritizes profitability irrespective of the product life-cycle needs to be shifted towards the circular economy, which focuses on sustainability. Government legislation and consumer behavior have forced major industries such as automotive, aerospace, and marine to seek out and adapt to sustainable lightweight composites. Therefore, there is a high demand for research in the development of next-generation green, sustainable, and lightweight composites with lesser carbon footprints. These materials can not only overcome natural resource limitations, but they are also safer, eco-friendly, biodegradable, and versatile in nature [2]. Nowadays, a variety of green composites are widely explored for their wide real-life applicability in various sectors including

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automotive, aircraft, biomedical, building construction, and their interiors [3].

In this context, the increasing amount of industrial and domestic waste materials that need to be disposed off in a safe and economical way can be considered a good opportunity to produce clean secondary raw materials, which can aid in reducing costs and conserving resources [4]. Recycling many of these waste materials can overcome the problems that arise during their management, including air and water pollution and climate change that might disturb many ecosystems. Most importantly, these waste materials have the potential to be used as reinforcements and matrices, which can influence the properties of prepared composite materials. Though polymer composites are much explored and used for many practical applications, biopolymers are less investigated as matrix materials. Chitosan is an abundantly available, recyclable, and eco-friendly linear biopolymer obtained by the deacetylation of chitin in crustacean shells generated as industrial food waste. This sea-food waste material can be combined with carbonaceous materials, agriculture residues, and even metals to manufacture composites on an industrial scale [5]. Long-lasting chitosan films [3] can be easily formed, which has a certain permeability to oxygen, carbon dioxide, and water vapor. The films display broad prospective real-life applications due to their attractive biocompatibility, antibacterial properties, biodegradability, low toxicity, and metal binding ability [6,7]. There are several reports on the use of chitosan composites in biomedical sector [8], agro-waste management, agriculture, wastewater treatment [9,10], food packaging [11], cosmetics, textile and paper industry [11]. Chitosan can function as a cross-linking agent between fibers inside the paper to improve the tensile strength and water absorption of the paper. Chitosan composites with waste glass, $\text{CaCO}_3/\text{Ca}(\text{PO}_4)_2$, clay, coconut husk, Fe_3O_4 , Ag, PVA/ TiO_2 , PLGA-PEG, alginate, carbon-dots, RGO/Ag, zeolite, and NTs- NH_2 /EGDE have been reported [12–21]. Kong et al., reported specific

effects of calcium acetate on the self-assembly of chitosan molecules [22].

Solid waste from tons of glasses and their disposal causes contamination to the environment [23]. Several studies report waste glass powders in many applications, including road pavement, cement, concrete, etc. [12,24,25]. Recent literature shows evidence of improvement in the mechanical properties of chitosan while using glass as reinforcement [26]. Seashells are yet another waste material that accumulates on beaches that can produce foul smell due to the decaying of leftover flesh attached to shells or the decomposition of the salts in them into H_2S , NH_3 , and other organic compounds [27]. Seashells have little to no commercial value and are generally dumped into the sea or deposited in landfills that account for a hefty disposal cost [28]. However, they can be recycled and processed to be utilized as fine aggregate, coarse aggregate, or as a cement replacement in brick production [29,30].

Based on the existing literature, the present study focuses on the use of chitosan as the polymer matrix, along with seashells and waste glass as reinforcements in developing eco-friendly biocomposites. The biopolymer chitosan contains abundant amino and hydroxyl groups enabling strong inter/intramolecular hydrogen bonds, and could be complexed with metal ions [22,31]. Therefore, calcium ions can act as cross-linking agents, making similar compact reticular structures through hydrogen bonds or salt bonds between chitosan molecules [22]. In this regard, seashells that have a high calcium content can be used as a sustainable calcium source for complexation with chitosan. Further, the effect of these reinforcements on the intrinsic properties of the chitosan matrix is investigated.

2. Materials and methods

2.1 Materials

Chitosan with 85% deacetylation was procured from marine chemicals (Kerala, India). Discarded short neck transparent whiskey bottles were used as the waste glass source, whereas the

seashells were collected from the Arabian Sea coast. Glacial acetic acid used for the solvent casting process was obtained from Sigma-Aldrich.

