Innovative Infrastructure Solutions (2023) 8:287
https://doi.org/10.1007/s41062-023-01253-z

TECHNICAL PAPER

The impact of using natural waste biopolymer cement on the properties of traditional/fibrous concrete

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Received: 16 May 2023 / Accepted: 19 September 2023 / Published online: 11 October 2023

Abstract
The naturally occurring wastes contain a large number of active groups. In this study, shrimp shell wastes were modified chemically to form chitosan. When mixing concrete with a natural polymer the result revealed a synergistic impact on the characteristics and functionality of the concrete structure. The formed chitosan was characterized by Fourier-Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). Five concrete mixes were designed to achieve the study objective. For certain concrete mixes, admixtures such as a natural polymer (chitosan), and chemical (superplasticizer) were added with 0.05% by weight of the cement content. Those admixtures were added to study their behavior on the characteristics of the concrete mixes, and then compare test results with control concrete mixes. Also, the purpose of the experiment was expanded to study the impact of adding the admixtures to fibrous concrete, as this fibrous concrete faces interlocking due to steel fiber's presence in the fresh concrete mixture. The results indicated that concrete-embedded chitosan exhibited significant enhancement in the mechanical properties. Further, the surface shape of concrete was characterized by the presence of chitosan crystallites which spread and filled the spaces in the chitosan structure. Also, it's noted that chitosan can delay the rate of cement hydration to a small value, which may help in hot weathering concrete.

Keywords Chitosan polymer material · Sustainable materials · Recycling seafood wastes · Biopolymer cement · Green concrete

Introduction

In recent decades, sustainability has become an important issue in the construction industry. In this direction, it has become necessary to use environmentally friendly materials or to use environmental waste in construction. Moreover, the corrosion of reinforcing steel has been considered one of the greatest factors affecting the sustainability of concrete structures, especially in harsh environmental conditions. Therefore, engineers and researchers in this field have focused on replacing the reinforcing steel with other non-corroded materials or adding materials to the concrete mixes that limit the access of moisture to the reinforcing steel. On the other hand, the second-most significant and naturally abundant biopolymer is chitin, behind cellulose. It is produced from seafood wastes which are available at a rate of 10^{10}–10^{11} tons per year but rarely used for concrete technology applications [1]. Chitosan is the primary derivative of chitin by the deacetylation process. It is a biopolymer made of polysaccharides and involved in cement applications but to a smaller extent than other polysaccharides like starch, cellulose, and its derived compounds. Furthermore, nature creates stiff habitats for a variety of living things by combining a mineral calcium carbonate filler with an organic chitin matrix to inspire composites that have good mechanical characteristics and durability in the face of harsh environments [1]. The chemical composition of concrete has been altered by adding chitosan to enhance the material's characteristics. Glucosamine and N-acetylglucosamine make up chitosan, a linear polymer derived from chitin. It has a distinct cationic behavior, a hydrophilic surface, and strong biocompatibility,

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which promote cell proliferation, bond strength, and differentiation [2]. Chitosan and the polymers derived from it can be employed as admixtures for cement, and concrete for various purposes, such as superplasticizers, anti-dispersants, retarders, etc. For self-packing cement, polylactic acid, a chitosan derivative, can inhibit alkali silicic acid [3]. Natural strong composite materials such as chitin derivations could be used as serve as inspiration for improving long-term properties of concrete in order to create more durable concrete [1]. Chitosan's efficacy as a potential rheological modifier, and heavy metals retention admixture was examined by [4]. The study showed that the molecular weight, dosages, and surface groups of chitosan all affect how it affects rheology. They proposed that chitosan could lessen viscosity by producing electrostatic repulsions between polymer chains due to its higher charge density. Moreover, they discovered that chitosan with a higher deacetylation degree had a higher water retention value. Also, they observed that the insolubility of chitosan non-alkaline pH caused the set retardation effect, which was explained by the adsorption of precipitants onto anhydrous state particles of cement.

In a different investigation by [3] cement pastes containing nonionic, and ionic chitosan derivatives were examined. It was discovered that ionic chitosan exhibits a greater thickening effect and water retention capacity than nonionic chitosan. They discovered how chitosan interacts with cement particles, causing a flocculating effect and a delay in the cement phase's hydration. The chitosan solutions significantly enhance the handling characteristics of cement. The mechanical characteristics of cement paste containing different chitin concentrations exposed to chemically demanding conditions and at various ages using nanoscopic and macroscopic examinations were studied by [5]. They noted that the mechanical performance decreased when chitin was added to the cement paste and observed that chitin lowered the surface roughness of the paste of cement using an atomic force microscope (AFM), which was associated with a hardening action and the production of aggregate in the distribution of particle sizes of chitin polymers. They also observed a strong correlation between cement paste's macroscopic characteristics and its nanoscale flexibility and adhesion.

Chitosan and regolith were used to create Martian biolith, and its mortar performance was evaluated by [6]. According to differential scanning calorimetry and Fourier transform infrared (FTIR) research, they did not discover any chemical interactions between chitosan and regolith. In 1:75 ratios (chitosan: regolith), they noticed a considerable rise in flexural strength, which fell off at 1:100 ratios. The compressive strength also decreased after the 1:100 ratios. [7] studied how chitin affected mortar cement. According to the experimental results, chitin caused cement particles to repel one another electrostatically, delaying the final setting time by up to 78 min, likely by electrostatic repulsion of cement particles. Moreover, chitin made fresh cement paste viscous. The increased mobility of concrete is blamed for these various effects. Chitin also markedly boosted twenty-eight days' compressive strength by up to 12% and flexural strength by 40% when combined with chitin by 0.05 wt% of cement.

Recent explosive development in the construction sector has alerted engineers to the necessity of sustainability and the usage of eco-friendly materials. The use of renewable, sustainable, and biodegradable biopolymers as admixtures in concrete and mortar mixtures has a lot of potential. The researchers [8] demonstrated that adding chitosan, xanthan gum, and guar gum as an admixture enhances the characteristics of mortars used to encapsulate heavy metals. Chitosan is added to mortar to counteract the negative effects of heavy metal encapsulation on its workability, setting time, and compressive strength. The crosslinking properties of guar gum and xanthan gum, along with the addition of boric acid, in the mortar matrix system increase the mortar's compressive strength by up to 30% and lower the leaching of heavy metals to less than 0.001 mg/L. The workability of fresh-state mortar is enhanced by lignosulphonate as a plasticizer. The ability of fresh-state mortar to retain water improved by up to 98.8% with the addition of cellulose ethers to the mortar mixture. The use of biopolymers improves the physical and leaching characteristics of mortar and concrete, according to the data listed above.

