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Effects of Green Mussel Shells (*Perna viridis*) and Chitosan Extracted from Milkfish (*Chanos chanos*) Scales on the Compressive Strength of Mortar and Concrete

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Abstract: It is estimated that in the construction industry, cement production contributes to 7% of global CO_2 emissions. Because of this, alternative materials, including biological resources and wastes, are being explored to determine their viability as substitutes for conventional concrete aggregates. This study investigates the feasibility of using green mussel shells (GMSs) as a partial cement replacement and chitosan derived from milkfish scales as an additive in concrete. Addressing environmental concerns tied to cement production, the research evaluates the potential of GMSs and chitosan to enhance mortar and concrete properties. This study was conducted in two phases: phase one focused on mortar with varying percentages of GMSs (0%, 5%, 10%, 15%, and 20%) and chitosan (0%, 0.25%, 0.50%, 0.75%, and 1%), while phase two applied the phase one results that resulted in the highest compressive strength of concrete. The results indicate that 10% GMS and 0.25% chitosan improved mortar strength by 38.74%, although high GMS levels reduced workability. In concrete, 10% GMS without chitosan decreased compressive strength by up to 47% due to magnesium impurities in GMSs, verified by FTIR analysis. This study highlights GMSs' and chitosan's potential but emphasizes impurity management for its application feasibility.

Keywords: green mussel shells; chitosan; waste utilization in concrete; sustainable construction; biological wastes

Academic Editors: Zoltán Lakner and Anita Boros

Received: 7 November 2024
Revised: 22 December 2024
Accepted: 28 December 2024
Published: 31 December 2024

Citation: Lejano, B.; Elevado, K.J.; Chua, L.M.; Cuartero, S.R.; Fabian, V.P.; Rase, A.Y. Effects of Green Mussel Shells (*Perna viridis*) and Chitosan Extracted from Milkfish (*Chanos chanos*) Scales on the Compressive Strength of Mortar and Concrete. *Resources* **2025**, *14*, 9. https://doi.org/10.3390/resources14010009

1. Introduction

Annually, the world produces roughly 1.6 billion tons of cement, responsible for approximately 7% of the carbon dioxide released into the atmosphere. As such, while cement is an indispensable material with which plenty of construction projects are completed, it is also responsible for a considerable amount of pollution and copious amounts of greenhouse gases released into the atmosphere [1]. Aside from this, cement production is considered one of the most energy-intensive in the manufacturing industry, requiring around 3.2–6.3 GJ of thermal energy per ton of clinker [2]. The aforementioned concerns have compelled the construction industry to shift towards sustainable practices. Various studies have explored the use of alternative materials, such as waste products in cement, and incorporating them in the production of concrete while adhering to established standards.

Green mussel shells (GMSs), locally referred to in the Philippines as Tahong, have garnered attention as a potential supplementary cementitious material (SCM) obtained from waste. Green mussels (*Perna viridis*) are extensively cultivated in Southeast Asia, including the Philippines, but the challenge of disposing of their shells has become significant. Southeast Asia generates approximately 18.75% of global shellfish waste [3,4]. In the Philippines alone, shells constitute 40% of the 250,000 metric tons of seafood waste produced annually, where the majority end up in landfills [5].

GMSs are rich in calcium carbonate (CaCO3), which can be converted to calcium oxide (CaO) or lime through heating. Because of this, GMSs were found to be a potential partial substitute for cement since 60% of cement is composed of lime [6]. This property is responsible for the development of the strength and soundness of cement. Studies have shown that GMSs can enhance the compressive strength of concrete from 21.32 MPa to 31.62 MPa but may decrease its workability, particularly at lower water/cement ratios. However, the use of green mussel shells as partial aggregates of concrete in high quantities was found to have a negative effect on its overall strength [4,6,7]. The decrease in strength was attributed to the reaction of the excess lime with the silica present in the mix. Such a reaction leads to major concerns regarding the durability of concrete and concrete structures [8]. As the lime reacts with the silica, the creation of ASR gel causes problems for the concrete to develop, such as cracking. This is due to the gel created by the reaction absorbing moisture from the atmosphere, and with the moisture absorbed, the gel slowly swells and increases its size, putting the concrete under increased tensile stress [9]. In addition, the periostracum of the green mussel shell contains magnesium, and previous studies found that magnesium, with unreacted phosphate, causes the expansion of cement in concrete, leading to lower strength as well as a higher porosity [10,11]. In a previous study, increased magnesium content in concrete was found to increase concrete deterioration, where corrosion and concrete peeling were observed on the concrete samples, particularly at its edges [12].

Another promising material for concrete production is chitosan, a natural polymer derived from the exoskeletons of crustaceans, fish scales, insects, and fungi. In the Philippines, milkfish (*Chanos chanos*) yield higher production than any other fish since they have the ability to adapt to different cultural conditions [13,14]. The amount of fish scales produced can become a source of chitosan. In the construction industry, chitosan, a biodegradable and natural source, can be used in ready-mixed concrete as an admixture. Studies have shown that chitosan can increase the fresh unit weight of concrete while decreasing its air content. When used in concrete production, it can also increase both the early and late stages of concrete compressive strength. Additionally, natural admixtures such as chitosan can decrease the cost of concrete, as chitosan does not require an immense amount of work and energy for production while also decreasing the corresponding environmental emissions [15].

Previous studies have also shown that chitosan exhibits some efficiency as a plasticizer in concrete. Increased performance was observed in terms of application and fluidity of cement paste compared to Portland cement or polycarboxylate plasticizers while also exhibiting a strong retarding effect when it comes to cement hydration. In addition, chitosan was found to effectively lower the water content of the fresh concrete and produced a greater 28-day compressive strength at about 1.12% for the concrete with the chitosan additive compared to the control setup of concrete without any additives and admixture. It was also determined that the chitosan samples used, when compared to a commonly used plasticizer, had a lower slump but a longer setting time due to water retention, as it took around 90 min for the plasticizer to have a reduction in its slump, while the chitosan took around 120 min before its slump was reduced [16]. Meanwhile, another study found that chitosan-derived plasticizers increased the 28th-day compressive strength of concrete at 13.3% and 10.9% with a 0.69 water/cement ratio. The increase in compressive strength due to the addition of chitosan may be attributed to factors such as an increase in unit weight leading to a reduction of air content. Furthermore, it has been mentioned that the water-reducing properties of chitosan significantly increase the compressive strength of concrete [15]. These similar studies served as a framework for this study that utilized chitosan from milkfish scales as an admixture for concrete.

The utilization of waste products as an intervention in construction materials has been studied broadly in the civil engineering field to help reduce its negative impact on the environment. GMSs and fish scales are two of the most discarded wastes in the seafood section, and studies have shown that GMS contains lime and chitosan can adsorb water. Because of this, the feasibility of GMSs as a partial cement replacement and milkfish scales-derived chitosan as an additive to improve the properties of concrete was investigated in this study to optimize waste utilization within the civil engineering industry.

Various research regarding the application of GMSs and fish scales-derived chitosan in improving the properties of concrete have been studied independently in the past. Some studies have utilized GMSs as a partial replacement for cement and chitosan as an admixture [6,15]. However, the likelihood of the availability of resources, where both materials are applied to concrete at the same time and milkfish scales are used as a source of chitosan, is minimal. As such, this research aids in understanding the effects of GMSs and milkfish scales-derived chitosan on the properties of concrete, such as workability and compressive strength. This study addresses certain research gaps in concrete by investigating the simultaneous use of these biological waste materials in concrete production.

2. Materials and Methods

The study carried out a two-phase experiment, namely Phase 1 for the mortar testing, followed by Phase 2 for the concrete testing. The experiment started with sourcing out the seafood waste materials, GMSs, and milkfish scales. Ordinary Portland cement (OPC) was utilized in both experiments, while aggregates varied. In particular, this study used OPC by Republic Cement. In Phase 1, Ottawa sand was utilized following ASTM C109-20 [17], while standard sand and gravel were procured from a local construction supplier for the concrete phase. Figure 1 shows the research methodology, supplemented by the discussions in the succeeding sub-parts of this article.