2.2 Preparation of composite samples

Seashells were cleaned and scrubbed to remove any dirt, washed thoroughly using distilled water and dried in an oven at 50°C for five days before finely grounded using a mortar and pestle. The particles were further pulverized using a planetary ball milling machine [32]. The waste bottles were washed with distilled water, dried, crushed and then pulverized using the ball milling machine. The pulverized seashell and waste glass samples were then sieved to obtain 45 µm particle size.

About 300 mg of chitosan was dissolved in 10 mL of a 2% aqueous acetic acid solution. Precalculated amount of seashell and/or glass powder/s were dispersed in the above chitosan solution and rigorously mixed using magnetic stirrer for 3 h at room temperature to obtain uniform dispersion. Eight samples with matrix and reinforcement(s) composition(s) as provided in **Table 1** were prepared and poured into petri dishes of ~50 mm diameter. Further, the samples were allowed to dry at 80°C for 24 h. The formed films were peeled off, neutralized using 1% sodium hydroxide, washed with water, dried and the films were stored in a desiccator for further studies. The weight percentages of the components added are presented in **Table 1**.

Table 1 Weight percentages of each component initially added to prepare the composite film samples.

Sample	Chitosan (C)	Seashell powder (S)	Glass powder (G)
CSG100	100	0	0
CSG550	50	50	0
CSG541	50	40	10
CSG532	50	30	20
CSG522	50	25	25
CSG523	50	20	30
CSG514	50	10	40
CSG505	50	0	50

2.3 Characterization of composite samples

The powdered glass and seashell samples and the prepared composite films were examined using a Carl Zeiss EVO 18 Analytical Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-Ray Spectrometer (EDS) after gold sputtering. Fourier Transform Infrared (FTIR) spectra were recorded using an Attenuated Total Reflectance (ATR) Shimadzu-IR Spirit analyzer, with a frequency range of 4000–400 cm⁻¹. X-ray diffraction (XRD) data of the samples were acquired using a X-ray powder diffractometer (Rigaku Miniflex 600 (5th gen) with Ni-filter and Cu Kα radiation source at a scattering range (2θ) of 5° to 80° (4° per minute).

Swelling degree (SD) was studied by dipping the pre-weighed dry samples into distilled water for different time periods at ambient room temperature [33]. The SD was calculated by recording the weight of the samples before (W_d) and after dipping (W_w) in water using the formula given below. The experiment was performed in triplicates and the average value was recorded and was performed as per ASTM D570.

$$\%SD = \frac{W_w - W_d}{W_d} \times 100$$

The hardness of the samples was measured using a Vickers Hardness Tester, in accordance with ASTM E384 under dry conditions at room temperature. The tested samples were cut to a size of 7 mm × 5 mm for hardness test and the experiment was performed in triplicates.

3. Results and discussion

The polysaccharide chitosan obtained by the deacetylation of chitin, nano-sized seashell powder and waste glass powder were used as natural and sustainable materials for the preparation of green composites. Among the various types of processing methods, such as solution casting, dipping, spray coating, compression molding, freeze casting and drying, blending, and layer-by-layer processing [1], the commonly known solvent casting method was

adopted for the preparation of composite samples [34].

3.1 Preparation of composite samples

Eight samples: i) chitosan alone (CSG100), ii) two binary composites with equal weight percentages of a) seashells & chitosan (CSG550) and b) glass & chitosan (CSG505), and iii) five ternary composites with different weight percentages of seashells and glass (CSG541, CSG532, CSG522, CSG523, CSG514), while the weight percentage of chitosan being constant. The calcium carbonate in seashells reacts with acetic acid to produce calcium acetate, which on hydrolysis serves as the source for calcium ions. Chitosan can adsorb calcium ions and the NH_2 and OH groups of the biopolymer can co-ordinate with calcium ions [35]. The amount of reinforcements: seashell powder, calcium ions and glass powder in 300 mg of chitosan matrix is depicted in **Table 2**.

Table 2 Weight in milligrams of each component in the composite samples containing 300 mg of chitosan.