In the construction industry, cellulose ether-based admixtures that increase viscosity and retain water are frequently employed to enhance the qualities of concrete and ready-mix mortars. The researchers [9] studied the effects of alternative natural viscosity-enhancing admixtures at dosages of 0.1%, 0.5%, and 1% of the cement binder weight, including (sodium salt of alginic acid, carrageenan, diutan gum, xanthan gum, and hydroxypropyl derivatives of guar gum and chitosan). Isothermal calorimetry is used in the study to examine the heat flow and total heat produced during the reaction starting with the water addition to the system. The results showed that all examined biopolymers made of polysaccharides exhibited a consistent ability to set retarding. While the retarding effects of other additives did not significantly change with the amount of biopolymer in the tested range of doses, hydroxypropyl guaran and diutan gum did. In contrast to cellulose ethers, the investigated admixtures were less effective at delaying the accelerating period and reducing the overall heat produced during the process. If the set-retarding ability is not suitable for the mixture's intended purpose, another admixture other than hydroxypropyl guar gum or diutan gum should be selected; otherwise, the benefit over cellulose ethers won't be very substantial. The authors [10], utilized steel slag as a fine aggregate and examined the application of a chitosan-based polymer (CBP), a biomimetic polymer, to cement mortar. Chitosan, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride and 3-(3,4-dihydroxyphenyl)propionic acid were used in an amide coupling reactions to create the CBP. The CBP helped to increase the compressive strength and tensile strength of cement mortar when added to cement mortar made with natural sand or aggregate made from blast furnace slag. However, when CBP was added to mortar mixtures containing ferronickel slag as an aggregate, the tensile strength dropped by 5.7–9.4%. By [11], in situ shrinking microfibers, as opposed to conventional passive reinforcing microfibers, can cause precompression of the matrix and increase resistance to external stresses, resulting in stronger composite constructions. These microfibers respond to in situ stimuli such as heat, pH, or moisture variations. A variety of cementitious specimens, including active and passive non-shrinking fibers as well as control samples, were made. Compression and three-point bending tests were used to compare the samples' mechanical characteristics. In compression tests and three-point bending tests, the ideal microfibre weight percentages for HAS microfibers were 0.5 wt% and 1.0 wt%, respectively. In three-point bending tests, the ideal weight percentage for pHAS microfibers was 0.5 wt%. At the ideal weight percentages of HAS microfibers, 45% more maximum compression strengths and 124% more maximum bending strengths were obtained compared to heat-passive microfiber specimens. Additionally, when compared to pH passive microfiber specimens, the maximum bending strengths of three-point bending tests increased by 145% with 0.5 weight percent of pHAS microfibers.

The effect of fibers added to the concrete was studied by numerous investigations as well and [12] used recycled soft drink aluminum cans as fiber reinforcement in the concrete to examine the behavior of the material, in particular its compressive and flexural strength. Finding the maximum amount of fibers to mix into the concrete is another aim of the research. Ordinary Portland Cement (OPC) concrete was made to achieve a mean strength of 30 MPa with no more than 30 mm of the slump by adhering to the standard mix design. OPC concrete with 0%, 1%, and 2% soft drink aluminum fiber was made based on cement weight and had the same workability. The relevant results showed that because of loss of bonding caused by an excess of fiber, concrete with 2% fiber has the least strength, according to the negative reaction. In general, 1% is the ideal amount to provide the best compressive strength. Further, [13] reported that Glass fiber reinforced polymer (GFRP) sheets and steel fibers were used to examine high-performance traditional and lightweight fibrous concrete. Fiber could influence how quickly and wide cracks in concrete would propagate. However, incorporating fibers can make concrete fail in a semi-ductile or ductile behavior. The author conducted an experimental program to obtain the ideal percentage of corrugated steel fibers of 0.5%, 1%, or 1.5%. The experimental results were relevant in that the optimum steel fiber percentage was 1%. Moreover, [14] examined how axially compressed concrete with various steel fiber contents deteriorated mechanically and microscopic properties under a chemical erosion and freeze–thaw environment. To investigate the durability behavior under various environmental conditions for up to 28 days, including tap water, 3.5% sodium chloride solution, 10% sodium sulfate solution, 5% sulfuric acid solution, 2 mol/L sodium hydroxide solution, and 100 freeze–thaw cycles, concrete cylinders with three types of steel fiber contents (0%, 1%, and 2%) were chosen. With increases in the chemical erosion cycle, the microstructure and axial bearing capacity of the specimens varied with different fiber contents, and changes in the specimen's mass and pH were measured. The degree of deterioration was assessed using the law of microcracks, and a numerical analysis model was developed to determine the reliability of the structure with various fiber contents. The findings demonstrate that the addition of steel fibers can significantly increase concrete's axial bearing capacity and that chemical erosion and freeze–thaw environments can accelerate the failure of fiber-reinforced concrete. The ideal amount of steel fiber is 1% for situations with sodium chloride and sodium sulfate, and 2% for environments with freeze–thaw cycles, diluted sulfuric acid, and sodium hydroxide. The freeze–thaw cycle and mechanical test of concrete were simulated and examined using the finite element program Abaqus, which confirmed the validity of the test results.

To this end, natural polymers such as chitosan are promising materials for obtaining environmentally friendly concrete with distinctive properties. The use of shrimp shell residues in the manufacture of polymers is an interesting idea during the coming period because it achieves improved properties of concrete, in addition to recycling food waste. On the other hand, the literature is based on cement mortar and lacks coverage of concrete behavior. Also, steel fibers in concrete at a content of 1% significantly improve the mechanical properties of concrete. Ultimately, the experimental program was performed to investigate the validity of using natural chitosan as admixtures instead of chemical admixtures, in addition to studying the effect of adding steel fibers on the behavior of concrete.

Scope of the research

The research aims to study the use of a natural polymeric material produced from shrimp shells to improve the behavior of fresh and hardened concrete. This idea will contribute to solving the problems of marine waste disposal and preserving the environment, in addition to using a natural admixture in the concrete mix as an alternative to other chemical admixtures. The laboratory production of the chitosan from the waste shrimp shells was conducted, and then

Table 1 Physical and mechanical properties of used cement

Property	Test result	Acceptable limit [15]
Cement fineness by blaine test specific surface area (cm^2/gm)	3625	–
Initial setting time (minutes)	143	Not less than 60 min
Final setting time (minutes)	188	–
Cement soundness (Le Chatelier) in (mm)	3	Not more than 10 mm
Compressive Strength 2 Days (MPa)	26.6	Not less than 10.0 MPa
Compressive strength 28 days (MPa)	55.2	Not less than 42.5 MPa And not more than 62.5 MPa

Table 2 Physical properties of the used crushed stone

Test	Results	Acceptable limit [16]
Specific gravity	2.76	–
Unit weight (t/m^3)	1.74	–
Materials passing no. 200 sieve	1.75	Less than 3%
Absorption %	1.76	Less than 2.5%
Abrasion (Los Anglos)	16.90	Less than 30%
Crushing factor	19.85	Less than 30%
Impact	18.95	Less than 45%

Table 3 Physical properties of the used sand

Test	Results	Acceptable limit [16]
Specific gravity	2.55	–
Unit weight	1.63	–
Materials finer than No. 200 Sieve	1.95	Less than 3%
Absorption %	1.30	Less than 2%

Table 4 Properties of the used steel fibers

Property		Value* *Obtained data from a supplier
Shape		End hooked
Chemical composition Low carbon drawn wire Conforming to AISI 1010	C	0.08–0.10%
	Si	0.05–0.1.%
	MN	0.6–0.80%
	P	Max 0.015%
	S	Max 0.030%
Length (mm)		25
Thickness (mm)		1
Aspect ratio		25
Unit weight (t/m^3)		7.80
Young's modulus (MPa)		2×10^5
Tensile strength (MPa)		Not less than 1000

the complete chemical and physical characterization of the produced chitosan was presented. Also, characterization methods including Fourier-Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) were carried out. Biopolymer cement is a Portland cement with natural polymer chitosan as an aqueous solution, the aqueous solution acting as an admixture for concrete mixes. Chitosan from waste shrimp shells was processed for evaluating the concrete mixes without or with the addition of steel fibers and compared the results by the same concrete ingredient mix with a chemical superplasticizers admixture. The investigation of the tested concrete mixes extended to include the fresh and hardened properties. The study helps in recycling seafood waste to achieve sustainable trends, reduce concrete costs, and minimize the usage of chemical admixtures in concrete mixes.

