

Article

Nanomodified Concrete with Enhanced Characteristics Based on River Snail Shell Powder

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Abstract: The utilization of aquaculture waste, such as snail shells, is a severe issue. These shells are common in water-sources and are a by-product of sifting sand for masonry and concrete work. Calcium-rich river shells are of great interest for cement building materials. In this regard, the purpose of this article was to develop a nanomodified concrete with improved characteristics based on the powder of snail shells. Experimental studies have confirmed the effectiveness of the use of river shells in concrete without a decrease in strength characteristics and deterioration of other properties. It has been found that the optimal replacement by the snail shell powder that replaced cement is in the amount of 6%. By the nanomodification of concrete with the powdered shells of river snails, it was possible to achieve an increase in compressive strength up to 12%, axial compressive strength—up to 8%, tensile strength in bending—up to 9%, axial tensile strength—up to 11%, elastic modulus—up to 8%. Concrete nanomodification with snail shell powder in the amount of 6% contributed to a reduction of deformations of up to 7%. The study of the microstructure of concrete samples nanomodified with snail shell powder confirmed the obtained dependences of the cement's properties on the nanomodifier dosage, as well as the most effective dosage of snail shell powder.

Keywords: river snail shell concrete; nanomodification; sustainable concrete; concrete composition; concrete microstructure



Citation: Stel'makh, S.A.; Shcherban', E.M.; Beskopylny, A.N.; Mailyan, L.R.; Meskhi, B.; Beskopylny, N.; Dotsenko, N.; Kotenko, M. Nanomodified Concrete with Enhanced Characteristics Based on River Snail Shell Powder. *Appl. Sci.* **2022**, *12*, 7839. <https://doi.org/10.3390/app12157839>

Academic Editor: Carlos Thomas

Received: 21 July 2022

Accepted: 1 August 2022

Published: 4 August 2022

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1. Introduction

Currently, the accumulated waste from agriculture and aquaculture is a severe environmental problem. At the same time, the actual direction of building materials science and concrete technology is the utilization of industrial, agricultural waste, aquaculture waste and other types of waste as components for concrete [1–16]. At the same time, it is important to maintain the quality of concrete at the proper level, and often find ways to improve the properties of concrete through recycled waste. This approach makes it possible to achieve a complex environmental and economic effect. It is comprised, first, improving the technological properties of concrete and concrete mixtures. Secondly, there is an environmental effect due to waste disposal. Thirdly, there is an economic effect due to the reduction in the cost of raw materials and, as a result, the cost of production of new improved concretes. The advantage of this will be a decrease in the percentage of rejects

due to obtaining a higher quality micro- and macrostructure of concrete, improving its strength and other characteristics.

An overview of previous studies on the types, dosages and uses of aquaculture waste is presented in Table 1.

Table 1. Purpose of shells in cement materials and their influence on properties.

Destination of Aquaculture Waste	Source	Dosage and Effect of Aquaculture Waste
As an Additive to the Material		
Asphalt modifier	[17]	The addition of seashell powder as an asphalt modifier was studied at 5, 10 and 15%. “Seashell powder improves the consistency, hardness, and high temperature performance of the bituminous binder, but weakens its low temperature performance; shell powder increases elasticity, recovery characteristics and resistance to residual deformation of bituminous binders, improves rheological properties at high temperatures; shell powder has minimal effect on the crack resistance of bituminous binders at very low temperatures”
Additive in building materials	[18]	Modification of the surface of particles of crushed oyster shell waste by grinding in a high-energy ball mill makes it possible to obtain fine materials that can be used in building materials and as aggregates for concrete
Cleaning of drains	[19]	Pyrolysis of waste oyster shells under certain conditions removes phosphates from wastewater
Expansion additive in cement mortar	[20]	The volumetric expansion of “the calcined oyster shell powder during hydration compensated for the autogenous shrinkage of the mortar at an early age”. Excessive introduction of such a powder led to a decrease in the rate of compressive strength development.
As a replacement part of the material		
Replacing a piece of plaster	[21]	Replacement of 40 and 50% gypsum for refractory materials. The strength was reduced to 80% when exposed to sulfates and cyclic freeze–thaw. When exposed to acids, an increase in strength was observed during the first three weeks and its further decrease [17].
As a substitute for limestone in cement clinker	[22]	“Oyster and scallop shells are suitable substitutes for limestone as a raw material for cement” [23]
Fine aggregate replacement	[1,3,23–26]	Effect of the particle size of oyster shell instead of 20% river sand on compressive strength, flexural strength, and modulus of elasticity of mortar, as well as its workability. A finer powder contributes to obtaining the maximum characteristics of the solution [24]. Replacing part of the aggregate (5, 10, 20%) with oyster shell powder led to a decrease in the workability of concrete, left the compressive strength unchanged or increased it compared to conventional concrete, and the modulus of elasticity decreased to 10%. The setting time remained unchanged when the fine aggregate was replaced with oyster shell powder up to 20% [25,26]. The use of mussel shells in cement coating mortars as a substitute for conventional sand at various proportions of 25, 50 and 75% has been investigated. The most effective dosage is 25% [27]. “The use of coarse-grained shell aggregate improves the workability of the concrete. Concrete containing up to 50% shell aggregate as a partial replacement for fine or coarse aggregate has a density greater than 2100 kg/m ³ . Up to 20% of natural fine aggregate and up to 50% of coarse aggregate can be replaced with ground shells to obtain concrete of sufficient density and strength. The most effective dosage of shells is 5%” [1].