Sample	Seashell powder initially added	Seashell powder present in composite	Calcium ions formed in the composite	Glass powder
CSG100	0	0	0	0
CSG550	300	133.5	66.6	0
CSG541	240	73.5	66.6	60
CSG532	180	13.5	66.6	120
CSG522	150	0	60	150
CSG523	120	0	48	180
CSG514	60	0	24	240
CSG505	0	0	0	300

3.2 Surface morphology and elemental analysis

The SEM images were used to analyze the physical morphology of chitosan as well as that of powdered glass and seashells. The particle size of bulk chitosan powder ranged from few to hundred micrometers with a flaky texture as shown in **SF1a**. The seashell particles obtained after the ball milling process were irregularly shaped crystallites of ~ 230 nm size as presented in **SF1b**. The powdered glass particles were comparatively bigger compared to that of seashell powder (**SF1c**). The elemental composition of the raw materials: powdered glass and seashells were analyzed by single point EDX mapping. The elemental composition of the seashell nanoparticles (**SF1d**) showed that the

NPs contained 46.76% oxygen, 25.91% calcium, and 27.32% carbon. The analysis confirms that the composition of NPs from seashells was approximately 100% of CaCO_3 . The glass powder had majorly silicon (24.26%), carbon (15.16%), oxygen (48.53%), and traces of sodium (5.83%), calcium (5.24%) and magnesium (0.95%) as presented in **SF1e**.

The SEM images as shown in **Figure 1** were analyzed to probe into the morphologies of the green composite films. The surface textures of chitosan composite films were found to vary from the chitosan film upon addition of seashell and/or glass powders. The pure chitosan film displayed an irregular or lamellar type surface structure. The surface morphology of CSG550, CSG541, CSG522, CSG514 and CSG505 displayed more uniform surface morphology compared to the CSG100 matrix alone film. Interestingly, CSG532 and CSG523 exhibited entirely different surface morphology compared to the remaining five composite films. Rod shaped long filamentous stacked structures were densely arranged in the SEM visuals of CSG532, whereas highly porous crystallite clusters were observed on the surface of CSG523.

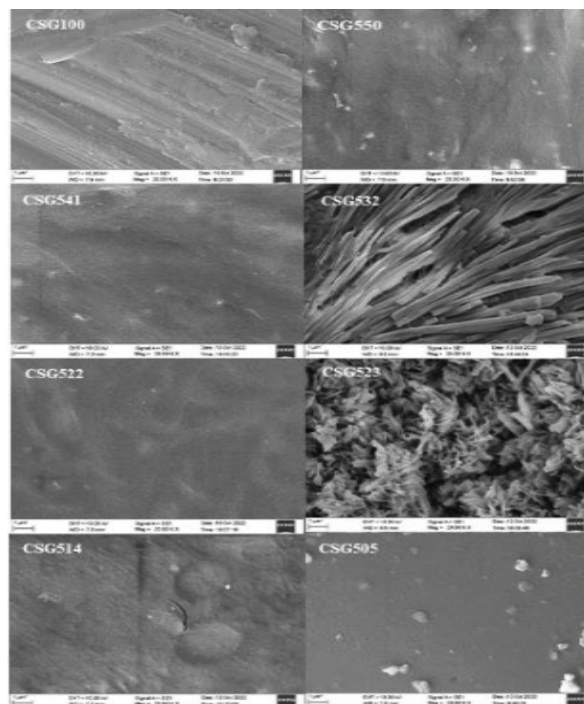


Figure 1. SEM images of pure chitosan film (CSG100), and its green composites with powdered seashells and glass as reinforcements.

Further the elemental compositions of the green films were explored using EDS plots as shown in **Figure 2**. The EDS of the pure biopolymer CSG100 displayed the presence of carbon, which is present in the molecular framework and elements such as oxygen as part of the cyclic ring and the functional groups in addition to nitrogen of the amine group. The CSG550 displayed mainly calcium from the seashells in addition to carbon, oxygen and nitrogen of chitosan, whereas sodium, silicon and glass was observed in CSG505 film apart from the elements present in chitosan. The ternary composites exhibited the presence of carbon, oxygen and nitrogen of chitosan, calcium from seashells as well as calcium and silicon from glass.