Experimental program

Properties of the used materials

The materials used to produce specified concrete were tested according to specifications and codes. CEM I 42.5 N, "Portland Cement" was tested according to [15]. Crushed size two dolomite stone was tested according to [16] and siliceous clean sand was also tested according to [16]. Tables 1, 2 and 3 show the test results for used concrete mixture ingredient materials. On the other hand, steel fibers with end-hooked shapes were used in certain concrete mixes with a percentage of 1%. The properties of the used steel fibers are presented in Table 4 which shows the datasheet obtained from the supplier. Jumbo shrimps were purchased from Suez City in Egypt to use its waste shells in producing chitosan. Sodium hydroxide (NaOH), Hydrochloric acid (HCl), and acetic acid were purchased from Aldrich Chemical Company, Egypt. Those chemicals helped to produce chitosan, then diluted to the required concentration for the methodology with distilled water without further purification. The admixtures such as superplasticizer (ViscoCrete®-3425) [17], or produced chitosan were added to concrete with the same percentage in certain concrete mixes and stacked with the recommended percentage of 0.05% of cement content as reported by [7]. Five concrete mixes were designed according to [18] and cast to achieve the aims of the study.

Each mix was cast with six standard samples of cubes (150 × 150 × 150 in mm), cylinders (150 × 300 in mm), and prisms (100 × 100 × 500 in mm) to test three samples after seven days and the other three samples after twenty-eight days. Table 5 shows the details of concrete mixes including ingredient quantities. However, The following Sect. "Extraction and characterization of chitosan". shows the extraction method and characterization of chitosan. Also, the section included the chitosan characterized by FT-IR to identify the functional groups, XRD to analyze the crystallinity of the product, and TGA to study the thermal stability.

Extraction and characterization of chitosan

The extraction of chitosan material from shrimp shell waste can be carried out by four different methods, in the current research, the optimum method was used because it gives the most thermal stability and the highest degree of deacetylation for produced chitosan as reported by [19]. To remove the loose tissue from the shrimp shells, it's washed, dried, and grind to obtain dry powder as shown in Fig. 1. The demineralization step of the extraction procedure involved washing shrimp shell wastes in 4% HCl (1.3N) at a ratio of 14 ml:1g (w/v) at room temperature for 24 h. The product was washed under running tap water to neutralize. The solid was collected, cleaned with distilled water, and vacuum-dried afterward. Then, via 5% NaOH (1.25N) in a solution of 12ml:1g (w/v) at 90°C over a period of 24 h, the deproteinization has been processing was initiated. The deproteinized product was collected and washed with distilled water, then deacetylated with stirring by adding 70% NaOH (17.5 N) with a ratio of 14ml:1g (w/v) at room temperature for 75 h. The deacetylated solid was collected and washed with distilled water, then dried in a vacuum, producing the required chitosan material.

Figure 2 displays the FTIR spectroscopic analysis of the chitosan which was generated. Two characteristic bands of chitosan peaking at 3447 cm^{-1} and 3258 cm^{-1}. The bands are attributed to NH stretching from non-acetylated 2-amino glucose primary amine (NH_2) in the chitosan chain. The

Table 5 Details of ingredients quantities for the studied mixes

Mix	Cement content kg/m^3	Sand kg/m^3	Dol kg/m^3	Water content kg/m^3	Superplasticizers kg/m^3	Chitosan kg/m^3	Steel fiber kg/m^3
Control	350	612	1228	180	–	–	–
SP-0.05%					17.5	–	–
CH-0.05%					–	17.5	–
SP-0.05%-SF-1%					17.5	–	78.0
CH-0.05%-SF-1%					–	17.5	78.0

