

PREPARATION AND CHARACTERIZATION OF CHITIN HYDROGEL COMPOSITED WITH HALLOYSITE CLAY SOLUTION VIA PHASE INVERSION

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In this study, halloysite clay (HC), a reinforcing nanofiller, was mixed with 1 and 1.5% chitin solutions to prepare chitin–halloysite clay composite hydrogel by phase inversion under water vapor atmosphere at 25 °C. Chitin, extracted chemically from crab shell, was dissolved in *N,N*-dimethyl acetamide in the presence of 5% lithium chloride (DMAc/5% LiCl), and then different amounts of HC solution (0, 3, 5 and 7%) were added to evaluate the effect of HC on the fundamental properties of the obtained composite hydrogels. After the green route of preparation, the diameter and thickness of the hydrogel samples seemed to remain the same, while varying the concentrations of chitin and inorganic filler solution. As a result, in the case of the 1% chitin hydrogel, the tensile strength of the composite films increased from 335.9 to 489.8 kPa, while the elongation was around 61.3 and 86.0% with the addition of 0 and 7% HC solution. With the increase in the chitin content to 1.5%, the mechanical strength of the resultant composite hydrogels was enhanced. Moreover, the reduction in the equilibrium water content confirmed the formation of a composite hydrogel incorporating a well dispersed nanofiller, with good interfacial interaction between the nanofiller and the biopolymer matrix.

Keywords: chitin, clay, composite hydrogel, phase inversion

INTRODUCTION

Hydrogels are hydrophilic structures capable of holding large amounts of water in their three-dimensional networks.^{1,2} Hydrogel materials based on biopolymers have attracted very much interest in recent years.^{3–6} Biopolymers, which are plant- or animal-derived macromolecules, are normally biodegradable, which may be relevant in biomedical applications, as they are susceptible to human enzymes.⁷ Many carbohydrate-based biopolymers have a long history of safe use and are well documented in terms of biocompatibility, biodegradability and low toxicity.⁸

Among hydrogel materials, chitin is one of the biopolymers primarily found in nature. This polymer is widely distributed as a structural component of crustacean exoskeletons,⁹ insects,¹⁰ arthropods,¹¹ as well as in the cell walls of most fungi¹² and algae.¹³ Chitin is composed of insoluble linear homopolymers, such as β -(1 \rightarrow 4)-N-acetyl-D-glucosamine¹⁴ (Fig. 1a), and has found applications in many fields, such as the

food industry,¹⁵ biomedical materials,¹⁵ pharmaceuticals,¹⁶ agriculture,¹⁷ textiles,¹⁸ cosmetics¹⁹ and water treatment.^{20,21} However, the chitin hydrogel has been reported to have poor solubility in solvents, which limits its uses.²² Moreover, as reported by Pradip K. Dutt, the mechanical strength of the chitin hydrogel was not good enough for several applications.²³ This highlights the major disadvantage of neat hydrogels being their mechanical weakness, leading to restrictions in applications.^{24,25}

It has been reported that the physical properties of chitin hydrogels could be improved in terms of tensile strength, while preparing them under high water vapor temperature conditions.²⁶ Nowadays, combining a polymer hydrogel network with nanoparticles, such as metals, non-metals, metal oxides, and polymeric moieties, holds the promise of providing superior functionality to the resulting composite material.^{27,28} The use of an inorganic reinforcing

agent, mainly clays, can represent a way of improving the mechanical strength of composite hydrogels.²⁹⁻³¹ Moreover, the introduction of clay materials into the hydrogel improves its elasticity and permeability, allowing them to adsorb different substances, due to some predominant properties, including low interfacial tension and a variety of functional groups, which provide high adsorption capacities.³² In line with this approach, the present work focuses on a halloysite filler to reinforce a chitin biopolymer-based hydrogel.

Halloysite clay (HC) occurs in nature as a hydrated mineral, consisting of rolled aluminosilicate sheets, with an ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, similar to kaolinite, except for the presence of an additional water monolayer between the adjacent layers³³ (Fig. 1b). When $n = 2$, the mineral is called halloysite-10Å due to its layer space of 10Å, reversibly dehydrated form halloysite-7Å with $n = 0$. Chemically, the external surface of the groups has a tetrahedral sheet composed of siloxane groups (SiO_4), whereas the inner surface is occupied by octahedral sheets of aluminosilicate groups (Al-OH).³⁴ In addition, the low contents of

silanols/aluminous on the cylindrical surface lead to the relative hydrophobicity of this inorganic material. The most significant specialty of halloysites, compared to other layered silicates, is that the tubular nanostructures of HC can ensure their high aspect ratio, which helps reinforce polymers in composites by optimizing the load transfer for different polymeric matrixes, due to the weak secondary interaction among the nanotubes.³⁵ Based on these properties, the strength, modulus, stiffness and impact resistance of polymers can be increased simultaneously by the incorporation of HC into the composites.³⁶ Due to its environmental friendliness, high water resistance, good mechanical strength and biocompatible characteristics, HC has been investigated for many applications, for example, as reinforcement agent in drug delivery,³⁷ as catalyst of polymer degradation,³⁸ and templates.³⁹ However, the most concerning disadvantage of HC is that this inorganic filler may aggregate in solutions or in a polymer matrix, leading to a reduction of relevant properties of the prepared materials.⁴⁰⁻⁴²