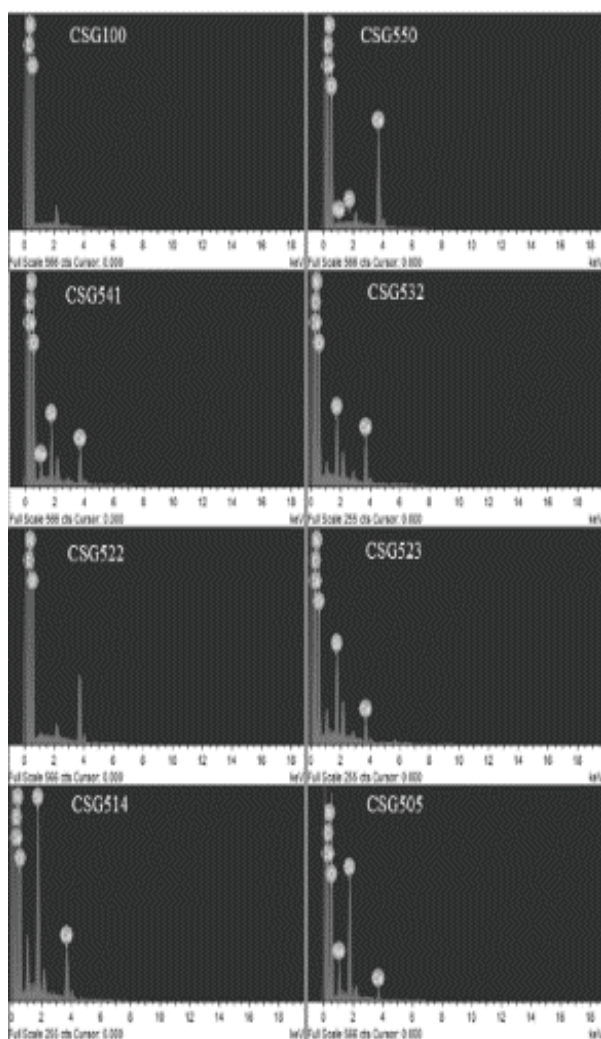


Figure 2. EDS plots with elemental composition of pure chitosan film (CSG100), and green composites prepared from chitosan, powdered seashells, and powdered glass.

3.3 FTIR spectral data studies

The FTIR spectra of the individual raw materials and the composite films with different mass fraction of the reinforcements were further analyzed. The spectrum of the pure chitosan sample (**SF2a**) was characterized by a broad absorption in the $3200\text{--}3500\text{ cm}^{-1}$ range due to NH_2 and OH groups, in addition to C=O amide II stretch and N-H bend (amide I) at 1649 cm^{-1} and 1552 cm^{-1} , respectively. The polysaccharide skeletal C-O stretching vibrational peaks were observed at 894 cm^{-1} , 992 cm^{-1} and 1070 cm^{-1} , whereas anti-symmetric stretching (C-O-C bridge) at 1152 cm^{-1} . The deformation and axial stretching of N-group were detected at 1307 cm^{-1} and 1374 cm^{-1} in the fingerprint region [36–38]. The spectral data obtained as presented in **SF2b** for seashell powder revealed broad absorption peaks at 1786 cm^{-1} , 1450 cm^{-1} , 1082 cm^{-1} , 857 cm^{-1} , and 709 cm^{-1} , which are common characteristic features of the carbonate ions in calcium carbonate and are the fundamental modes of vibration for this molecule [39]. The FTIR spectra of crushed glass showed characteristic features of Si-O-Si unit: asymmetric stretching at 992 cm^{-1} and symmetric stretching at 755 cm^{-1} [40].

The chemical interactions of chitosan macromolecules with added reinforcements were studied by analyzing the IR spectra portrayed in **Figure 3**. The composites displayed variations in the vibrational frequencies from the respective component materials. The characteristic broad peak of pure chitosan was found to narrow down in composites due to the breakage in inter-chain hydrogen bonding. An appreciable shift in the $-\text{NH}_2$ or $-\text{OH}$ absorption peaks was observed in all the composites due to probable co-ordination with the calcium ions, except the binary composite CSG505, which had only glass as the reinforcement material. Further, the peaks at 1649 cm^{-1} and 1552 cm^{-1} of pure chitosan CSG100 sample shifted to 1604 cm^{-1} and 1525 cm^{-1} in the other composites suggesting coordination with calcium ions [35]. The IR spectrum of the binary composite CSG505 shows the characteristic band of both chitosan and Si-O-Si at 942 cm^{-1} and 772 cm^{-1} . When the glass powder is embedded into the chitosan matrix, the

NH₂/OH stretch is shifted to a lower wavenumber compared to the bands in the pure chitosan film.