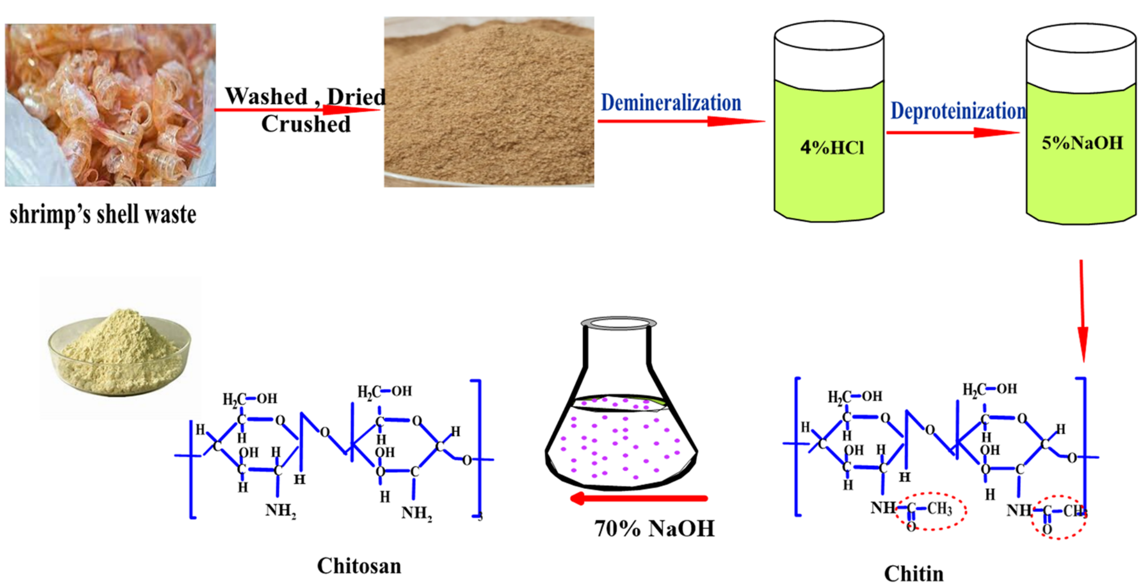

Fig. 1 The extraction of chitosan material from shrimp's shell waste

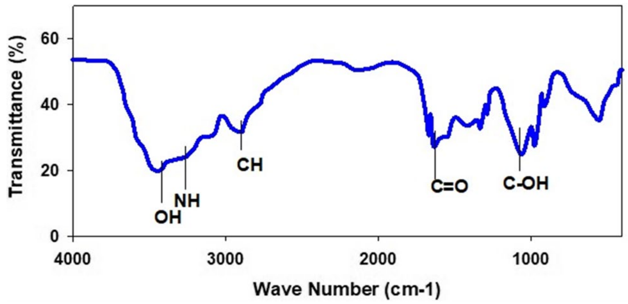

Fig. 2 Infrared spectra of chitosan prepared from shrimp shells

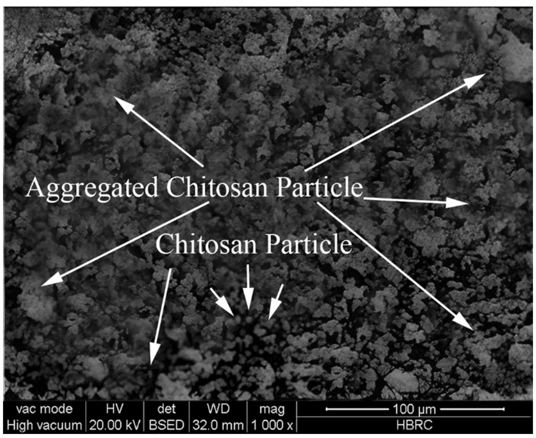

Fig. 3 SEM of chitosan prepared from shrimp shells

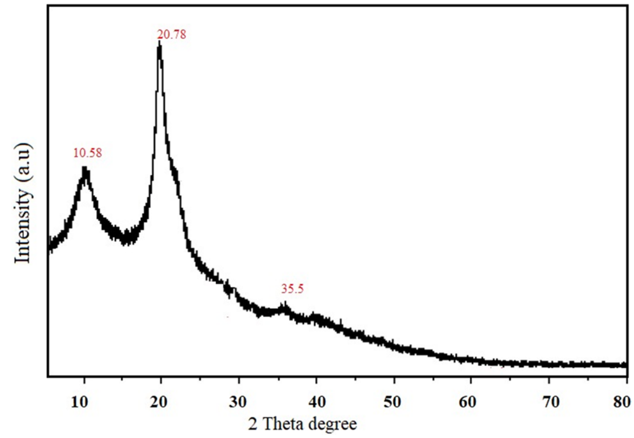

Fig. 4 X-ray diffraction pattern of chitosan prepared from shrimp shell wastes

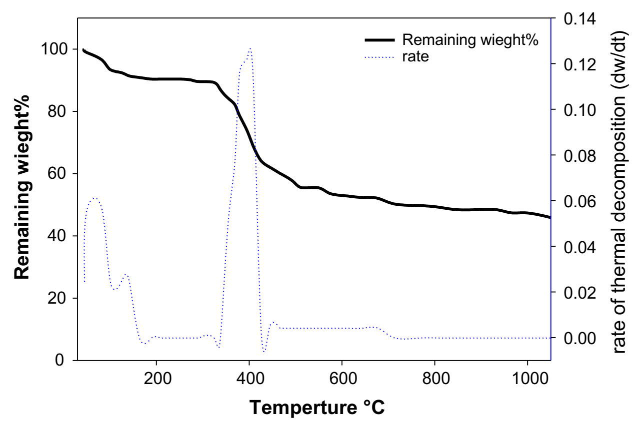

Fig. 5 TGA thermograms of chitosan prepared from shrimp shell wastes

minor band centered around 3447 cm^{-1} can be assigned to OH stretching, 2922 cm^{-1} (C–H stretch), and 1641 cm^{-1} (N–H bend) [20]. Additionally, stretching vibrations of the alcohol groups are seen at 1317.2 cm^{-1} and 1156.9 cm^{-1} for the C–N stretching vibration and at 1061.7 cm^{-1} and 1032.3 cm^{-1}. The peaks at 1641 cm^{-1} and 1598 cm^{-1} in the initial chitosan were attributed to the carbonyl stretching (C=O) of the secondary amide and primary amine bending (NH), respectively [21].

The chitosan which is produced from jumbo shrimp shell wastes was analyzed by SEM, and the captured scan is shown in Fig. 3. It seems from the captured scan that the surface of the chitosan has a pore structure with a rough surface. A continuous and uniform porous structure is an interaction feature between the chitosan molecules.

The produced chitosan from shrimp shell wastes is subjected to X-ray diffraction analysis as shown in Fig. 4, it produces a diffractogram with three peaks at 10.58, 20.78, and 35.5 that are indicative of crystalline areas According to the previous studies, [22–24], the two distinctive broad diffraction peaks at 2 around 10.58 and 20.78, which are typical fingerprints of semi-crystalline chitosan and may indicate crystalline form. However, broad bands appear at the angle 2 = 35°, indicating that the structure is ordered in the amorphous part.

Chitosan was subjected to TGA analysis in an inert/reducing environment to assess the effects of pyrolysis on its structural characteristics. Figure 5 shows the TGA profile, which presents two main weight losses the first one at 100 °C due to the loss of physisorbed water molecules (7.5 wt.%, i.e., chitosan is a hydro scope material, and the second one in the 250–400 °C range due to the degradation of the structure of the polysaccharides with the formation of volatiles products. According to previous studies, water, carbon dioxide, carbon monoxide, NH_3, and N-containing heteroaromatic compounds are formed during the breakdown of chitosan, principally pyrazines, pyridines, and pyrroles. The curve profile also demonstrates the very slow degradation at higher temperatures (beyond 450 °C), with the release of CH_4 and subsequent development of a carbonaceous residue (27% by weight) at 1000 °C by a

Table 6 Properties of chitosan

Test	Results
Color	Yellow
Shape	Powder
Color after acidic solution	Faint yellow
pH	7.6
Viscosity	150–200 mPa.s
Bulk denstity	0.15–0.3 gm/cm^3
Molecular weight	300 KDa
Chemical composition	
C	29.10%
H	3.60%
N	5.41%
Degree of deacetylation	77.51%

dehydrogenation process [20]. Table 6 shows the properties of chitosan.

Concrete mixing, curing, and testing

Chitosan was prepared with deionized water (0.05% by weight of cement content) with an ultrasonic tip for 15 min at 100W, chitosan powder 2.5 g dispersed in 1000 ml deionized water. The suspensions were mechanically stirred while cement powder was added to the aqueous medium. The concrete ingredients were transported to start the mixing process. Coarse aggregate is put into a concrete mixer followed by fine aggregate. The cement was mixed with a certain admixture (superplasticizer or chitosan) and water and then put into the concrete mixer. In order to prevent segregation or honeycomb, a vibrator rod was used to obtain well-compacting concrete. After filling the standard mold with fresh concrete, a trowel was used to smooth and level the surface of the samples. All molds were disassembled after twenty-four hours, and then the concrete underwent water curing till the day of the testing to prevent the evaporation of the water, which is necessary for cement hardening (evaporation generates cracks in the concrete, especially in the early time after pouring, where the strength of the cohesiveness of the cement is still insufficient to resist those cracks). In fact, the curing process was conducted by immersing the concrete samples in the water tank as the traditional method for all concrete samples to compare the results of different concrete mixes under the same curing conditions. It is worth mentioning that the steel fibers in certain concrete mixes were added in three batches to reduce the possibility of balling. Ultimately, the concrete standard samples (cubes, cylinders, and prisms) were tested after seven and twenty-eight days, to obtain the compressive strength, indirect tensile strength, and flexural strength, respectively according to [25]. In detail, a universal testing machine (2000 kN capacity) was used to test the cubes under the effect of axial compressive forces, and the cylinders were tested horizontally to determine the indirect tensile strength. Furthermore, the prisms were tested by test setup to achieve the dividing of the machine load into two points load to obtain a pure bending moment without shear forces in the region of the maximum bending moment.

Result, analysis, and discussion

Fresh concrete properties

In this section, the slump test was carried out to study the behavior of chitosan on fresh concrete Properties. The slump test was performed to evaluate the effect of the admixtures (superplasticizers or chitosan) and fiber content in the concrete mixture on the consistency. It seems from Fig. 6 that the slump value for SP-0.05% and SP-0.05%-SF-1% mixes was increased by 94.64% and 53.57%, respectively in comparison to the control mix because the water covered the surface of the superplasticizer particles which lead to decreasing the friction between the concrete mixture. Moreover, the slump value for CH-0.05% and CH-0.05%-SF-1% decreased by 14.29% and 23.21%, respectively compared to the control mix. As can be observed, adding chitosan to fresh concrete increased its viscosity and had a modest thickening effect, which caused a decrease in fluidity. The obtained slump values comply with the outcomes attained and support the predictions [4]. Also, there was a decrease in a slump value by 10.42% in the case of CH-0.05%-SF-1% concrete mix when compared to CH-0.05% concrete mix. Along the same lines, the slump value decreased by 21.10% for the SP-0.05%-SF-1% concrete mix compared with the SP-0.05% concrete mix. Hence, the steel fiber content has shown to be

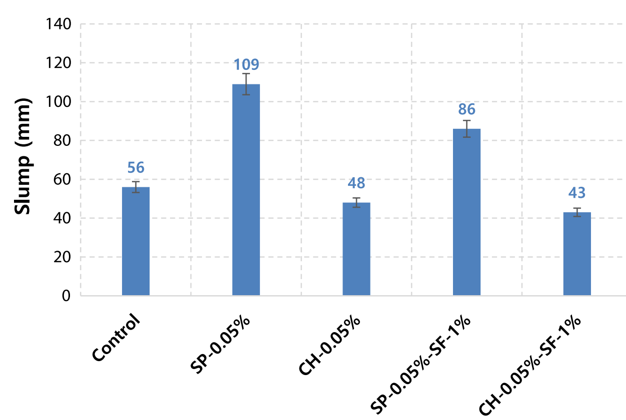

Fig. 6 Effect of the addition of admixtures on the slump values of fresh cement mortars

a great influence on concrete mobility reducing the slump values. The fibers act as a barrier to coarse aggregate movement reducing the material's mobility. However, by using chitosan in the concrete mix as a natural admixture, the slump decreased, so, the workability decreased and a delay in cement hydration was observed but still, superplasticizer admixture achieved the desired slump values.