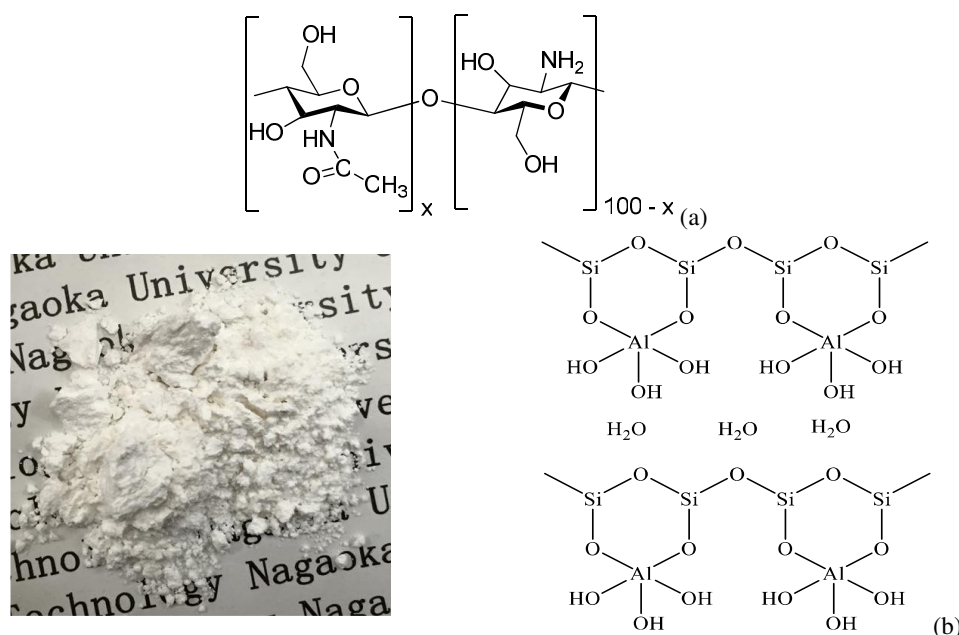


Figure 1: Chemical structure of natural chitin (a) and the appearance of halloysite clay with its structure (b)

In our previous study, dispersing a higher concentration of HC directly in the chitin solution could enhance the mechanical strength of the hydrogel, but it led to a reduction in the adsorption performance of the material towards heavy metal ion in aqueous medium.²¹ It might

have been caused by the fact that the HC particles tended to agglomerate, leading to a decrease in pore volume and size distribution. This phenomenon has been also reported in the case of a cellulose composite reinforced with a high amount of silica nanofiller.⁴³ In order to improve

the properties of composite materials, it is necessary to ensure a good dispersion of fillers within the matrix, and a homogeneous distribution of nanoparticles in the polymer is strongly required. It has been reported that ultrasonic waves generated by an ultrasonic horn were successfully used to disperse titanium dioxide nanoparticles into epoxy resin.⁴⁴ Ultrasound was used to produce the cavitation effect by the formation of bubbles which get trapped in the polymer matrix and nanofillers. Besides, this acoustic cavitation effect can lead to breaking up agglomerates, thus improving the dispersion of nanofillers.⁴⁵ Therefore, to overcome the issue of HC forming agglomerates, ultrasonic pretreatment could assist in dispersing HC in aqueous environment,⁴⁶ which is expected to influence some related properties, such as mechanical ones.

In the present study, chitin–halloysite clay composite hydrogels were prepared by phase inversion, and coagulated in water vapor at 25 °C. The research aimed to study the effect of HC content and chitin concentration on the ultrasonically assisted formation of the composite hydrogels and their physical properties.

EXPERIMENTAL

Materials

Red snow crab shells (genus *Chionoecetes*) were collected in Teradomari, Niigata, Japan. All chemicals used in the preparation of chitin and chitin-halloysite nanoclay hydrogel composites were of analytical grade. Halloysite clay (HC) was received from Sigma-Aldrich, with the main element composition confirmed by X-ray fluorescence (XRF) as 44% Al₂O₃ and 44.6% SiO₂. Other chemicals were used without any further purification, including hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), *N,N*-dimethyl acetamide (DMAc), lithium chloride (LiCl), and ethanol, which were products of Nacalai Tesque, Inc. (Tokyo, Japan). Prior to use, DMAc was stored with KOH for over five days, and LiCl was dried in a vacuum oven at 80 °C for 24 h to remove any traces of moisture.