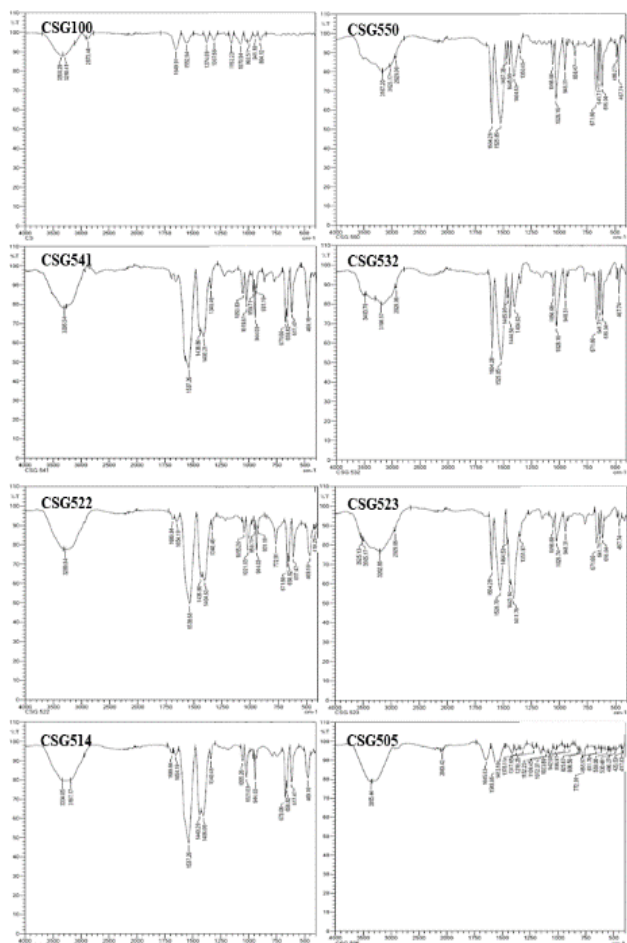


Figure 3. FTIR spectra of pure chitosan film (CSG500), and green composites prepared from chitosan, powdered seashells, and powdered glass.

X-ray diffraction analysis

The raw materials were initially characterized by recording their XRD spectra (**SF3**). The XRD patterns of chitosan with semi-crystalline structure displayed a very intense fingerprint diffraction peak at 2θ of $\sim 20^\circ$, corresponding to (110) plane as presented in **SF3a** [41]. The XRD plots (**SF3b**) indicated the diffraction peaks at 2θ values around 25.8° , 26.8° , 32.6° , 35.6° , 37.4° , 38° , 45.4° , 47.9° and 52° , which revealed that the seashells were mainly composed of calcium carbonate as per previous observations. The XRD pattern of the waste glass powder displayed its non-crystalline or amorphous nature with broad band at 2θ of $\sim 20^\circ$, which are typical of glassy materials [42].

Further, the X-ray diffraction plots as presented in **Figure 4** were examined to investigate the microstructure and crystalline nature of composites. A shift as well as a decrease in intensity of the XRD peaks were observed in all the binary and ternary composites, compared to that of the pure chitosan film. The decrease in peak intensity at 2θ value of $\sim 20^\circ$ and the peaks at 26.1 , 27.1 , 48.4 , 52.3 due to the incorporation of seashells was observed in the diffractogram of CSG550. Moreover, the intensity of the peaks due to seashells were found to decrease in CSG541 and further in CSG532, confirming the reduced percentage of seashells due to their reaction with aqueous solution of 2% acetic acid. The films of CSG514 displayed two weakly intense peaks with diffraction maxima at $2\theta = 8.6^\circ$ and 26° .