Tests were performed to identify their physical properties according to ASTM. The results are presented in Table 1. Aside from this, equipment and materials such as a Digi Mortar Mixer, 2″ × 2″ Phenolic Board Molds, Half Bagger Concrete Mixer, 4″ × 8″ Cylindrical Molds, and a Universal Testing Machine (UTM) were employed to mix, mold, and test the mortar and concrete specimens.

Table 1. Physical properties of sand and gravel.

Property	ASTM Designation	Sand	ASTM Designation	Gravel
Fineness Modulus	C33-18 [18]	2.41	C33-18	7.67
Moisture Content (%)	C566-19 [19]	7.87	C566-19	0.39
Specific Gravity	C128-22 [20]	2.62	C127-15 [21]	2.85
Absorption (%)	C128	3.93	C127	0.99
Dry Unit Weight (kg/m^3)		-	C29-23 [22]	1553.44

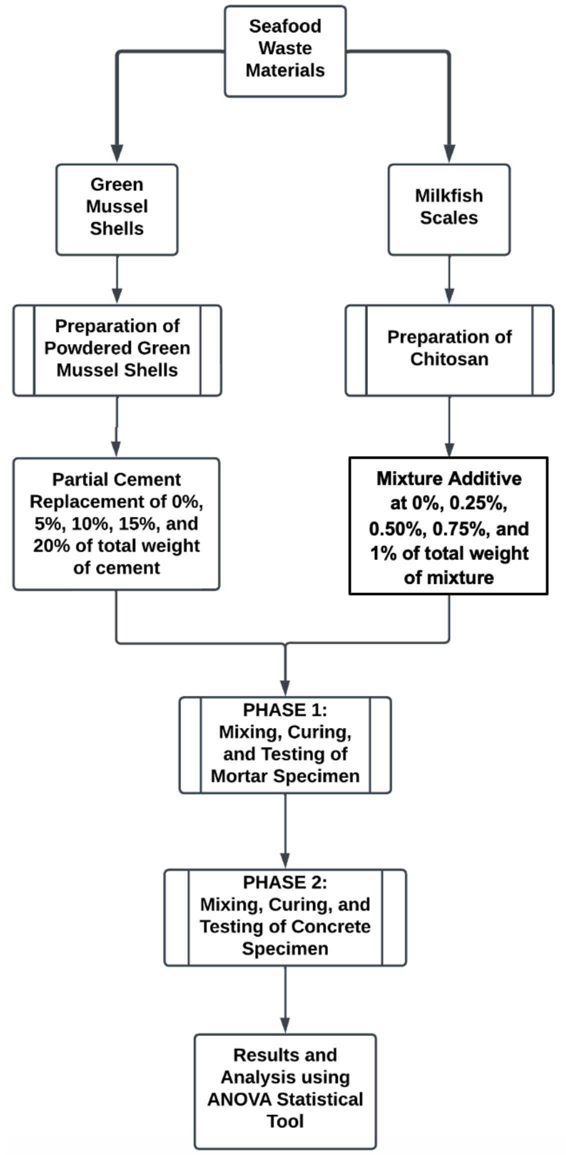


Figure 1. Research methodology.

2.1. Collection and Processing of Green Mussel Shells

Before mixing, GMSs were procured from Kaymig Seafood Grill and Restaurant in Dampa Seaside Market in Pasay City, Philippines. The shells were heated in a pan and stirred for three hours, ensuring they were brittle enough for processing. Subsequently, they were pulverized into consistent powdered form using a mortar and pestle or a hammer until they passed through a number 50 sieve or 300-micrometer diameter opening. The ones that passed through the sieve were used in the experiment, while others underwent the process again. Figures 2a, 2b, and 2c show the experimental photos when the GMSs were heated, pulverized, and sieved, respectively.

(**a**) (**b**) (**c**)

Figure 2. Experimental photos when (**a**) heating, (**b**) pulverizing, and (**c**) sieving the green mussel shells.

2.2. Collection of Milkfisk Scales and Extraction of Chitosan

The milkfish scales were also obtained from a wet market in Libertad, Pasay City, Philippines. The milkfish scales were cleaned using distilled water and dried using the oven for 24 h and sat for another 24 h at room temperature, ensuring improved quality of the extracted chitosan. Demineralization was performed by submerging the dried scales in a 2% HCl solution for 16 h at room temperature with a solid solvent ratio of 1:5 (weight-to-volume). The residue was washed until it reached neutral pH and was oven-dried for 12 h. Subsequently, deproteinization was executed by submerging the scale residue in a 4% NaOH solution for 20 h at room temperature with a solid-to-solvent ratio of 1:5. The residue was washed until it reached neutral pH and was oven-dried for 12 h. The last step for extraction involved submerging the residue for another 20 h in a 4% NaOH solution for deacetylation, but at 60 $\pm$ 5 °C with a solid/solvent ratio of 1:10. The residue was washed and oven-dried for 4 h at about 40 $\pm$ 5 °C. Figures 3a and 3b display the deacetylation and straining of the chitosan samples, respectively.

(**a**) (**b**)

Figure 3. Experimental photos of (**a**) deacetylation of chitosan samples and (**b**) straining of chitosan samples for drying.

The characterization of the chitosan involved determining its percentage yield and Fourier Transform Infrared Radiation (FTIR) graph. The percentage yield was determined to show how much chitosan yielded from the fish scales using the formula presented in Equation (1):

$$\text{Yield (\%)} = (\text{Amount of chitosan obtained})/(\text{Amount of fish scales used}) \times 100\%, \quad (1)$$

The FTIR helped determine the different functional groups or compounds present in the chitin, which aided in determining what specific component or group might affect the properties of the mortar and concrete produced.

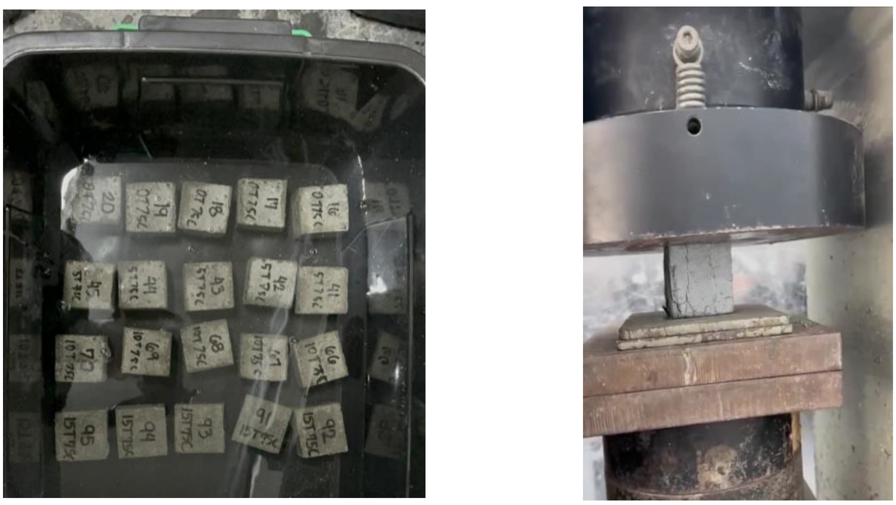
2.3. Processing and Testing of Mortar Mix

In the first phase of the study, the mix design of the mortar was developed using ASTM C109-20 [17]. The mix design of the mortar per 1 cubic meter is presented in Table 2. The different ratios of GMSs as partial cement replacement and chitosan as an additive were also considered in the process. The GMS/cement weight ratios were 0%, 5%, 10%, 15%, and 20%, while the chitosan/mixture weight ratios were 0%, 0.25%, 0.50%, 0.75%, and 1%. With this, a total of 25 cases were produced. Each case had 5 cube specimens, which had a size of 2″ × 2″, for a total of 125 specimens produced in Phase 1.

Table 2. Mix design of mortar mix per 1 cubic meter.

Material	Amount
Cement	635.7 kg
Sand	1748.1 kg
Water	307.7 L

All mortar specimens were mixed using a Digi Mortar Mixer by Tinius Olsen. The specimens were cured underwater for 28 days before being subjected to the compressive strength test. Figures 4a and 4b show the curing and testing of mortar specimens, respectively. The compressive strength was computed using the resulting maximum load in UTM over the surface area of the face of the specimen that was subjected to loading.