Methods

Extraction of chitin from crab shells

It is known that crustacean shells are composed of minerals, protein and chitin, in different percentages varying among species.^{47,48} Chitin is chemically extracted from crab shell due to the interest in using waste by-products as biopolymer sources. In the present study, chitin was obtained from crab shells by the chemical method, as shown in Figure 2, with some modifications.⁴⁹ Briefly, 10 g of crab shells were

treated with 300 mL of 1 N HCl aqueous solution at room temperature for 24 h for demineralization. Then, the deproteinization process was carried out in 300 mL of 1 N NaOH aqueous solution at 90 °C for 5 h. Next, 300 mL of ethanol solution was added, and the alkalized crab shells were bleached at 60 °C for 5 h. After each step, the solid part was filtered off through a stainless-steel sieve and washed with distilled water to neutral pH. The initial, acid-treated and alkalized crab shells, as well as the extracted chitin, are displayed in Figure 3. As can be seen, the color of the crab shell was reddish, while the extracted chitin was light pink. The yield of chitin from the crab shells after the purification reached about $40.2 \pm 2.30\%$.

Preparation of chitin hydrogel composited with halloysite clay

The fabrication of chitin and composite hydrogels was carried out by dissolving purified chitin in DMAc with 5% LiCl solvent system, at room temperature, to obtain 1 and 1.5% viscous solutions. According to the available literature, the concentration of 5% LiCl in DMAc could be considered as optimum for dissolving chitin at room temperature.²

In the case of HC, a similar solvent system was used to prepare 50% HC solution in DMAc/5% LiCl, in an ultrasonic bath for 1 h at room temperature. Then, various ratios of pretreated HC solution were added into the chitin solution at 0, 3, 5 and 7%, followed by stirring for 24 h at room temperature to prepare homogenous solutions. About 10 g of each solution was poured into a glass dish, having 91 mm in diameter, and placed into a container (120x120x60 mm³), then 50 mL of distilled water was added into the container without directly contacting these solutions. The pristine chitin hydrogels and composite hydrogels, containing different ratios of HC solutions, were coagulated by phase inversion under water vapor at 25 °C within 24 h. Afterwards, all the hydrogel samples were washed with distilled water several times to remove traces of solvent before measurements. The samples were denoted as C (chitin concentration) H (amount of HC solution). For example, the chitin hydrogel prepared at 1% chitin solution and coagulated in the presence of 5% HC solution was named as C1H5.

Characterization

After storing for 24 h in the container, the obtained hydrogel samples were taken out from the glass dishes and washed with an excess amount of distilled water to remove any traces of solvent. The thickness and diameter of the neat hydrogel and composite hydrogels with different chitin and HC concentrations were measured by a technical ruler and a thickness gauge. At least three samples were repeatedly measured to obtain the average values.