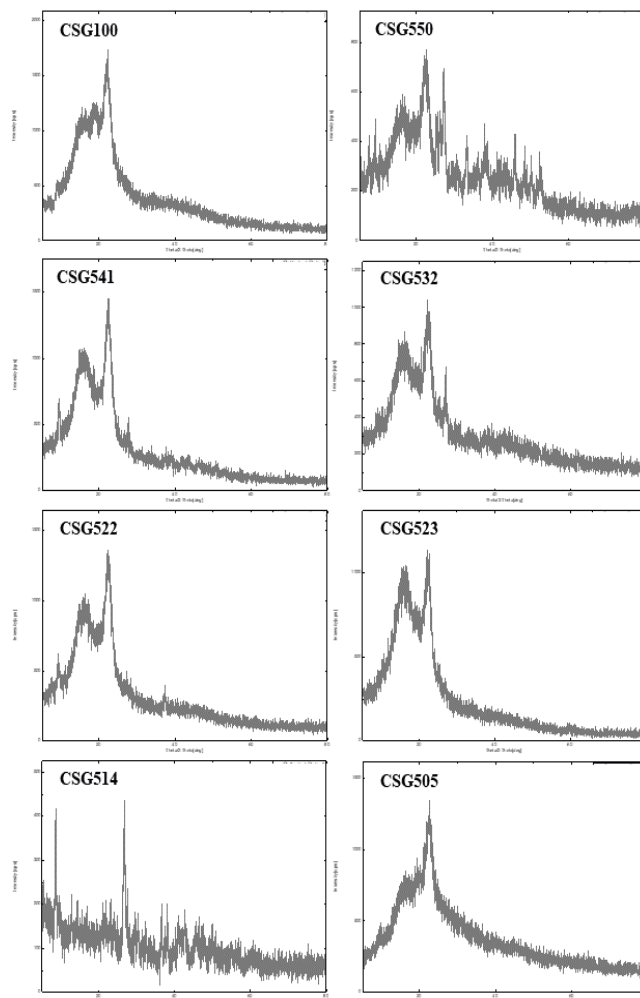


Figure 4. XRD plots of pure chitosan film (CSG100), and green composites prepared from chitosan, powdered seashells, and powdered glass.

Swelling degree studies

One major drawback of chitosan as a natural material for real-life application is its hydrophilic nature, or high degree of moisture absorption [43]. SD is an important factor used to measure the hydrophilicity or moisture absorption, which enables to determine the suitable application of the studied composite materials. Chitosan is basic in nature due to the presence of primary amino groups that gets converted to a polyelectrolyte when these amino groups are protonated [44]. The %SD of the synthesized composite samples was studied in distilled water.

Figure 5a shows the variations in the degree of swelling of the seven samples having different composition of the added reinforcements with respect to the pure chitosan sample. It is observed that the sample with chitosan alone had a higher water uptake as expected, which increases with time compared to its original dry mass [12]. It is noticed from the plots that the addition of reinforcements was found to appreciably reduce the swelling behavior of pure chitosan. Interestingly, the %SD was very less and remained constant when seashells/calcium percentage in the composite was high when compared to glass. Thus, CSG550 and CSG541 are the best films in terms of minimum swelling rate among all the composites. Interestingly, the %SD did not vary even after 24 h of immersion in water. It is also important to note that CSG532 and CSG523 exhibited completely different surface textures compared pure chitosan and the remaining five composites with more fibrous like structures in the SEM images.