(**a**) (**b**)

Figure 4. Mortar samples subjected to (**a**) curing and (**b**) testing.

2.4. Processing and Testing of Concrete Mix

The second phase of the study focused on the mixing and compressive strength testing of concrete specimens while adhering to ASTM C192-14 [23] and ASTM C39-21 [24], respectively. The cases considered were the setups that resulted in the highest compressive strength for the GMS-only setup, the chitosan-only setup, and the combination of the GMS and chitosan setup from the first phase (mortar). The ACI mix design for concrete was utilized to ensure the mixture of each setup. These were subjected to controlled water/cement ratios of 0.4, 0.5, and 0.6, resulting in 12 cases, including the controlled setup. Each case had 5 cylindrical specimens, with a size of $4'' \times 8''$, for a total of 60 concrete specimens for Phase 1. A half-bagger concrete mixer by Saturn was used for the mixing of all concrete specimens.

After mixing the concrete aggregates in a half-bagger concrete mixer, a slump test was performed on fresh concrete following ASTM C143-12 [25] prior to molding to determine its workability. The specimens were cured underwater for 28 days before they were tested to determine their compressive strength.

3. Results

3.1. Chitosan and GMS Analysis

3.1.1. Percentage Yield

Equation (1) was used in determining the chitosan yield. The weight of the milkfish scales used to extract the chitosan totaled 10,379 g, while the extracted chitosan totaled about 2103 g.

A resulting percentage yield of 20.26% was obtained, which is within the acceptable range for milkfish scales of around 20–30% [26,27]. The value falling at the lower range of acceptance may be attributed to the extra weight of contaminants, as the study used milkfish scales that were already waste materials compared to previous studies that sourced fresh scales.

3.1.2. Chitosan FTIR Analysis

Figure 5 displays the FTIR spectra of the chitosan utilized in the study, which was compared to the commercial chitosan at 400–4000 cm^{-1} [28]. The key peaks shown in the graph correspond to the verification of the properties. The peak at ~3370.92 cm^{-1} indicates N-H and O-H bonds, suggesting the presence of aliphatic amines and alcohols, which has a retardation effect on the water evaporation on concrete, explaining the increase of workability [29]. On the other hand, the peak at ~2974.51 cm^{-1} confirms the amino polysaccharide structure that is typical of chitosan. Peaks at 1641.65–1337.17 cm^{-1} reveal residual N-acetyl groups from chitin deacetylation, while the 1035.55 cm^{-1} peak shows a C-O-C bridge. These peaks are common in the samples of other papers that were processed using FTIR analysis, confirming that the chitosan used in the study is the compound itself [28].

Chemically processed chitosan with its corresponding chemical compounds has lots of uses, especially in the fields of medicine and materials science. In a study conducted by Ke et al., the material properties of chitosan were reviewed as an antimicrobial agent, which was used as a food additive or preservative, a component in cosmetics, and hydrogel films in pharmaceutical applications [30]. In terms of material science, chitosan is used as an additive for concrete in some studies, although not in its pure form, but rather as a compound that involves its structure. It can also serve as chitin nanofibers and nanocrystals in cement, protection of Bacillus pseudofirmus bacteria for a self-healing concrete, anti-corrosive coating for reinforced concrete, and a superplasticizer for concrete [15,31–33].

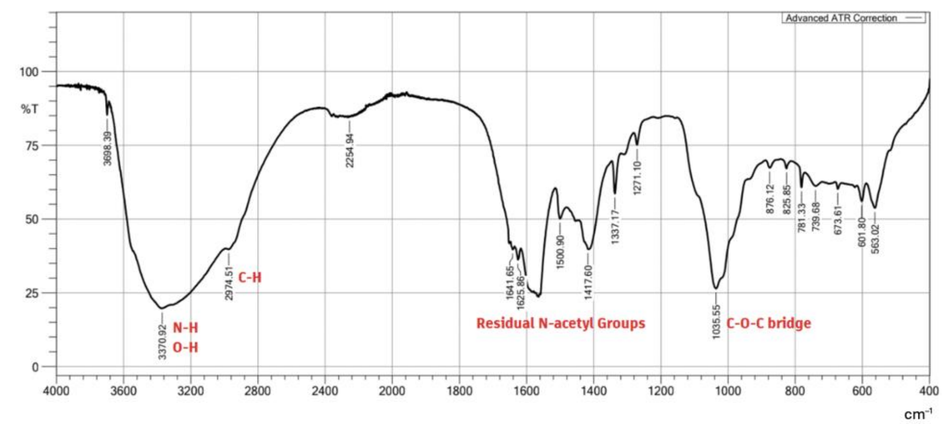


Figure 5. FTIR spectra of dried chitosan samples.

3.1.3. GMS FTIR Analysis

Figure 6 displays the FTIR spectra for the GMSs used in this study, which were compared to the FTIR spectra of limestone and $CaCO_3$ with and without Mg^{2+} at 400–4000 cm^{-1} [34,35]. The GMSa graph shows similar peaks compared to both graphs of the related literature at around 2356.35 cm^{-1}, indicating the possible presence of dolomite, a limestone rich in $CaCO_3$ and Magnesium Carbonate. The peaks at 1472.17, 860.32, and 712.39 cm^{-1} in Figure 5 show the presence of $CaCO_3$ with low magnesium content [34]. Lastly, the peak at 1082.95 cm^{-1} can be attributed to the presence of magnesium cations, which is an impurity that can lead to lower 28-day compressive strength compared to its 7-day compressive strength, which expands the cement and also increases the rate of deterioration [7,10,12,35].

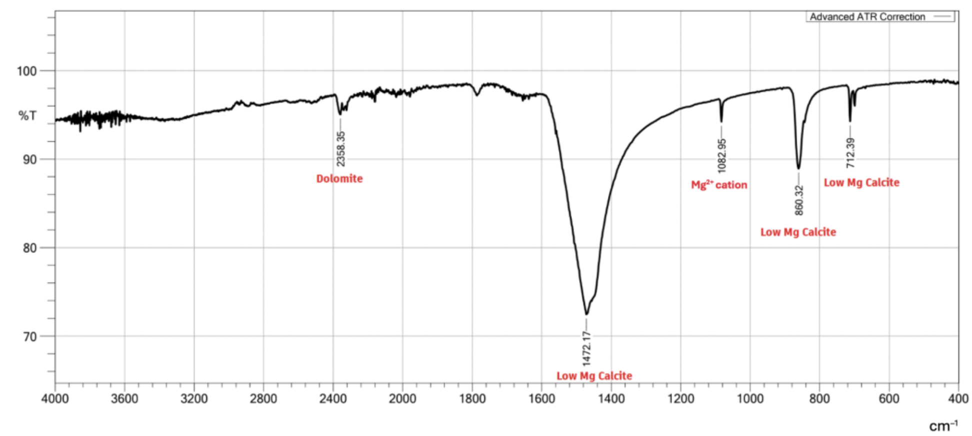


Figure 6. FTIR spectra of GMS samples.

3.2. Mortar Results and Analysis

3.2.1. Flow Table Test

Figure 7 shows the comparison of the different values in the flow table test for the mortar samples at different additive percentages based on the weight of the mixture of chitosan. It is shown that the flow of the controlled setup was 140.88 mm, and the chitosan-only setup had a maximum flow of 142.73 mm with 0.50% chitosan additive, which increased by 1.31%. However, with 0.25% chitosan additive, a decrease in flow was observed with a 14.66% difference. This low flow value can be attributed to the retardation of the cement hydration while mixing the mortar sample, as the flow table test was instantly conducted after following the ASTM C109-20 [17] procedure for mixing. As the workability is dependent on the overall mix design of the mortar samples, it cannot be compared to different studies, and other studies initially measured the setting time of their samples before determining the workability by using the flow table test.