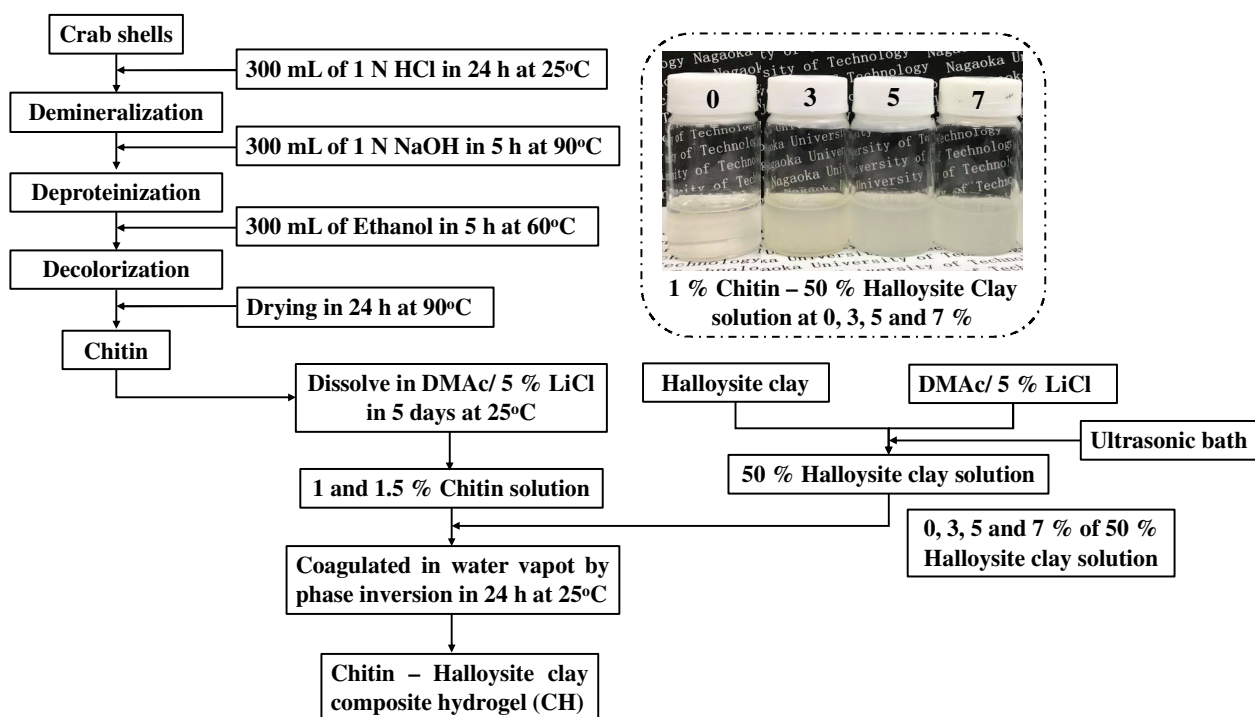


Figure 2: Procedure of chitin extraction from crab shell and preparation of chitin-halloysite clay composite hydrogel

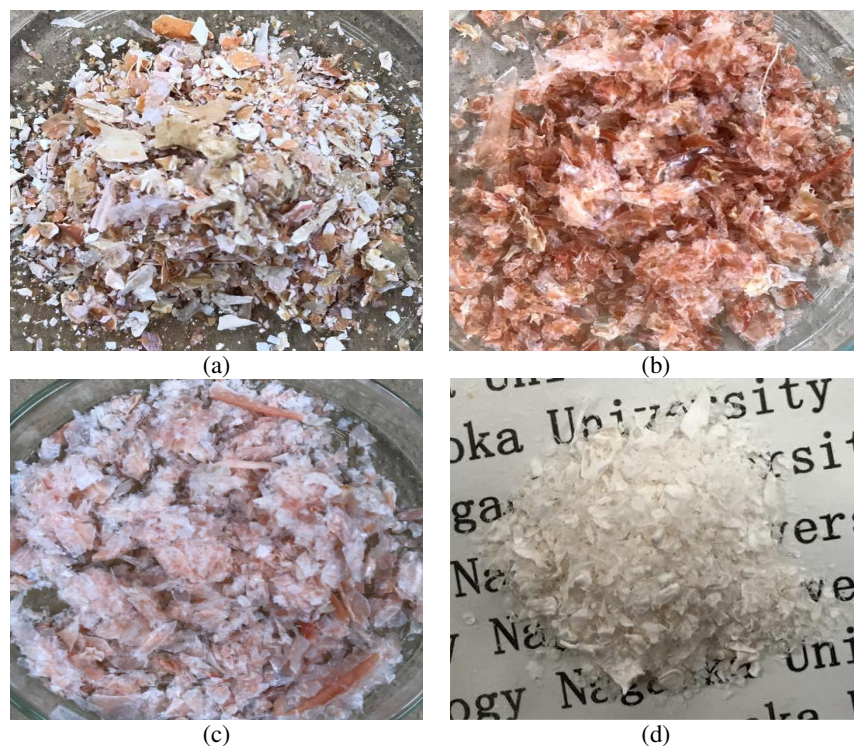


Figure 3: Initial appearance of crab shell (a), and after acid (b) and alkali treatments (c); purified chitin (d)

To characterize the interaction between constituents in the composites, Fourier transform infrared spectroscopy (FT-IR) of the hydrogels was conducted with a JASCO FT-IR/4100 spectrometer. About 1 g of dry hydrogel films was well ground with 9 g of KBr. Afterwards, the mixed samples were pressed to prepare a thin and transparent plate, which was scanned in the transmittance mode. Spectra were taken from 4000 to 400 cm^{-1} wavelength, with the resolution of 2 cm^{-1} . The degree of acetylation (DA) of the resultant chitin was calculated according to a method reported earlier⁵⁰ by the following equation:

$$\text{DA (\%)} = (A_{1650}/A_{3450})/1.33 \times 100 \quad (1)$$

where A_{1650} and A_{3450} refer to the absorbance of peaks at 1650 and 3450 cm^{-1} , related to the bands of amide I and the hydroxyl group, respectively, in the FT-IR spectra.