Table 1. Cont.

Destination of Aquaculture Waste	Source	Dosage and Effect of Aquaculture Waste
Coarse aggregate replacement	[27–30]	The use of shell waste without crushing, filled with foam, in foam concrete as a volume replacement for coarse aggregate 0, 20, 50, 80 and 100% led to a decrease in shrinkage, fresh concrete density, and an increase in fresh concrete fluidity. At the same time, the rate of strength reduction was lower than that of the control foam concrete [20]. Used 10, 15, 20, 25, 30, 40, 50% replacement of coarse aggregate in concrete with crushed shells. This replacement of the aggregate reduced workability and compressive strength with increasing percentage of barnacles. 10% and 20% replacement made it possible to obtain the required design values for compressive strength and workability.
Replacing part of the binder in heavy concrete and mortar	[2,31–40]	The use of seashells with fly ash in addition to gravel slurry to form an unfired earthen building material result in higher compressive strength compared to conventional earthen building materials, allowing for thinner walls [31]. The use of a ternary binder system (10% oyster shells + 5% lithium slag (LS) + 5% crushed blast-furnace granulated slag (GGBFS)) results in a strength equivalent to the reference samples and a decrease in permeability. Oyster shell powder and blast-furnace slag were separately and jointly used as a binder “replacement up to 30%. The compressive strength was about equal to or slightly better than controls when replacing part of the cement with 30% blast furnace slag or 10% oyster shell powder and 20% slag” [32]. The use of seashell powder (4–30% by weight of cement) and natural pozzolan (up to 30% by weight of cement) in solutions significantly reduces the environmental impact while maintaining a similar compressive strength compared to conventional Portland cement [34,35]. Four types of seashell waste have been used as a replacement for cement (5, 10, 15, 20% by weight) to make a mixture for masonry and plaster. Due to this, it was possible to reduce water demand and increase the setting time of the solutions. At the same time, the strength remained sufficient, shrinkage and thermal conductivity decreased in comparison with conventional cement. Seashells can be used as a substitute for cement in masonry and plaster mortars, improving their workability [36]. Replacement in the range of 5–15% reduces strength at an early age and improves mechanical performance after long periods of concrete hardening, reduces concrete workability [37]. Ground seashell has been used as a replacement for 2, 4, 6% and 8% cement. The most effective for compressive strength was a dosage of 4%. Shelled concrete showed a lower compressive strength and elastic modulus compared to conventional concrete, but greater flexural tensile strength and axial tension [38]. An increase in compressive strength after 28 days of concrete hardening was achieved up to 7.5%, and in axial tensile strength—up to 3.5%. The optimal replacement ratio is 5% [39,40].

Partial replacement of the binder with recycled seashells [2] not only affects the characteristics of concrete, but also, at optimal dosages, helps to save expensive binder, reduce production costs, and reduce environmental impact. At the same time, an important direction in expanding the scope of aquaculture wastes is their use as a substitute for aggregates for concrete and mortar, including in road construction [41–43]. At the same time, the strength of such materials is often noticeably lower than that of conventional concrete, but nevertheless, it can be used in products and structures of a reduced level of responsibility [2,41,42].

In addition, freshwater shells have also been studied for their applicability in building materials; in particular, their preferred crystallographic orientation has been studied in

detail [43]. Of no small importance in studies of the possibility of using aquaculture waste in cement composites is the study of the mechanism of “the effect of such waste on the synthesis, characteristics, and hydration of cement” [44], as well as the preparation and characterization of CaCO₃ microparticles/polypropylene composites [45]. The “reuse of shell waste to promote sustainable shellfish aquaculture is also an important task in the studies of many authors” [46,47].