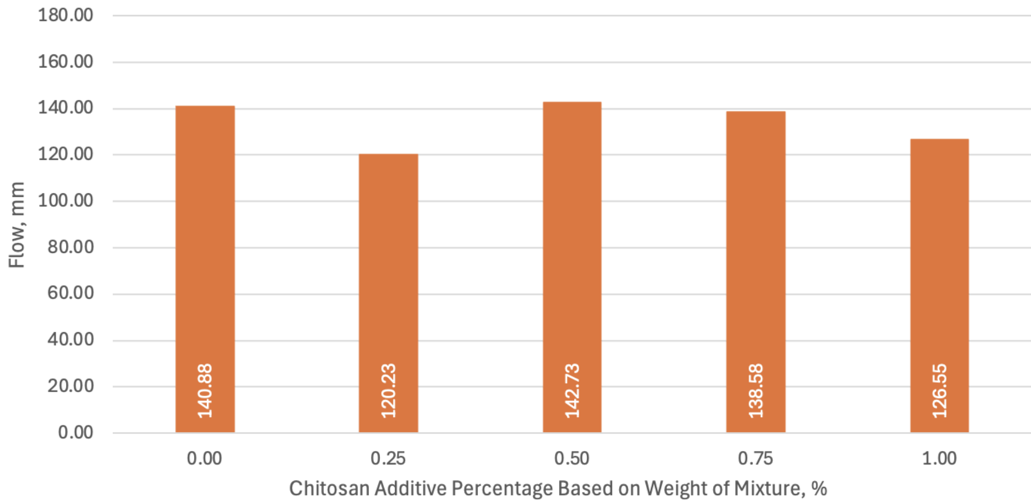


Figure 7. Flow table test results of samples with varying chitosan additives.

The setup that contains only GMSs had a maximum flow of 157.78 mm with a 15% GMS partial cement replacement, which increased by 12% in comparison to the flow of the control mixture. On the other hand, the 10% GMS partial cement replacement generated the lowest increase in the flow of the GMS-only setups, with a 5.41% difference from the control setup. With a 5% GMS partial cement replacement, the flow had decreased by 5.03%. These results are illustrated in Figure 8.

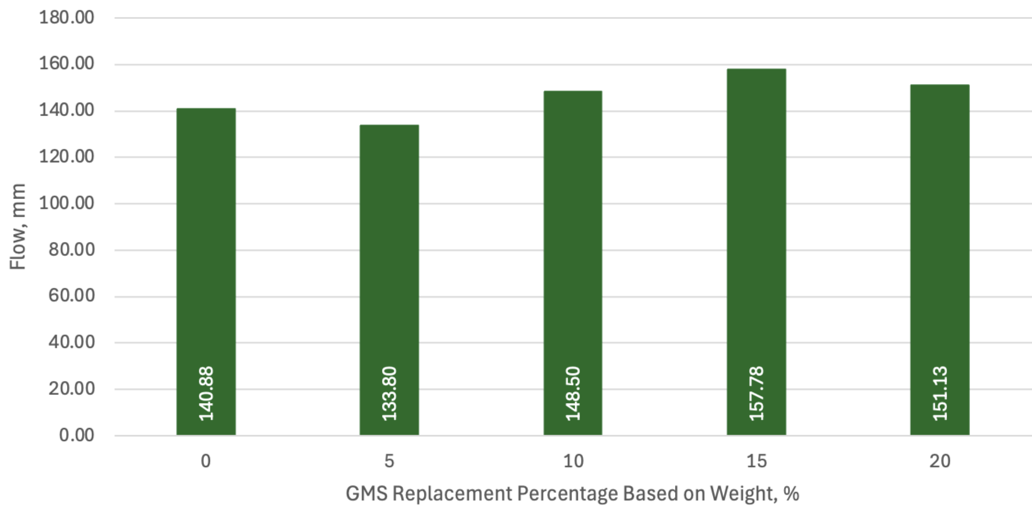


Figure 8. Flow table results of mortar samples with varying GMSs as partial cement replacement.

Figure 9 shows the flow table results of mortar samples with varying GMS percentages as a cement replacement and chitosan as an additive percentage. When GMSs and chitosan were combined, the maximum value of flow for mortar samples was found to be 176.65 mm, which was a 25.39% increase from the control sample. In contrast to the initial presumptions of the study, the flow values indicate that the addition of GMSs in mortar mixtures enhances the overall workability of the mortar samples. This improvement may be significant in the construction industry since it can lead to more efficient construction processes in terms of easier handling, placement, and finishing of mortar. Furthermore, these advantages are particularly important for masonry construction and plastering in hot climates, such as in the Philippines, to mitigate challenges posed by rapid drying and difficult working conditions [36].

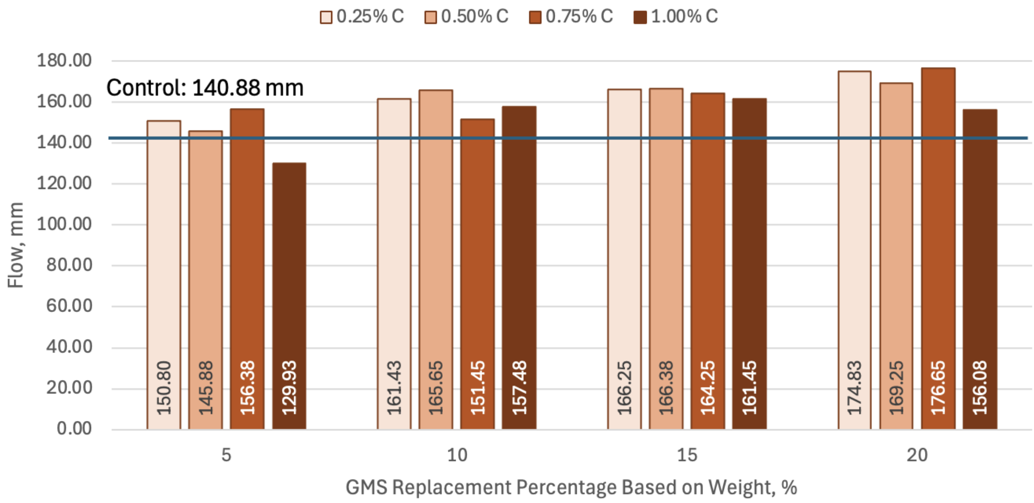


Figure 9. Flow table results of mortar samples with varying GMS percentages as cement replacement and chitosan as additive percentage.

3.2.2. Compressive Strength Test of Mortar Samples

Figure 10 shows the corresponding compressive strength of the mortar samples. It is shown that the controlled setup produced an average strength of 10.17 MPa, while the highest average produced for the chitosan-only setups produced a strength of 14.79 MPa, which came from the 0.25% mix. The compressive strength of the 0.25% chitosan additive had an increase of 45.43% compared to the controlled setup. On the other hand, the GMS-only setups produced the highest average compressive strength of 12.80 MPa, which is from the 10% setup, as shown in Figure 9. Compared to the control setup, the compressive strength of 10% GMS as a CRP is higher by 25.86%.

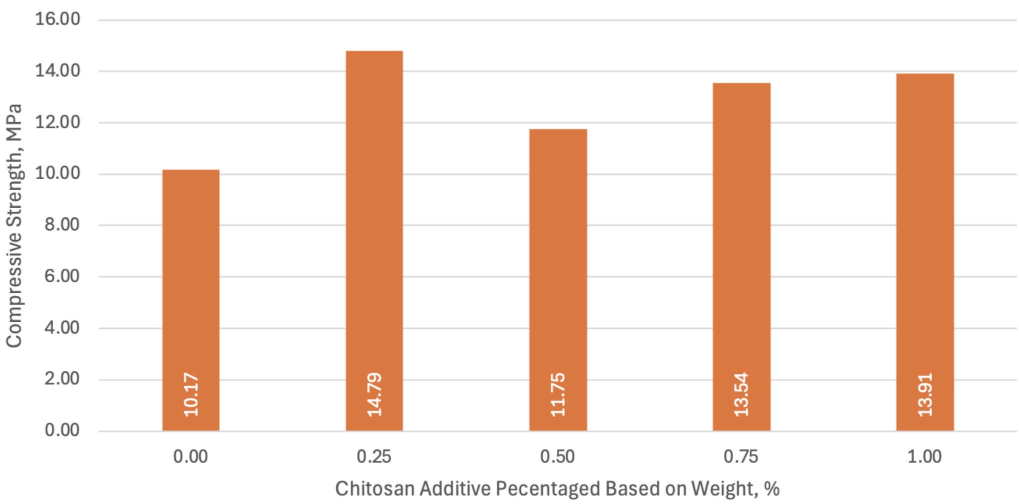


Figure 10. Compressive strength of mortar samples at varying chitosan additive percentages after 28 days of curing period.