Mechanical properties of hardened concrete

Density is one of the most essential concrete features because it integrates the mechanical properties of concrete, such as compressive strength, indirect tensile strength, and flexural strength. The results of the concrete samples were investigated to ensure quality control and to determine the degree of confidence in the obtained results. However, any result value of the tested sample is less than or more than 25% of the value of the mean results (the repeated three samples) at the same testing time excluded according to [26]. In fact, this did not happen in all the tested mixes. Table 7 shows the test results for concrete samples (three repeated samples). It was noted that the percentage of strengths variation ranged from 2.26 to 4.91% (less than 5%) which means the confidence is more than 95%.

The direct tensile strength may be calculated as 0.85 of the indirect tensile strength (f_s), or 0.6 of flexural strength (f_f), which is well-known according to [26]. Therefore, the indirect tensile strength (f_s) ranged from 10.75 to 13.62% of concrete compressive strength (f_{cu}). As well as, the ratio of flexural strength (f_f) to compressive strength (f_{cu}) ranged from 21.50 to 29.81%. Also, noted that the direct tensile strength may be taken as 10.92% (average value based on indirect tensile strength) of the compressive strength (f_{cu}) or as 15.25% (average value based on flexural strength) of the compressive strength (f_{cu}), see Table 8 which represent the mean strengths for the concrete mixes.

Table 7 Test results for all concrete samples

Concrete mix	Mechanical properties	Testing time	Sample (1)	Sample (2)	Sample (3)	Range (MPa)	% of variation
Control	Compressive strength (MPa)	7 Days	20.05	20.80	20.35	0.75	3.68
		28 Days	30.23	30.64	31.23	1.00	3.26
	Indirect tensile strength (MPa)	7 Days	2.45	2.39	2.36	0.09	3.75
		28 Days	3.35	3.22	3.33	0.13	3.94
	Flexural strength (MPa)	7 Days	4.47	4.32	4.41	0.15	3.41
		28 Days	6.76	6.55	6.49	0.27	4.09
SP-0.05%	Compressive strength (MPa)	7 Days	22.68	23.81	23.11	1.13	4.87
		28 Days	32.58	31.34	31.18	1.40	4.42
	Indirect tensile strength (MPa)	7 Days	2.91	2.95	2.84	0.11	3.79
		28 Days	4.09	4.01	3.90	0.19	4.75
	Flexural strength (MPa)	7 Days	5.35	5.23	5.32	0.12	2.26
		28 Days	8.06	7.83	8.11	0.28	3.50
CH-0.05%	Compressive strength (MPa)	7 Days	24.10	23.58	24.62	1.04	4.32
		28 Days	33.05	33.01	32.04	1.01	3.09
	Indirect tensile strength (MPa)	7 Days	3.27	3.18	3.15	0.12	3.75
		28 Days	4.39	4.49	4.32	0.17	3.86
	Flexural strength (MPa)	7 Days	6.32	6.20	6.08	0.24	3.87
		28 Days	9.00	9.25	9.35	0.35	3.80
SP-0.05%-SF-1%	Compressive strength (MPa)	7 Days	25.60	26.80	26.20	1.20	4.58
		28 Days	36.00	35.80	34.70	1.30	3.66
	Indirect tensile strength (MPa)	7 Days	3.57	3.48	3.45	0.12	3.43
		28 Days	4.81	4.60	4.69	0.21	4.47
	Flexural strength (MPa)	7 Days	6.53	6.36	6.31	0.22	3.44
		28 Days	9.44	9.25	9.51	0.26	2.77
CH-0.05%-SF-1%	Compressive strength (MPa)	7 Days	27.41	28.33	27.96	0.92	3.30
		28 Days	36.00	36.89	37.81	1.81	4.91
	Indirect tensile strength (MPa)	7 Days	3.86	3.81	3.73	0.13	3.42
		28 Days	5.22	5.10	4.98	0.24	4.71
	Flexural strength (MPa)	7 Days	7.93	7.79	7.98	0.19	2.41
		28 Days	10.80	11.10	11.10	0.30	2.73

Table 8 The mean test results for different mixes after seven and twenty-eight days

Concrete mix	Density (t/m^3)	Age (Days)	Compressive Strength (MPa)—f_{cu}	Indirect Tensile Strength (MPa)—f_s	Flexural Strength (MPa)—f_f	f_s/ f_{cu} (%)	f_f/ f_{cu} (%)	0.85 f_s (MPa)	0.6f_f (MPa)	0.85f_s/ f_{cu} (%)	0.6f_f/ f_{cu} (%)
Control	2.32	7	20.4	2.4	4.4	11.76	21.57	2.04	2.64	10.00	12.94
		28	30.7	3.3	6.6	10.75	21.50	2.81	3.96	9.14	12.90
SP-0.05%	2.33	7	23.2	2.9	5.3	12.50	22.84	2.47	3.18	10.63	13.71
		28	31.7	4.0	8.0	12.62	25.24	3.40	4.80	10.73	15.14
CH-0.05%	2.34	7	24.1	3.2	6.2	13.28	25.73	2.72	3.72	11.29	15.44
		28	32.7	4.4	9.2	13.46	28.13	3.74	5.52	11.44	16.88
SP-0.05%-SF-1%	2.42	7	26.2	3.5	6.4	13.36	24.43	2.98	3.84	11.35	14.66
		28	35.5	4.7	9.4	13.24	26.48	4.00	5.64	11.25	15.89
CH-0.05%-SF-1%	2.45	7	27.9	3.8	7.9	13.62	28.32	3.23	4.74	11.58	16.99
		28	36.9	5.1	11.0	13.82	29.81	4.34	6.60	11.75	17.89

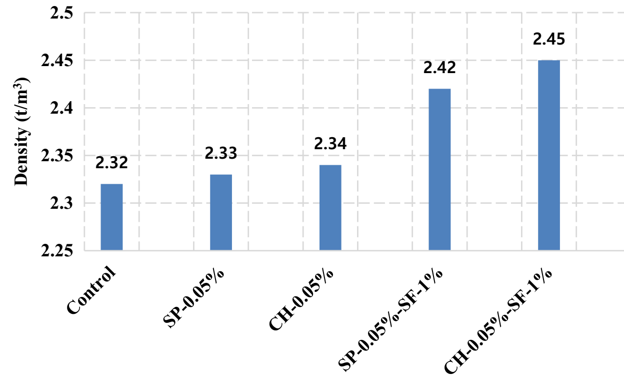

Fig. 7 Density for different mixes

Density

The presence of superplasticizer and chitosan affects the hardened density of the concrete standard samples. Table 8 recorded densities for all concrete mixes in this study. From Fig. 7 the concrete density increases with the presence of chitosan and superplasticizer in concrete. A 4.49% difference in density was observed between concrete mixes CH-0.05% and CH-0.05%-SF-1%. A 3.72% difference was observed between concrete mixes SP-0.05% and SP-0.05%-SF-1%. The admixtures based on a natural polymer like chitosan in the cement compositions allow for a reduction in the total volume of the concrete pores and have a positive effect on the nature of their distribution which is confirmed by [27]. Additionally, their ability to occupy space in the concrete leads to a slight increase in the density of concrete. It is also necessary to consider chitosan is insoluble in alkaline and calcium ion-rich environments, leading to entanglement and an increase in viscosity. OH and NH_2 groups undergo ionization under alkaline conditions, forming negatively charged O^- and NH^- groups, with Chitosan having the largest degree of deacetylation resulting in a larger charge density confirmed by [28]. All steel fibers concrete mixes have a higher concrete density compared with concrete mixes without steel fiber because steel fibers have a higher density (7.85t/m3) which leads to an increase in the overall concrete density.