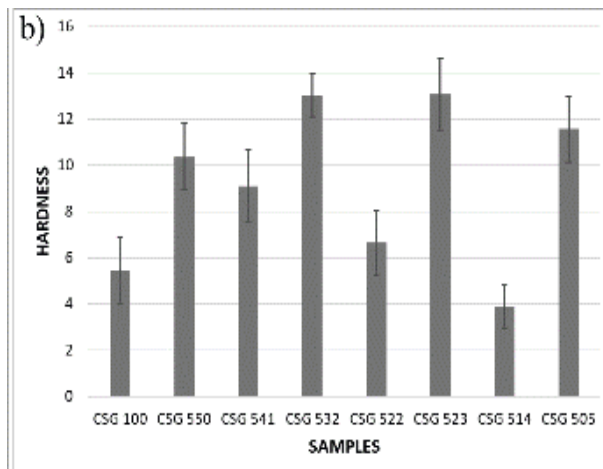
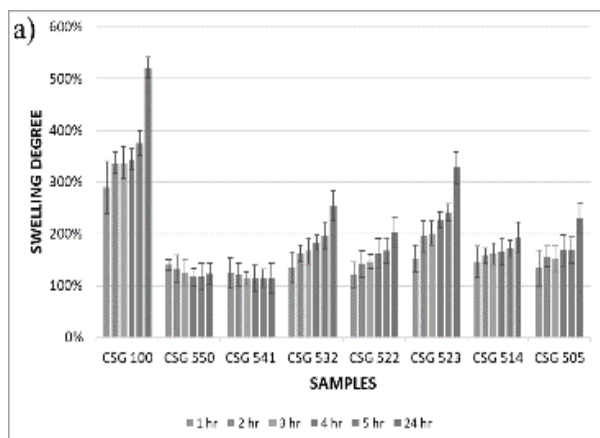


Figure 5 a) SD behavior and b) hardness of composite samples in comparison to chitosan film.

Hardness analysis

The small particle size of the reinforcements can influence the hardness of the composite as it facilitates their penetration into the chitosan matrix to increase the area of contact between the components of the prepared composite material. This could increase the interactions and interdependence between the matrix and the reinforcement to form a well-integrated system. The main functions of the reinforcement are to carry most of the load applied to composite and provide stiffness. Hardness is an important mechanical property, which is a measure of a material's resistance to localized plastic deformation under the influence of external stress. The hardness values obtained for the films are plotted in **Figure 5b**. The hardness increased by about 76% with introduction of seashell particulate as reinforcement signifying the role of reinforcement in increasing the hardness of chitosan films. With glass particulates added, the hardness increased by 125% as evident from the hardness values of CSG523 and CSG532 samples. Increased hardness of CSG523 and CSG532 can be attributed to increased presence of glass particulate. Silica is the major element in glass particulate and is also known to be harder than calcium carbonate which explains the increase in hardness in such composites. It should also be noted that these two samples had the highest hardness among all the samples, including those

samples with highest proportion of glass particulates. Relatively poor performance of samples with only increased glass particulates is due to the surface morphology of such samples. Though the proportion of glass particulates in CSG514 and CSG505 is more than CSG523 and CSG532, the surface morphology of the latter is responsible for their improved performance. Tubular structure is known to be rigid and thus provides more resistance to localized deformation. The improved performance of composites may also be because the glass particulate was bigger in size and thereby providing more surface to bear the indenting load. All the samples except CSG514 were found to be harder than the pure chitosan film. Poor performance of samples CSG514 and CSG522 may be attributed to voids underneath the surface thereby making it difficult to resist indentation. Thus, an optimized blend of seashells, calcium and waste glass can provide the chitosan bio-films maximum hardness for suitable applications.

Conclusions

In this study, seven composite samples with chitosan biopolymer as matrix and powdered seashells and/or glass as sustainable reinforcements were prepared using solvent casting method. The SEM, EDS, FTIR and XRD analysis direct towards the successful preparation of the composite films with different surface morphologies and interaction between the matrix and reinforcements. It is worth mentionable that two composites CSG532 and CSG523, which displayed unique rod-shaped crystalline structures in the SEM images were the hardest among all the seven composites. However, swelling degree was minimum in CSG550 and CSG541, when the seashell concentration was maximum in the composites. These results thus provide an experimental basis for the development of chitosan-seashell composites as sustainable source for calcium for possible application in bone tissue engineering. In addition, as the properties of the composites differ with the concentrations of seashell, calcium and glass focused future research on potential

applicability of these green composites as building materials and interiors of buildings can be explored. The green composites can also be investigated for their functional use in biomedicine, cosmetology, papermaking, wastewater treatment, agriculture, and pharmaceuticals.

Data availability

The supplementary material is available online. The data available upon reasonable request from the first author.

Declarations

Conflict of interest: The authors declare no conflict of interest with this work.

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