Figure 11 illustrates the compressive strength of mortar samples with varying GMSs as partial cement replacement. Similar to the study by Lejano [6], the partial cement replacement percentage of GMSs that generated the highest increase in compressive strength was 10%. However, concrete specimens were utilized in the experiment. It must also be noted that further increase of the GMS replacement, at a certain point, leads to lower compressive strength due to excess lime. According to Lejano [4], excess lime content during the lime-silica reaction may affect the soundness of concrete. Due to a higher content of GMSs, the creation of alkali–silica reaction (ASR) gel due to the reaction of lime with silica will cause cracking and swelling in the concrete. According to Figueira [8], this causes major concerns, including reduced strength and microstructural weaknesses, reducing its overall durability.

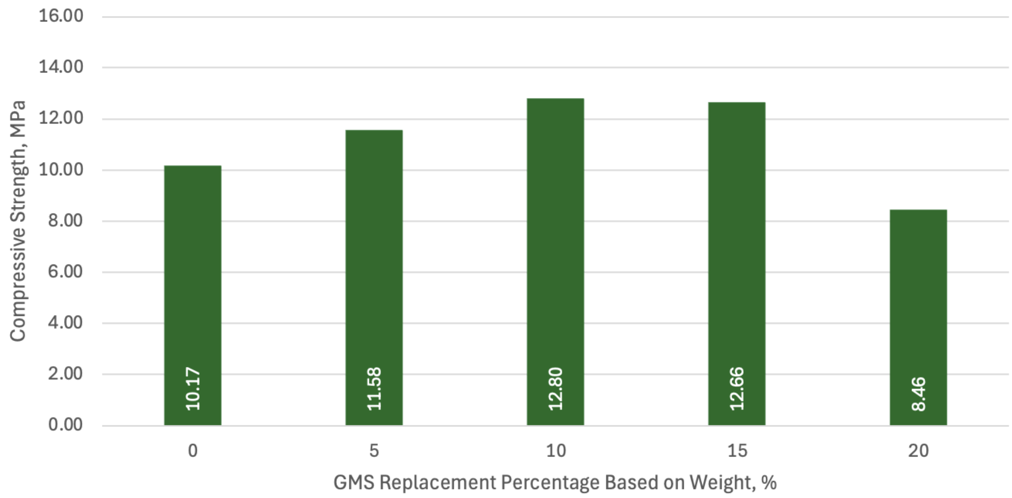


Figure 11. Compressive strength of mortar samples with varying GMS replacements after 28 days of curing period.

Figure 12 shows the compressive strength results of mortar samples when GMSs are utilized as a CRP with chitosan as an additive. The mix of both chitosan and GMSs produced the highest value of 14.11 MPa, which came from the mix of 10% GMS and 1% chitosan. The compressive strength of this mixture had a 38.74% increase compared to the control setup. Aside from this, when 10% GMS was mixed with 1% chitosan, a 10.23% increase in compressive strength was observed compared to the compressive strength of 10% GMS alone.

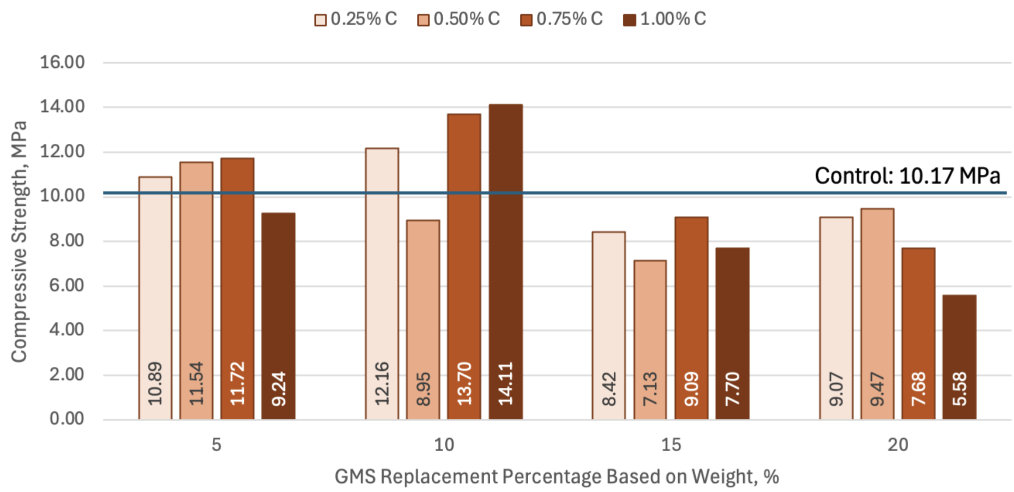


Figure 12. Compressive strength of mortar samples with varying GMS percentages as cement replacement and chitosan as additive percentages after 28 days of curing period.

Considering that the mortar mix with 10% GMS and 1% chitosan produced the highest compressive strength among the mixes in Phase 1, this proportion was carried over to Phase 2 of the experiment to compare the workability and compressive strength of the said materials in concrete. Table 3 presents the mix design used in preparing the concrete specimens, with a 0.4 water/cement ratio.

Table 3. Mix design (per cubic meter) for 0.4 water/cement ratio for control and 10% GMS with 1% chitosan setups.

Material	0% GMS and 0% Chitosan (Control)	10% GMS and 1% Chitosan
Cement, kg	512.50	461.25
GMS, kg	0	51.25
Water, kg	186.27	186.27
Gravel, kg	1029.28	1029.28
Sand, kg	679.61	679.61
Chitosan, kg	0	24.08

3.2.3. ANOVA Results of Mortar Specimens

Prior to conducting ANOVA, the experimental results were plotted in a Box and Whisker plot. Figures 13a, 13b, 13c, 13d, and 13e present the Box and Whisker plots representing the experimental data of 0%, 5%, 10%, 15%, and 20% GMS replacement, respectively, with varying amounts of chitosan. Based on the Box and Whisker plot of each group, a total of 9 out of 125 mortar samples were found to be outliers. These outliers were removed in the corresponding data set moving forward.

In confirming the validity of the compressive strength results for the ANOVA, the Shapiro–Wilk and Fligner–Killeen tests were used before starting the analysis. Table 4 shows the summary of F-values and *p*-values of the different variables to determine the applicability of ANOVA.

Table 4. Confirmation of the normality and homoscedasticity of the results.

Variable	F-Value	*p*-Value
Chitosan	0.968	0.4287
GMS	14.477	2.32×10^{-9}
Chitosan/GMS	2.081	0.0148

Based on the results shown in Table 4, with a computed *p*-value of 0.2048 for the Shapiro–Wilk normality test and 0.6863 *p*-value for the Fligner–Killeen test, the data follows normality and homoscedasticity and, as such, ANOVA can be performed and interpreted.

As shown in Table 5, the GMS and Chitosan/GMS setups yielded *p*-values of less than the significance level of 0.05, which indicates a significant difference between the strength of the setups compared to the control setup. On the other hand, the chitosan setup yielded a *p*-value of 0.4287, which is greater than the significance level. This would mean that there is no significant difference between the compressive strength of the chitosan-only samples and the controlled setup.

Table 5. ANOVA of mortar compressive strength.