Compressive strength

Figure 8 shows the mean compressive strength and age for different mixes. It noted that compressive strength increased by 13.73% and 18.14% (after seven days), 3.25%, and 6.51% (after twenty-eight days) for concrete mixes SP-0.05% and CH-0.05%, respectively compared with control concrete mixes. Further, the compressive strength increased by 28.43%, and 36.76% (after seven days), 15.63%, and 20.19% (after twenty-eight days) for concrete

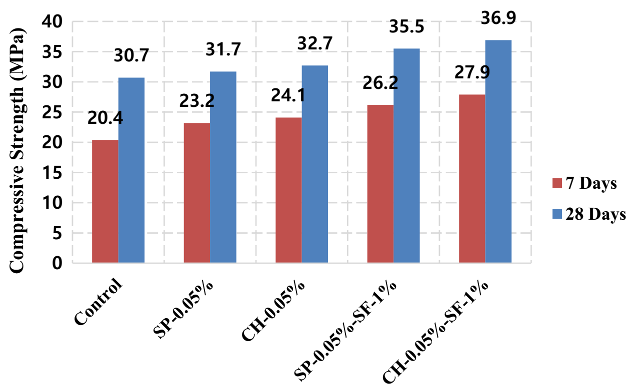

Fig. 8 Compressive strength and age for different mixes

mixes SP-0.05%-SF-1%, and CH-0.05%-SF-1%, respectively in comparison to control concrete mix. The presence of steel fibers with 1% enhanced the compressive strength of concrete mixes SP-0.05%-SF-1% and CH-0.05%-SF-1% by 12.93% and 15.77%, respectively after seven days in comparison to mixes without the addition of steel fibers. Moreover, the increase of compressive strength after twenty-eight days was 11.99% and 12.84%, respectively regarding concrete mixes SP-0.05%-SF-1% and CH-0.05%-SF-1%, and those increasing in comparison to concrete mixes without steel fibers. Adding chitosan to the concrete mixes instead of superplasticizer enhanced compressive strength by 3.88% and 3.15% after seven and twenty-eight days, respectively. Along the same lines, the compressive strength increased by 6.49% and 3.94% after seven and twenty-eight days, respectively in the case of adding steel fibers. Hence, the results revealed that the compressive strength of concrete significantly increased from seven days to twenty-eight days, and this may be attributable to the effect of polymer film that formed on the cement surface, filling mortar pores and enhancing compressive strength which was confirmed by [29].

The addition of chitosan with 0.05% by weight of cement increased the OH, NH, and COOH groups and branched chains pierced the liquid phase to disperse the effects of copolymer particles among the cement particles, leading to a sharp increase in the total pore volume, and promoted the hydration process leading to improved strength of the cement at an early stage. Therefore, in the long-term operation, the cement concrete chitosan will be subjected to the migration of moisture, corrosive substances, and microorganisms so chitosan is the most practical method for decreasing the size of the porous spaces in cement compositions. The addition of steel fibers is capable of arresting cement paste and contributes to concrete ingredients as a one-unit mass which finally leads to an increase in the compressive strength of the concrete mix. The new functional materials based on chitosan combined with concrete lead to an increase in the alkalinity of concrete leading to a decrease in the rate of corrosion, an increase in mechanical strength, and increased sustainability. The addition of chitosan improved the pH and solubility of Portland cement and extended its setting times. Figure 9 shows the relationship between the mean compressive strength and time for different concrete mixes.

Indirect tensile strength

The mean indirect tensile strength and age for different mixes are represented in Fig. 10. It seems that indirect tensile strength increased by 20.83% and 33.33% (after seven days), 21.21%, and 33.33% (after twenty-eight days) for concrete mixes SP-0.05%, and CH-0.05%, respectively compared with control concrete mix. Also, increased by 45.83%, and 58.33% (after seven days), 42.42%, and 54.54% (after twenty-eight days) for concrete mixes SP-0.05%-SF-1%, and CH-0.05%-SF-1%, respectively in comparison to control concrete mix. After seven days, adding steel fibers with 1% significantly enhanced the indirect tensile strength of

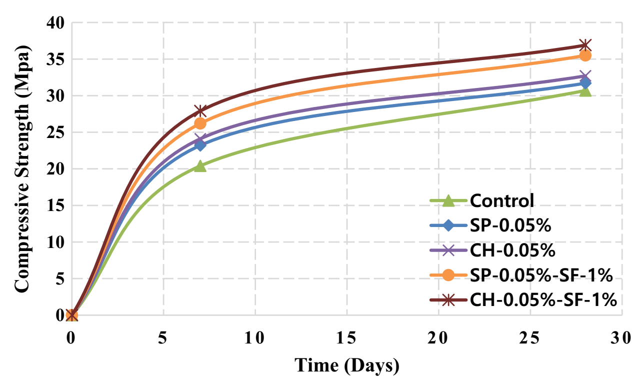

Fig. 9 Relationship between compressive strength and time for different mixes

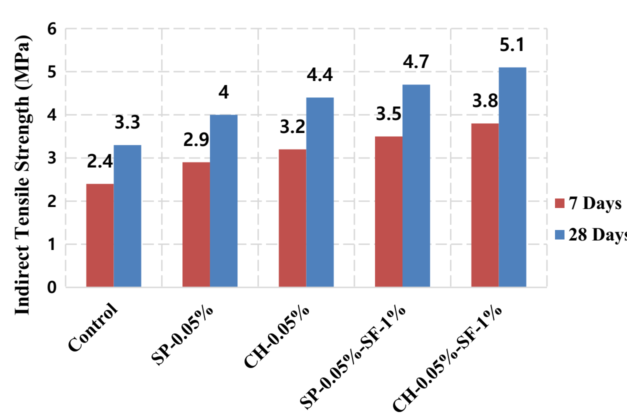

Fig. 10 Indirect tensile strength and age for different mixes

concrete mixes SP-0.05%-SF-1% and CH-0.05%-SF-1% by 20.69% and 18.75%, respectively but after twenty-eight days the indirect tensile strength increased by 17.50% and 15.91%, respectively for concrete mixes SP-0.05%-SF-1% and CH-0.05%-SF-1% in comparison to concrete mixes without steel fibers. Adding chitosan to concrete mixes instead of superplasticizer enhanced the indirect tensile strength by 10.34% and 10.00% after seven and twenty-eight days, respectively. Along the same lines for steel fiber mixes, the indirect tensile strength increased by 8.57% and 8.51% after seven and twenty-eight days, respectively.