Equilibrium water content (EWC) experiments for the neat and composite hydrogels were performed at room temperature by immersing 30 mm x 10 mm strips of the hydrogel samples in distilled water. After 24 h of soaking, to ensure equilibrium sorption, the swollen hydrogels were removed from the water, quickly wiped with tissue paper, and weighed. The saturated amount of water absorption was calculated by the following equation:

$$\text{EWC (\%)} = (m - m_0) \times 100/m_0 \quad (2)$$

where m_0 is the dry weight and m is the weight of the samples after 24-h immersion in distilled water.

To investigate the effect of HC on the mechanical properties of the prepared hydrogels, tensile strength and elongation at break were verified. Tensile strength is calculated by dividing the maximum load by the cross-sectional area. This test was carried out by using

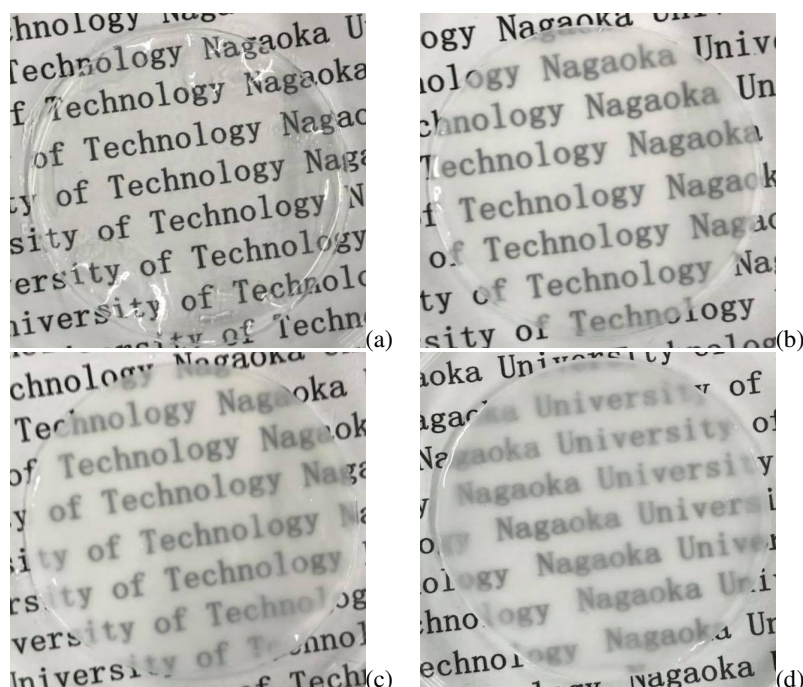
an LTS-500N-S20 (Minebea, Japan), with an operating head load of 5 kN at 23 °C and 50% RH. The hydrogel films (40 mm x 10 mm) were then placed between the grips of the testing machine. The initial length was fixed at 20 mm, and the speed of testing was 2 mm/min. The values of tensile strength and elongation at break were calculated using these equations:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Cross-sectional area}} \left(\frac{\text{N}}{\text{mm}^2} \right) \quad (3)$$

$$\text{Elongation at break (\%)} = \frac{\text{Elongation at rupture}}{\text{Initial gage length}} \times 100 \quad (4)$$

RESULTS AND DISCUSSION

The appearance of chitin hydrogels and composite films is displayed in Figure 4. As seen, the chitin hydrogel was transparent, while the hydrogel composites were opaque. Higher amounts of the chitin solution in the hydrogel caused more translucence in the appearance of the observed samples. In addition, with the increment in the HC solution in the hydrogels, the opaque white color became more intense. The shape of the chitin hydrogels and composite hydrogels was well preserved as the round-bottom glass dish. The thickness was in the range of 1.90-1.24 mm, when the diameter seemed to remain the same. Therefore, the presence of HC solution in the composite hydrogel did not have a significant effect on the size of the hydrogels. The diameter and thickness of the hydrogel samples prepared with various amounts of HC solution were summarized in Table 1.