Test	Test Statistic	*p*-Value
Shapiro–Wilk normality test	W = 0.98551	0.2048
Fligner–Killeen test of homogeneity of variances	X^2 = 20.183	0.6863

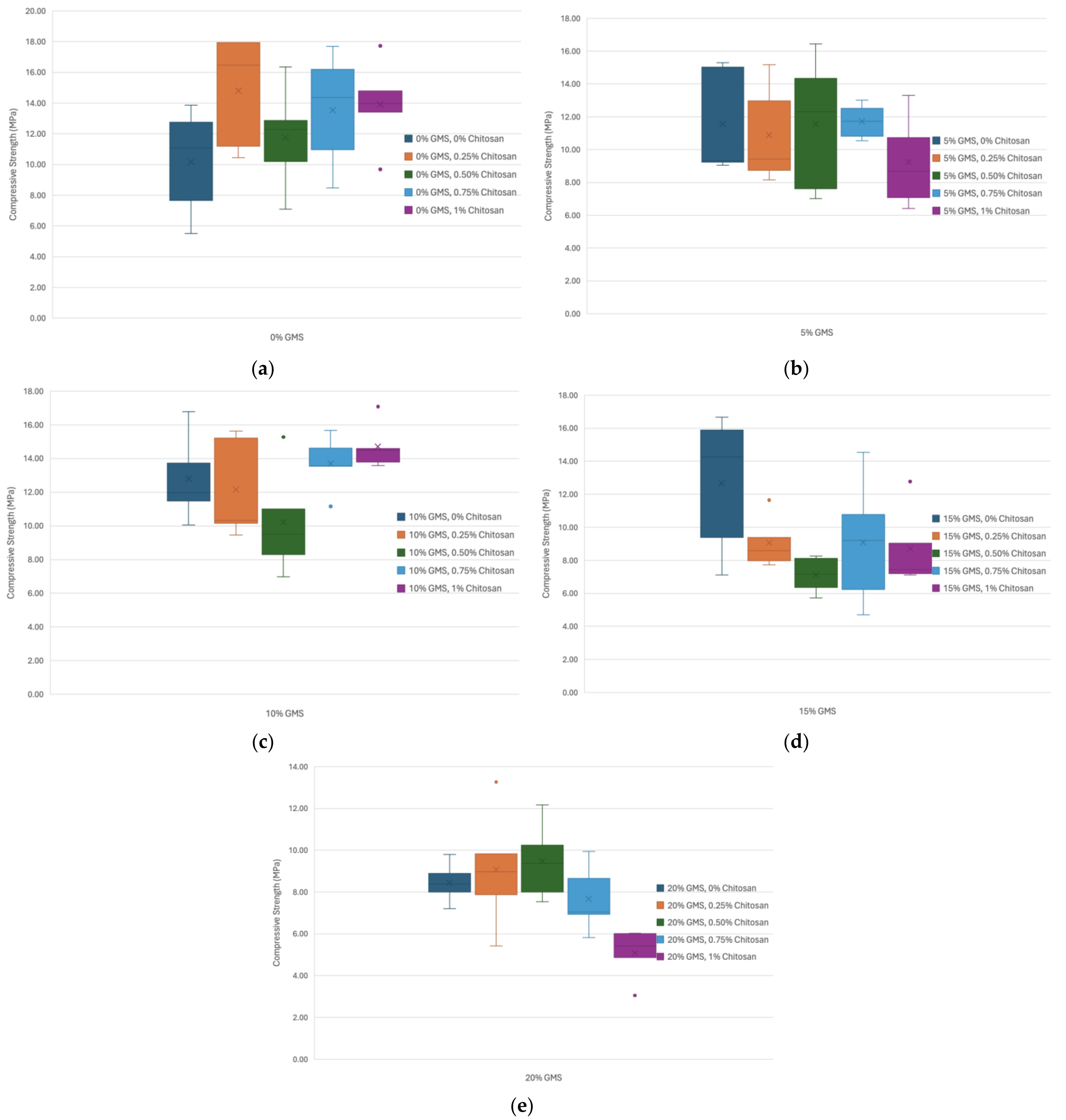


Figure 13. Box and Whisker plots for Phase 1 considering (**a**) 0% GMS, (**b**) 5% GMS, (**c**) 10% GMS, (**d**) 15% GMS, and (**e**) 20% GMS.

3.3. Concrete Results and Analysis

3.3.1. Slump Test

Figure 14 shows the comparison of the different values obtained from the slump test of the concrete samples. From the figure, it can be observed that the slump of the control setup at 0.40, 0.50, and 0.60 water/cement ratios is 85 mm, 155 mm, and 160 mm, respectively. Comparing this setup to the 0% GMS and 0.25% C setup, it can be seen that there was an increase of 10 mm in the slump for all of the mixes. In the 10% GMS and 0% C setup, a decrease in the slump, when compared to the control setup, was observed, with a 25 mm decrease in the 0.40 and 0.50 water/cement ratio mixes, while the 0.60 water/cement ratio sample had a 5 mm decrease in its slump. The 10% GMS and 1% C setup, when compared to the 10% GMS and 0% C setup, exhibited a 25 mm increase in the slump of the 0.40 w/c ratio mix, resulting in an equal slump with the 0.40 w/c ratio mix of the control setup. A 50 mm slump increase was observed from both the 0.50 w/c ratio mix and the 0.60 water/cement mix. However, only the 0.40 w/c ratio setups corresponded to the target slump of 75 mm to 100 mm in the mix design of concrete. The effect of utilizing GMSs as a CRP on the workability of concrete was observed to have decreased, similar to the study by Lejano [6]. Moreover, in accordance with the study by Lv [16], due to the ability of chitosan to adsorb water, the workability increased when 0.25% C is compared to the control setup and when 10% GMS and 1% C is compared to 10% GMS and 0% C.

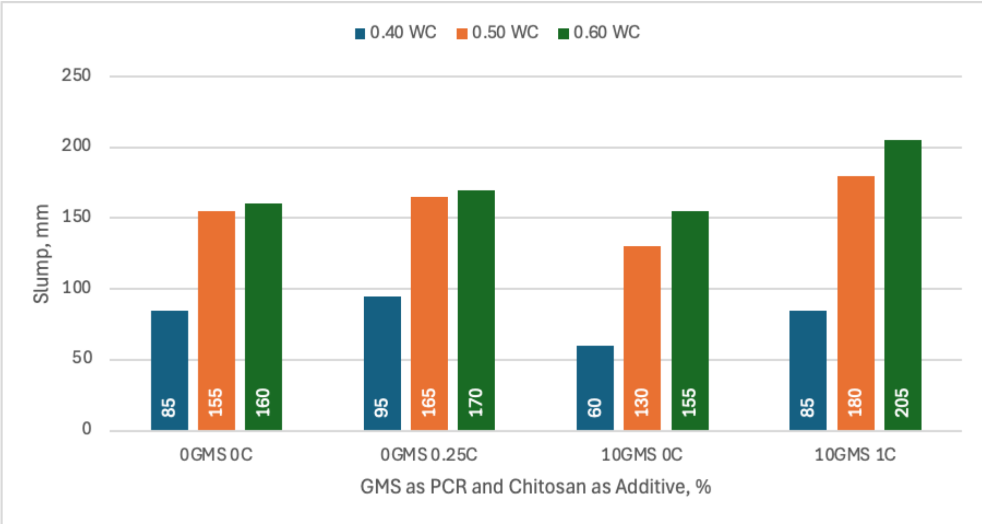


Figure 14. Slump test results of concrete samples.

3.3.2. Compressive Strength Test of Concrete Samples

Figure 15 shows the corresponding compressive strength of the concrete samples. The compressive strength values obtained by the control setup were 36.62 MPa, 33.45 MPa, and 22.90 MPa for 0.40, 0.50, and 0.60 w/c ratios, respectively. Correspondingly, the decreasing compressive strength of the concrete samples as the w/c ratios increased was expected due to the decrease of cement in the mixture. The results corroborate the theory that excess water in the concrete mixture produces greater voids among the aggregates. Furthermore, these voids are filled with air once the moisture evaporates, resulting in concrete specimens that are more porous. As such, a decrease in compressive strength was observed.

Comparing the control setup with 0.25% chitosan as an additive percentage and a 0% GMS cement replacement, there was an increase for all the samples, with the 0.40 w/c ratio having a value of 41.03 MPa with a percent increase of 12%, the 0.50 w/c ratio having a value of 34.93 MPa with a percent increase of 4%, and the 0.60 w/c ratio having a value of 25.73 MPa with a percent increase of 12%. These compressive strength increase rates are also similar to the 28th-day compressive strength increase rates due to chitosan-derived plasticizers mentioned by Arslan [15] at 13.3% and 10.9% with a 0.69 water/cement ratio. The compressive strength increase due to the addition of chitosan may be attributed to factors such as an increase in unit weight leading to a reduction of air content. Furthermore, it has been mentioned that the water-reducing properties of chitosan significantly increase the compressive strength of concrete.