Chitosan can put the water in a bound state, participate in further hydration processes of a binder, and enhance the curing process by swelling and actively calmative pores. Because of that, chitosan enhances the compressive strength of concrete mixes by achieving stronger mortar. The addition of steel fibers can arrest crack propagation and post-the-cracking mode. Those factors lead to an increase in the indirect tensile strength. Figure 11 presents the relationship between the mean indirect tensile strength of concrete mixes and time.

Flexural strength

The mean flexural strength and age for different mixes are represented in Fig. 12. It noted that flexural strength increased by 20.45% and 40.90% (after seven days), 21.21%, and 40.90% (after twenty-eight days) for concrete mixes SP-0.05%, and CH-0.05%, respectively in comparison to control concrete mix. Also, increased by 45.45%, 79.54% (after seven days), 42.42%, and 66.66% (after twenty-eight days) for concrete mixes SP-0.05%-SF-1%, and CH-0.05%-SF-1%, respectively in comparison to control concrete mix. The presence of steel fibers with 1% enhanced significantly the flexural strength of concrete mixes SP-0.05%-SF-1%, and CH-0.05%-SF-1% by 20.75%, and 27.42%, respectively after seven days. The increase of flexural strength after twenty-eight days was 17.50%, and 19.57%, respectively for concrete mixes SP-0.05%-SF-1% and CH-0.05%-SF-1%, and those increasing in comparison to concrete mixes without steel fibers. Adding chitosan to concrete mixes instead of superplasticizer enhanced the flexural strength by 16.98% and 15.00% after seven and twenty-eight days, respectively. Along the same lines for steel fiber mixes, the flexural strength increased by 23.44% and 19.57% after seven and twenty-eight days, respectively.

Figure 13 presents the relationship between the mean flexural strength of concrete mixes and time. The same trend appeared in the compressive and indirect tensile strengths and higher flexural strength noted at various ages of chitosan concrete mixes. The improvement in flexural strength behavior observed may be due to some sample homogeneity brought on by the complicated interaction of chitosan and its interactions with the hydrophilic paste of cement. Although chitosan is hygroscopic, the existence of functional groups such as NH, OH, and COOH in the substance ought to promote its absorption into the concrete matrix, which might compete with the hydration processes involved during the setting step. Since chitosan is chemically reduced (insoluble in water), chitosan acts as an internal fiber for concrete to

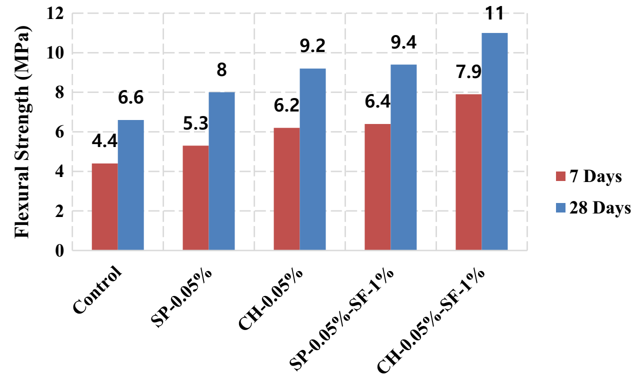

Fig. 12 Flexural strength and age for different mixes

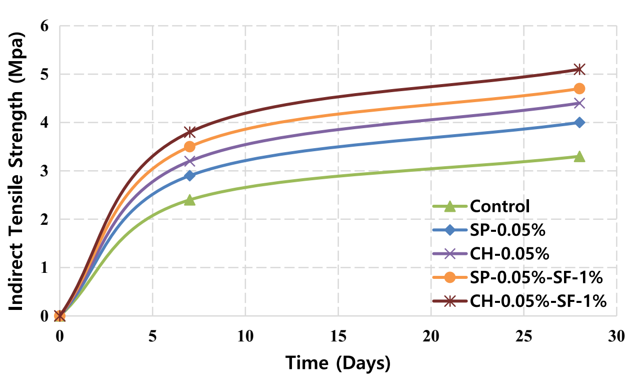

Fig. 11 Relationship between indirect tensile strength and time for different mixes

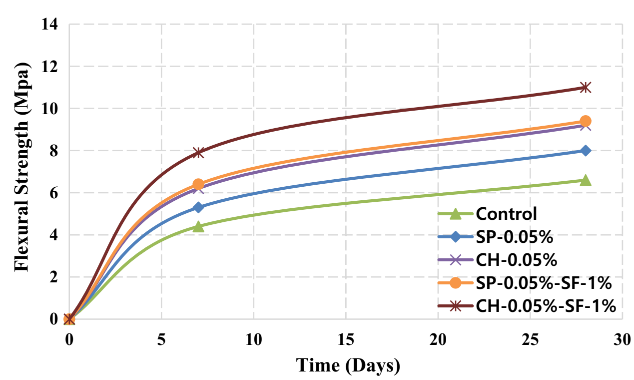

Fig. 13 Relationship between flexural strength and time for different mixes

enhance concrete internal properties and significantly record higher flexural strength. Also, the chemical functionalization of the concrete containing chitosan was a possible reason for improving the flexural strength due to bridge nano cracks and pores in addition to linking concrete elements internally with a resulting delay in crack propagation, which also complies with [30].

Microstructure

Figure 14 shows an SEM image of chitosan-doped, and hardened concrete at twenty-eight days. Due to the formation of a thicker and denser adsorbed on concrete, The SEM image of the chitosan-concrete sample shows that the hardened cement paste primarily has a loose porous structure with dense and has some rod-like crystals blocked in compact hardened cement paste of ring structure units and more short branched groups. On the other hand, chitosan concrete treatment encouraged the development of surfaces with debris and flaws as well as the occurrence of few cracks. When chitosan was added to the cement paste, it could strongly adhere to the cement surface because of the interactions of the multiple functional groups of OH, NH_2, and cement surface active groups (Al_2O_3, CaO, MgO, Fe_2O_3). Cement in a hydrous state mainly consists of tricalcium silicate C_3S (Ca_3SiO_5), dicalcium silicate C_2S (Ca_2SiO_4), tricalcium aluminate C_3A ($Ca_3Al_2O_6$), tetra calcium alumina ferrite C_4AF ($Ca_4AFe_2O_7$), as well as a small amount of clinker sulfate (Na_2SO_4, K_2SO_4) and gypsum ($CaSO_4.2H_2O$). In the hydration process, C_3A, C_4AF, C_3S, and C_2S will carry out a complex hydration reaction to form ettringite ($Ca_6Al_2(SO4)_3(OH)_{12}.26H_2O$), ($Ca_4Al_2(OH)_{12}.SO_4.6H_2O$), calcium hydroxide ($Ca(OH)_2$, CH), [31]. Thus, the amino groups (–NH_2) and hydroxyl groups (–OH) will be the dominant functional groups on the chitosan surface of the possible interactions in Fig. 15