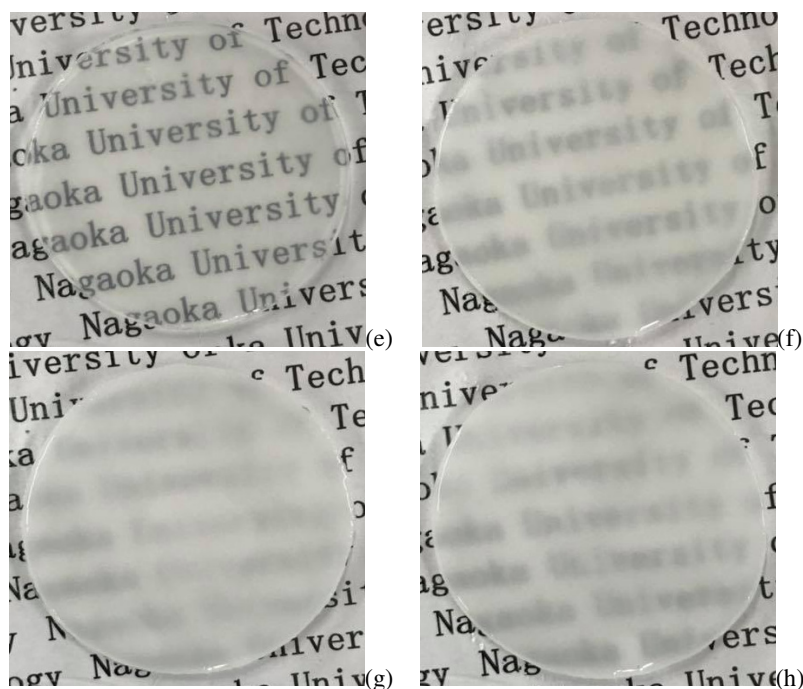


Figure 4: Images of hydrogel films with various ratios of halloysite clay solution: C1H0 – C1H7 (a-d) and C1.5H0 – C1.5H7 (e-h)

Table 1
Gravimetric ratio and physical properties of chitin hydrogel and composite hydrogels with various ratios of halloysite clay solution (n = 5 for each test)

Sample	Ratio for 10 g mixed solution		Thickness (mm)	Diameter (mm)	EWC (%)
	Chitin (g)	HC solution (g)			
C1H0	10	0	1.19 ± 0.01	47.5 ± 0.2	393.9 ± 31.7
C1H3	9.7	0.3	1.22 ± 0.01	47.8 ± 0.3	224.1 ± 17.1
C1H5	9.5	0.5	1.24 ± 0.06	47.8 ± 0.3	192.5 ± 25.0
C1H7	9.3	0.7	1.18 ± 0.15	48.0 ± 1.0	161.3 ± 10.0
C1.5H0	10	0	1.19 ± 0.03	47.0 ± 0.3	433.8 ± 16.7
C1.5H3	9.7	0.3	1.21 ± 0.01	48.0 ± 1.4	273.9 ± 31.9
C1.5H5	9.5	0.5	1.09 ± 0.16	47.0 ± 0.1	260.3 ± 30.9
C1.5H7	9.3	0.7	1.15 ± 0.08	46.8 ± 0.4	213.3 ± 14.9

According to the FT-IR spectrum, the calculated DA of the extracted chitin was about $81 \pm 3.0\%$. In addition, the FT-IR analysis in this study was used to confirm the initial form of the extracted chitin and the interaction of functional groups between chitin and the HC filler in the prepared composite hydrogel. In order to compare the obtained spectra, they are provided in Figure 5. As seen, the intensity of the peak at 827 cm^{-1} , attributed to the calcite compound, was reduced, after the acid and alkaline treatments (Fig. 5a). The results reveal that the specific functional groups in the purified chitin were the O–H stretching band at 3447 cm^{-1} , the C–H bonding at

$2888, 2932, 2960 \text{ cm}^{-1}$, the C–O stretching band at 1028 cm^{-1} and the C–O–C ring at 1155 cm^{-1} . In addition, the amide I bands at 1654 and 1626 cm^{-1} , and the amides II (N–H stretching) at 3294 and 1554 cm^{-1} indicated the alpha form of chitin. In the case of HC (Fig. 5 b), the peaks at 3692 cm^{-1} , 3619 cm^{-1} , 999 cm^{-1} and 910 cm^{-1} correspond, respectively, to the O–H stretching of the inner-surface hydroxyl groups, O–H stretching of inner hydroxyl group, and Si–O stretching and O–H deformation of Al–OH inside the hydroxyl group. The band at 1628 cm^{-1} corresponds to the O–H stretching vibration of adsorbed water, confirming the hydrated form of the sample. The FT-IR

spectra also showed the interaction between chitin and the HC filler. There was a slight shift of the absorption bands from 3692 to 3693 cm^{-1} , attributed to the Al-OH of HC^{51} upon addition of 5 and 7% of HC solution to the hydrogel samples.

As the intensity of the amide I band at 1626 cm^{-1} tended to decrease in the composite hydrogels from C1H3 to C1H7, the interfacial interaction between chitin and the HC solution was observed.