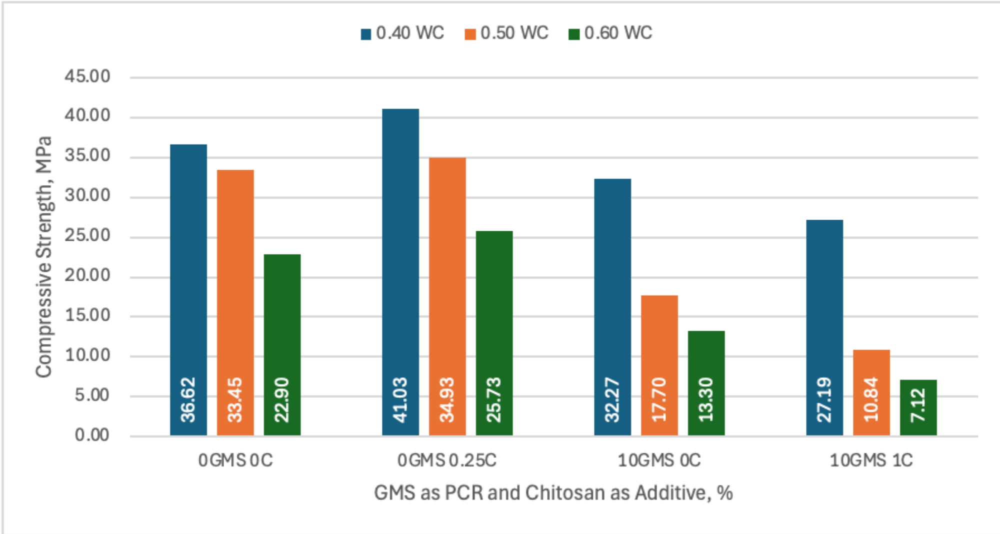


Figure 15. Compressive strength of concrete samples after 28 days of curing period.

However, a noticeable decrease in compressive strength can be observed in the 10% GMS and 0% chitosan samples, with the 0.40, 0.50, and 0.60 water/cement ratios producing values of 32.27 MPa, 17.70 MPa, and 13.30 MPa, respectively. These compressive strength values, when compared to the control setup, resulted in a percent decrease of 12% for the 0.40 w/c ratio mix, a percent decrease of 47% for the 0.50 w/c ratio mix, and a percent decrease of 42% for the 0.60 w/c ratio mix. The compressive strength decreased further when 10% GMS was added with 1% chitosan additive, with the 0.40, 0.50, and 0.60 w/c ratio samples having a compressive strength of 27.19 MPa, 10.84 MPa, and 7.12 MPa, respectively, with percent decreases of 26%, 68%, and 69%, respectively.

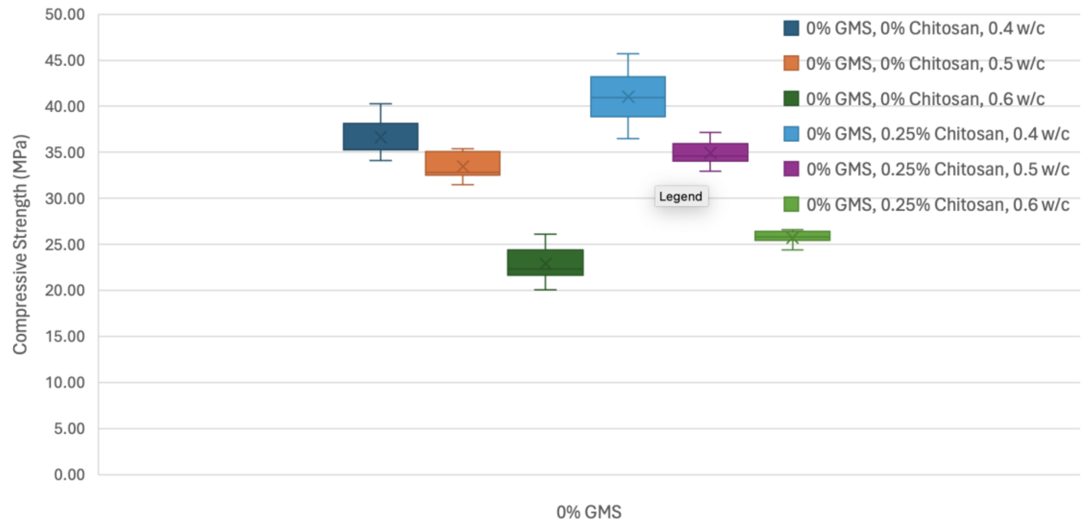
Compared to the study conducted by Lejano [6], there is a notable difference in the compressive strength values. As for the 0.40 and 0.50 w/c ratio with the 10% GMS replacement, the compressive strength values were 31.62 MPa and 23.27 MPa. With these values, when compared to the resulting compressive strengths of 32.27 MPa and 17.70 MPa, a 2.06% decrease and 23.94% increase were observed, respectively. Furthermore, a decrease in compressive strength due to GMS cement replacement contradicts findings from other studies.

Upon performing FTIR analysis, the GMSs used as a partial replacement for the concrete specimens were found to have the presence of magnesium cations. Magnesium, which can be found at the periostracum of the GMSs [11] and can be eliminated with the use of heat, can cause the expansion of the cement in concrete. In addition, the decrease in the compressive strength of the concrete mixture incorporated with GMSs can be attributed to this [10] since, according to a study conducted by Li [7], magnesium content in concrete will yield a decrease in compressive strength due to the rapid expansion of the cement which will result to a lower 28-day compressive strength compared to its 7-day compressive strength. This may explain the contradictions with regard to the results from the study conducted by Lejano [6]. However, while the magnesium content from the samples of that study is unknown, further factors, such as the lack of heat in processing the GMS, may also attributed to these conflicting results. As such, it is important for future studies to determine the chemical compositions of the materials being substituted to the conventional concrete aggregates, if possible.

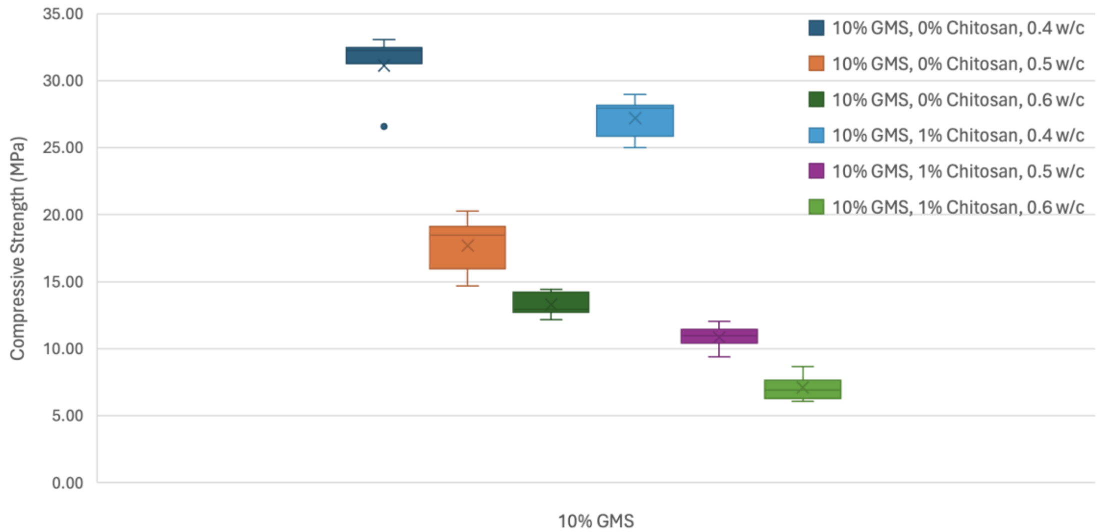
3.3.3. ANOVA Results of Concrete Specimens

Prior to conducting ANOVA, the experimental results were plotted in a Box and Whisker plot. Figures 16a and 16b present the Box and Whisker plots for the 0% and

10% GMS replacement, respectively, with varying amounts of chitosan and water/cement ratios. Based on the Box and Whisker plot for each group, only 1 out of 60 concrete samples was found to be an outlier, which was determined in the data set of 10% GMS and 0% chitosan with a 0.4 water/cement ratio. This data point was removed in the corresponding data set moving forward.