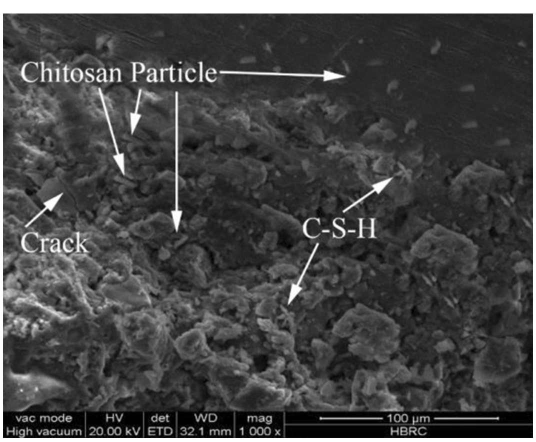

Fig. 14 SEM images of chitosan-based concrete

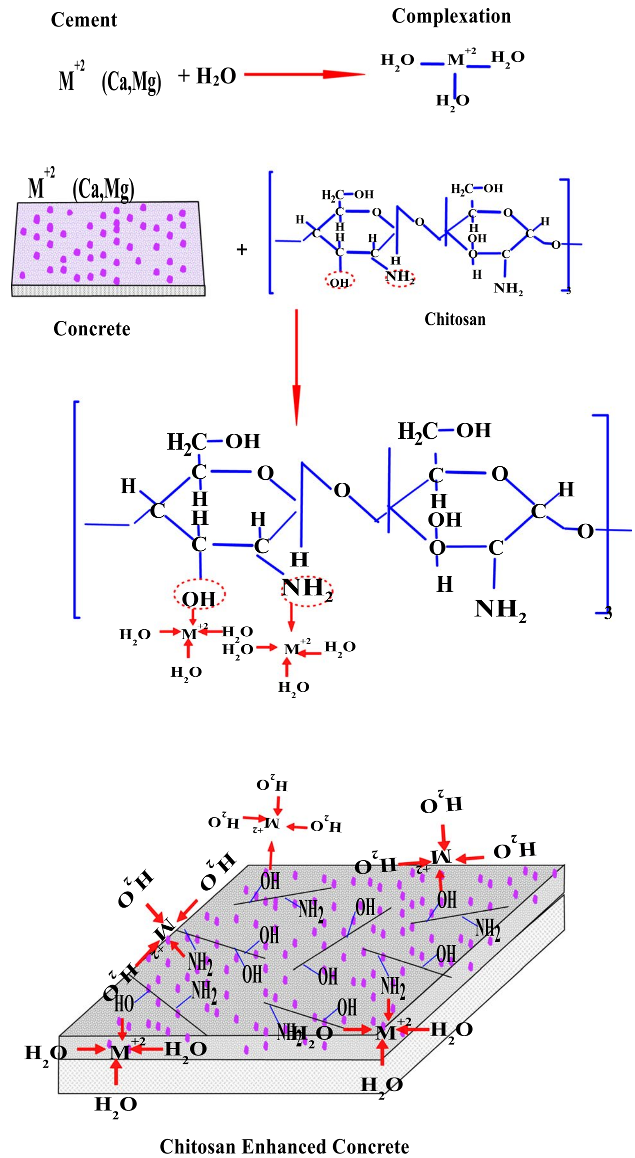

Fig. 15 The working mechanism of chitosan on the concrete surface

and states of chitosan with cement might exist as follows: (1) intercalation or the formation of an organo-mineral phase (OMP); the formation of OMP often occurs in the existence of cationic, anionic, and nonionic polymers that can form through micellization, intercalation, or coprecipitation. (2) adsorbed chitosan on the surface of cement particles which helps disperse cement agglomerates. The addition of chitosan in the current study increased the concrete alkalinity because chitosan raises the pH of the chitosan solution by protonating the amino groups in its amino acids [32]. These cement hydration products grow and aggregate together to form their unique structures, which are then affixed to concrete structures.

Conclusions

This study showed an innovative method to produce concrete mixed with natural polymers such as chitosan instead of chemical admixtures. To maximize the use of the research idea, steel fibers were added to further improve the mechanical properties. Based on the experimental study, the results showed powerful and ambitious conclusions and can be summarized in specific points as follows:

1. Compared to the control mix, the usage of chemical admixtures increased the slump value by 94.64% and increased by 53.57% in the case of adding steel fibers with 1%. On the contrary, if chitosan was used, the slump value decreased by 14.29% and decreased by 23.21% in the case of adding steel fibers with 1%. Moreover, adding 1% steel fibers in concrete mixes recorded a decreasing rate in a slump value by 10.42%, and 21.10% for chitosan and chemical admixture concrete mixes, respectively.
2. Chemical admixtures and chitosan concrete mixes enhanced the concrete density by trivial values of 0.43%, and 0.86%, respectively compared with the control mix. Therefore, adding steel fibers with 1% increases the concrete density by 4.31%, and 5.60% for chemical admixtures and chitosan concrete mixes, respectively in comparison to the control mix. The increasing rate due to adding steel fiber with 1% is 3.86%, and 4.70% in comparison to concrete mixes without steel fibers.
3. Compared to the control mix, the compressive strength increased by 13.73% and 18.14% (after seven days), 3.25%, and 6.51% (after twenty-eight days) for chemical admixture, and chitosan concrete mixes, respectively. Further, the compressive strength increased by 28.43%, and 36.76% (after seven days), 15.63%, and 20.19% (after twenty-eight days) for chemical admixture, and chitosan steel fiber concrete mixes, respectively. Adding steel fibers with 1% enhanced the compressive strength by 12.93% and 15.77% after seven days and increased by 11.99% and 12.84% after twenty-eight days for chemical admixture, and chitosan steel fiber concrete mixes, respectively in comparison to concrete mixes without steel fibers.
4. Adding chitosan to the concrete mixes instead of superplasticizer enhanced compressive strength by 3.88% and 3.15% after seven and twenty-eight days, respectively. Along the same lines, the compressive strength increased by 6.49% and 3.94% after seven and twenty-eight days, respectively in the case of adding steel fibers.
5. Compared to the control mix, the indirect tensile strength increased by 20.83% and 33.33% (after seven days), 21.21%, and 33.33% (after twenty-eight days). Also, increased by 45.83%, and 58.33% (after seven days), 42.42%, and 54.54% (after twenty-eight days). Furthermore, after seven days, adding steel fibers with 1% significantly enhanced the indirect tensile strength by 20.69% and 18.75% but after twenty-eight days increased by 17.50% and 15.91%, for chemical admixture, and chitosan steel fiber concrete mixes, respectively in comparison to concrete mixes without steel fibers.
6. Adding chitosan to concrete mixes instead of superplasticizer enhanced the indirect tensile strength by 10.34% and 10.00% after seven and twenty-eight days, respectively. Along the same lines for steel fiber mixes, the indirect tensile strength increased by 8.57% and 8.51% after seven and twenty-eight days, respectively.
7. Compared to the control mix, the flexural strength increased by 20.45% and 40.90% (after seven days), 21.21%, and 40.90% (after twenty-eight days). Also, increased by 45.45%, 79.54% (after seven days), 42.42%, and 66.66% (after twenty-eight days) for chemical admixtures and chitosan concrete mixes, respectively. The presence of steel fibers with 1% enhanced significantly the flexural strength by 20.75%, and 27.42%, after seven days and increased by 17.50%, and 19.57% after twenty-eight days, respectively for chemical admixture, and chitosan steel fiber concrete mixes, respectively in comparison to concrete mixes without steel fibers.
8. Adding chitosan to concrete mixes instead of superplasticizer enhanced the flexural strength by 16.98% and 15.00% after seven and twenty-eight days, respectively. Along the same lines for steel fiber mixes, the flexural strength increased by 23.44% and 19.57% after seven and twenty-eight days, respectively.
9. The SEM images show that the structure is dense and has some rod-like crystals blocked in compact hardened cement paste and a more compact structure. Also, the addition of chitosan allows for a reduction in the total volume of pores and has a positive effect on the strength characteristics of the cement compositions in comparison with synthetic polymers.

Therefore, even though these preliminary findings still require important improvement, the research provided a helpful starting point for developing the production of sustainable enhanced cementitious composites, such as biopolymer cement. Also, it's recommended to increase the percentage of chitosan in future research and add chitosan in a powder form as an additive for cement.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent For this type of study, formal consent is not required.

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