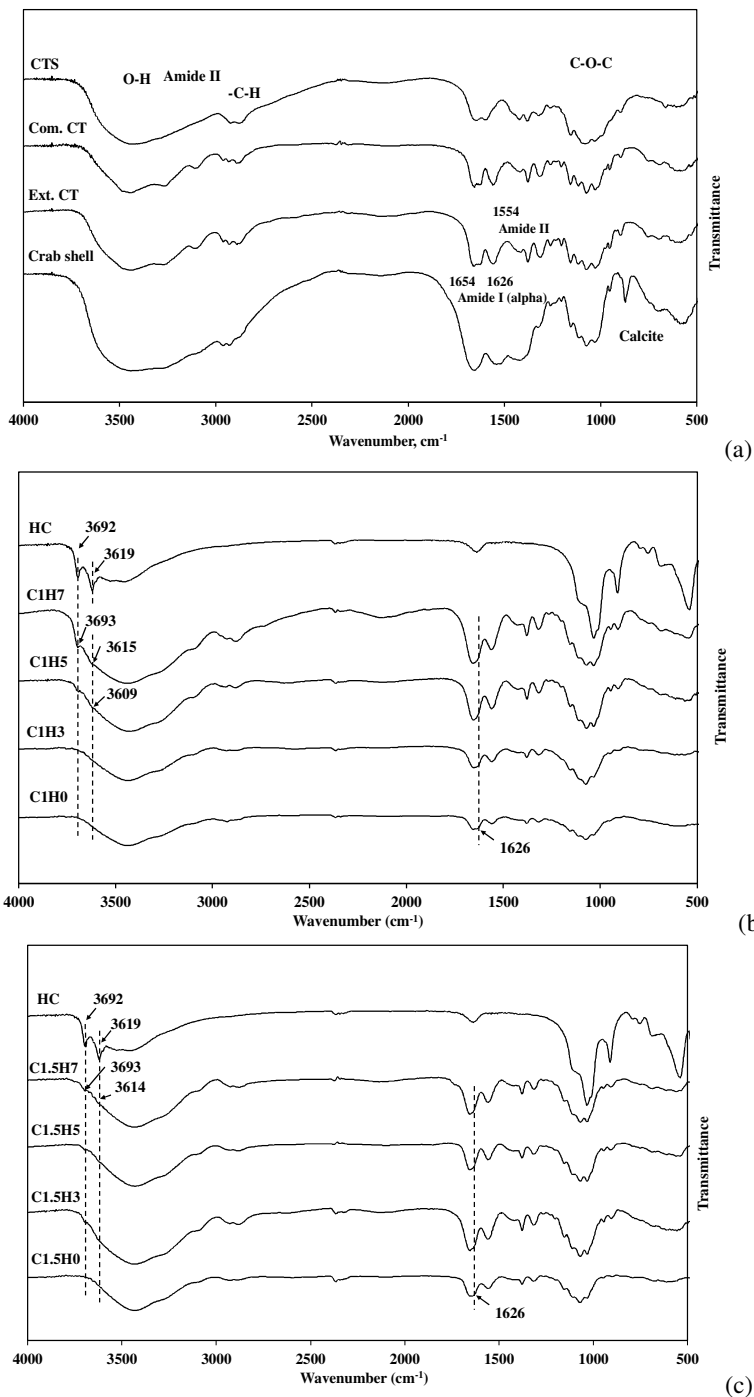


Figure 5: IR spectra of (a) extracted chitin (Ext. CT) in comparison with commercial chitin (Com. CT) and chitosan (CTS), and those of composite hydrogels based on 1% chitin (b) and 1.5% chitin (c)

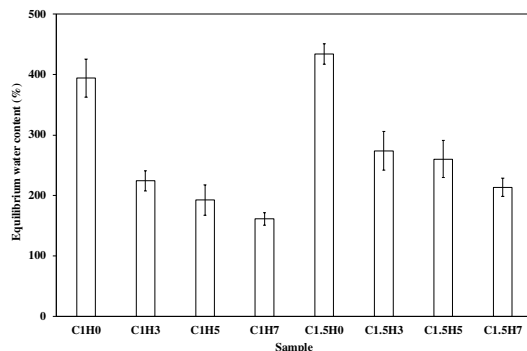


Figure 6: Equilibrium water content of hydrogel films with different halloysite clay amounts

It seemed to be the evidence for the formation of hydrogen bonding between the biopolymer matrix and the inorganic filler in the composite hydrogels. A similar tendency was recorded when the concentration of the chitin solution was 1.5% (Fig. 5c).