(**a**)



(**b**)

Figure 16. Box and Whisker plots for Phase 2 considering (**a**) 0% GMS and (**b**) 10% GMS, with varying chitosan content and water/cement ratios (w/c).

Table 6 summarizes the results obtained from the ANOVA statistical analysis of the concrete specimens having 0% GMS and 0.25% chitosan, considering the different water/cement ratios. The resulting *p*-values of the chitosan (0.00176) and water/cement ratio (3.45×10^{-13}) were lower than the critical value of 0.05 for a 95% confidence level. Hence, the analysis shows that both chitosan and water/cement ratios are significant factors that affect the compressive strength of concrete.

Table 6. ANOVA test results for 0% GMS and 0.25% chitosan.

Variable	F-Value	*p*-Value
Chitosan	12.15	0.00176
w/c	105.20	3.45×10^{13}

Another variable measured in this study was the effect of chitosan on the compressive strength of concrete, which is presented in Table 7. The table shows the ANOVA statistical analysis of the concrete specimens with 10% GMS and 0% chitosan at varying water/cement ratios. Similarly, the resulting *p*-values of the GMS composition (1.26×10^{-9}) and water/cement ratio (6.51×10^{-11}) at lower critical values for a 95% confidence level signify that both GMS and water/cement ratios are significant factors that affect the compressive strength of concrete.

Table 7. ANOVA test results for 10% GMS and 0% chitosan.

Variable	F-Value	*p*-Value
GMS	83.99	1.26×10^{-9}
w/c	65.98	6.51×10^{-11}

The ANOVA statistical analysis of the concrete specimens having 10% GMS and 1% chitosan at different water/cement ratios is presented in Table 8. The resulting *p*-values of the chitosan composition (4.47×10^{-9}) and water/cement ratio (2×10^{-16}) were lower than the critical value of 0.05 for a 95% confidence level. Consequently, the analysis shows that chitosan and water/cement ratios are significant factors that affect the compressive strength of concrete, given its composition.

Table 8. ANOVA test results for 10% GMS and 1% chitosan.

Variable	F-Value	*p*-Value
Chitosan	73.91	4.47×10^{-9}
w/c	306.72	2.00×10^{-16}

Table 9 presents the Duncan Post Hoc Test for the concrete specimens. The variables 0% and 0.25% in relation to chitosan highlight the effect of chitosan on compressive strength. A positive difference of 2.91 MPa indicates that adding chitosan to the concrete mix increases the compressive strength of the samples. This is also evident in the fact that the 0.25% chitosan replacement yields significantly larger compressive strength compared to the 0% replacement.

Table 9. Duncan Post Hoc Test for concrete compressive strength.

Setup	Variable	Difference (MPa)	*p*-Value
0% GMS	0% and 0.25% Chitosan	2.91	0.0018
0% Chitosan	0% and 10% GMS	−10.28	1.3×10^{-9}
10% GMS	0% and 1% Chitosan	−5.66	4.5×10^{-9}

Moreover, 0% and 10% GMS variables in Table 9 present the effect GMSs have on concrete. The obtained difference was −10.28 MPa, which signifies a negative influence on the compressive strength of the concrete samples. Correspondingly, the 10% GMS replacement was observed to have a lower compressive strength as compared to the 0% replacement. As such, a higher GMS percentage generally yields significantly lower compressive strength for this setup. Similarly, the interaction between chitosan and GMSs did not produce positive results, as highlighted by the negative difference of −5.66 MPa. This analysis supports the data presented earlier, as a 1.00% chitosan composition with 10% GMS produced significantly lower compressive strength compared to the 0% replacement.

4. Conclusions and Recommendations

This study identified the most desirable setup for achieving the highest compressive strength using ground mussel shell (GMS) as a partial cement replacement and chitosan derived from milkfish scales as an additive. A two-phase design was utilized in conducting the experiment, specifically using mortar and concrete specimens for a cost-effective sampling strategy.

In phase one, varying percentages of GMSs (0–20% at 5% increments) and chitosan (0–1% at 0.25% increments) were tested both individually and in combination. Results showed that 10% GMS cement replacement improved mortar compressive strength by 25.86%, and further increasing the GMS levels reduced the resulting strength due to adverse chemical reactions like ASR gel formation. Chitosan-only setups achieved the highest strength, with a 0.25% chitosan additive increasing the strength by 45.43%, though reducing flow by 14.66%. Based on the results in Phase 1, a combination of 10% GMS and 1% chitosan increased workability by 11.78% and compressive strength by 38.74%.

In Phase 2, chitosan enhanced both workability and compressive strength in concrete, while GMSs showed contrasting effects. A 10% GMS replacement alone in concrete reduced compressive strength by 12%, 47%, and 42% at varying water/cement ratios of 0.4, 0.5, and 0.6. When combined with 1% chitosan, this mix with 10% GMS decreased strength even further by 16%, 39%, and 46% at 0.4, 0.5, and 0.6 water/cement ratios, respectively, compared to the control mix. This was attributed to magnesium impurities in GMSs identified by FTIR analysis. These impurities likely caused cement expansion, accelerating deterioration. Additionally, the study found an inverse relationship between compressive strength and workability: as workability improved, compressive strength tended to decrease in concrete. These results were not in line with the initial hypothesis of the study, where a decrease in concrete compressive strength was obtained mainly due to the presence of magnesium impurities in the GMS samples. Furthermore, the results for both mortar and concrete samples differ from each other because the mortar specimens used a constant water/cement ratio in the design mix, as opposed to the setups of the concrete that used different w/c ratios for each setup. It was imperative to vary the water/cement ratios for Phase 2 to investigate the potential effects of GMSs and chitosan on the overall workability of concrete. The experimental results have shown that higher water/cement ratios result in lower concrete compressive strengths.

To further enhance this study, it is recommended to examine the differences in properties of green mussel shells from different sources, as well as seasons, as this could have a significant impact on the compressive strength of the samples. Such investigations could help determine the variability in quality and effectiveness of the shells based on their origin and the time of year they are harvested, potentially identifying optimal conditions for their use in the concrete mix. In addition, exploring various extraction methods for chitosan and processing methods for GMSs is recommended. Comparative studies on these methods could identify more efficient, cost-effective, or environmentally sustainable techniques for obtaining and preparing these materials. These comparative studies can be supplemented with economic analyses, such as cost–benefit analyses and life cycle cost analyses. Verification of green mussel shells processed through equipment, such as Fourier Transform Infrared Spectroscopy (FTIR) or energy-dispersive X-ray spectroscopy (EDX), is also recommended to ensure impurities, such as magnesium cations, are absent. Determining the optimal processing time for GMSs, along with exploring other effective processing methods, would further enhance the efficacy of these materials in concrete applications.

Author Contributions: B.L.: supervision, project administration, formal analysis, and conceptualization. K.J.E.: writing—review and editing, supervision, project administration, data curation, and conceptualization. L.M.C.: writing—original draft, visualization, validation, methodology, investigation, formal analysis, data curation, and conceptualization. S.R.C.: writing—original draft, visualization, validation, methodology, investigation, formal analysis, data curation, and conceptualization. V.P.F.: writing—original draft, visualization, validation, methodology, investigation, formal analysis, data curation, and conceptualization. A.Y.R.: writing—original draft, visualization, validation, methodology, investigation, formal analysis, data curation, and conceptualization. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Acknowledgments: The authors would like to acknowledge the Department of Civil Engineering of De La Salle University, Manila, Pasay City National Science High School, and the Department of Science and Technology-Science Education Institute for all their support in making this research possible.

Conflicts of Interest: The authors declare no conflicts of interest.

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