The swelling behavior of hydrogels is illustrated in Figure 6. As can be seen, with the increase in the HC loading from 0 to 7%, the EWC of the hydrogel samples decreased from 393.9 to 161.3% in the 1% chitin hydrogel. This value indicated that the pristine chitin hydrogel could be rapidly saturated (about 393.9%) due to the high affinity of water molecules to the hydroxyl groups of chitin segments. The combination with HC in the composite hydrogels seemed to limit the water content of the composite hydrogels because of the hydrophobicity of the HC, which could be observed for the C1H7 composite hydrogel (161.3%). Furthermore, the high aspect ratio property of its tubular nanostructure may allow HC to disperse easily into the chitin polymeric matrix to obtain a compact structure of the hydrogel films. A denser hydrogel structure diminished the accessibility of water molecules to the hydrophilic parts of polymer molecules; therefore, less water could penetrate into the composite hydrogel structure.³² In the case of the hydrogel samples prepared with 1.5% chitin solution, the EWC was found to be higher. As noted, the EWC value of C1.5H0 was 433.8% due to the stronger intensity of the chitin segment in the obtained samples. For the C1.5 composite hydrogels, when the amount of HC solution was increased from 3 to 7% in C1.5H3 and C1.5H7, these samples gained about 272.9 and 213.3% of water swelling, respectively. The findings of the study showed that, with the addition of HC solution, both the tensile strength and the

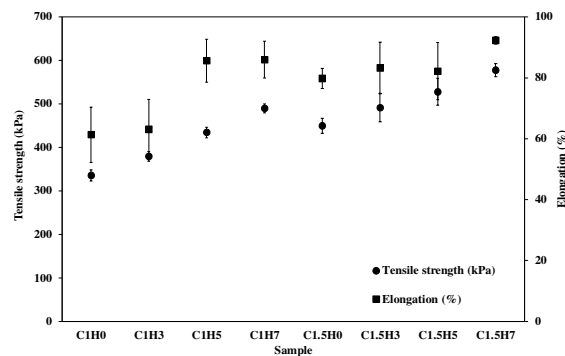


Figure 7: Tensile strength and elongation at break of hydrogel films with different halloysite clay amounts

elongation at break of the hydrogels increased (Fig. 7). Another study reported that, in the presence of inorganic fillers, the mechanical strength of the composite was improved through the increment in tensile strength, but the elongation at break reduced.²¹ However, in the above-mentioned experiment, HC was used in powder form to work as reinforcing agent. Meanwhile, in the present research, HC was prepared as solution, assisted by ultrasonic treatment to prevent the aggregation of the nanofiller within the polymer structures. Our results showed that the tensile strength increased from 335.9 to 489.8 kPa, when 0 and 7% HC solution was added, respectively. Notably, the elongation was relatively enhanced to 61.3% for C1H0 and 86% for C1H7. The reason could be related to the interfacial interaction between the hydroxyl groups of chitin and HC, as confirmed by FT-IR analysis. Thus, the stabilization of the hydrogel composites has been improved at higher nanofiller loading, resulting in the enhancement of tensile strength values.⁵²

This phenomenon was well-noted in the present study. This tendency might be due to the addition of HC in solution state, which caused the addition of a higher LiCl amount, compared to the previously cited research.²¹ It could be explained by the fact that a higher amount of Cl⁻ ion in the preparation of the HC solution might cause stronger affinity to water molecules. Therefore, the elongation at break increased when higher content of HC solution was added. A similar tendency was observed for higher chitin content in the hydrogel preparation. When using 1.5% chitin solution as a polymer matrix for the formation of hydrogel samples, the mechanical properties of the hydrogels gradually increased from 449.8 kPa and 79.8% for C1.5H0, and to 577.7 kPa and 92.3% for C1.5H7.

From these fundamental characterizations, it can be noted that, varying the chitin concentrations at 1 and 1.5% and the amount of HC solution from 0 to 7%, an improvement in the mechanical properties of the composite hydrogel was achieved, in addition to its well-known non-toxicity and biodegradability. The enhanced mechanical properties of such materials could make them suitable for potential applications in different areas, such as wastewater treatment or biomedical products.

CONCLUSION

Crab shells were successfully used as a source of chitin, owing to the interest it presents in the preparation of hydrogels. The study demonstrated that the chitin hydrogels obtained by a green preparation route, using a non-degraded solvent system and performed in ambient atmosphere, presented improved mechanical strength due to mixing with different ratios of natural halloysite clay (0 to 7%). Thus, the tensile strength of the composite hydrogels increased from 335.9 to 489.8 kPa, while the elongation rose from 61.3 and 86.0% for 0 and 7% additions of HC solution to 1% chitin hydrogel. With the increment to 1.5% chitin solution, the mechanical strength of the resultant composite hydrogels was enhanced. In addition, a reduction in the equilibrium water content confirmed the formation of a composite hydrogel with a well dispersed nanofiller, showing improved interfacial interaction between the nanofiller and the biopolymer matrix. Based on the findings, further investigations need to be made to address the suitability of the obtained composite hydrogel for various applications, such as in water remediation or biomedical materials.

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