One of the most common types of aquaculture waste is the shells of river snails. Such waste is common in water bodies, is a side waste when screening sand for masonry work and concrete work, and thus is a rather urgent environmental problem.

The basis of the shells of most mollusks is calcium. The snail is no exception. Also, in the composition of its shells, but in smaller quantities, manganese, zinc and iron are found. It is known that the shells of gastropods consist of three layers:

- (1) periostracum—outer thin layer, consisting of a protein—conchiolin;
- (2) ostracum—the middle layer of the shell, which consists of CaCO₃.
- (3) hypostracum or mother-of-pearl layer—the inner layer of the shell, consisting of CaCO₃ plates, which are wrapped with conchiolin [37].

Thus, summing up the results of the literature review, it can be summarized that quite a few studies are devoted to improving the properties of concrete by replacing part of the cement with shellfish powder and even less are devoted to freshwater. In general, in most of the studies studied, the mechanical properties of modified concrete only approach those of conventional concrete at certain dosages of powdered waste in the form of shells.

In this regard, the main aim of this work was to substantiate the obtaining nanomodified concrete with enhanced characteristics on the basis of the powder of snail shells.

The research objectives are:

- theoretical and practical substantiation of the possibility of the nanomodification;
- search for a rational dosage and formulation of concrete, and a rational dosage of nano-modifying powder of snail shells;
- search and determination of the rational composition and formulation of nanomodified concrete based on the powder of snail shells;
- development of recommendations for the actual production of concrete nanomodified with snail shell powder, taking into account its improved characteristics.

Scientific novelty is:

- achievement of theoretical evidence for the improvement of the micro- and macrostructure of concrete nanomodified by the powder of the shells of river snails;
- determination of the dependence and relationship between the composition, microstructure and properties of nanomodified concretes using snail shell powder;
- identification and fixation of fundamental and applied dependencies in the formation of the microstructure of a new type of nanomodified concrete.

The significance of the study is the practical applicability of the new knowledge gained and the development of existing ideas on nanomodification in the technology of concrete using aquaculture waste and the development of proposals for concrete production, justification in an approximate form of the economic effect and a preliminary assessment of the cost reduction of such concrete.

2. Materials and Methods

2.1. Materials

The binder used in the research was CEM I 52.5 N Portland cement without additives according to GOST 31108-2020 “Common cements”. Specifications were produced by JSC Novoroscement (Novorossiysk, Russia). The main characteristics, as well as chemical and mineralogical composition of Portland cement are presented in [16].

Granite crushed stone are presented in [16].

Quartz “sand was used as a fine aggregate according to” GOST 8736–2014 “Sand for construction works” produced by Arkhipovsky Quarry JSC (Arkhipovskoe village, Russia). Fine aggregate properties’ specifications are given in [16].

The powder of snail shells was used as a nanomodifying additive (Figure 1). The shells of river snails used as raw materials for the nanomodifier were collected on the banks of rivers located in the Rostov region and the Krasnodar region.



Figure 1. Appearance of snail shells: (a) after washing; (b) after grinding by pounding.

The chemical composition of snail shells is presented in Table 2.

Table 2. Chemical composition of RSSP.

Element	Amount, %
SiO ₂	0.95
Al ₂ O ₃	0.15
Fe ₂ O ₃	0.06
MgO	0.04
CaO	54.11
SO ₃	0.14
SO ₄	0.06
Na ₂ O	0.38
K ₂ O	0.03
Cl	0.01
LOI	41.95

Data were obtained by quantitative chemical analysis in the laboratory.

Figure 2 shows the particle size distribution curve of the river snail shell powder.

From the data in Figure 2, it follows that the RSSP powder particles had sizes from 2 to 60 µm. Of these, more than 40% are particles from 2 to 20 µm, 30% from 20 to 40 µm, and 30% from 40 to 60 µm.

The variants of experimental compositions with different dosages of RSSP are presented in Table 3.

2.2. Methods

The production of the powdered shells of river snails was carried out as follows. First, the collected shells were washed to remove contaminants. Then, after washing and drying under natural conditions, the shells of river snails were calcined in a muffle furnace SNOL 6.7/1300 AB UMEGA GROUP (Utena, Lithuania) at a temperature of 300 °C for 2.5 h to remove organic matter. After cooling in natural conditions, snail shells were crushed in a

laboratory jaw crusher, and then crushed to a fine powder state using an “Activator-4M mill [32], the detailed characteristics and parameters of which are presented in” [32].

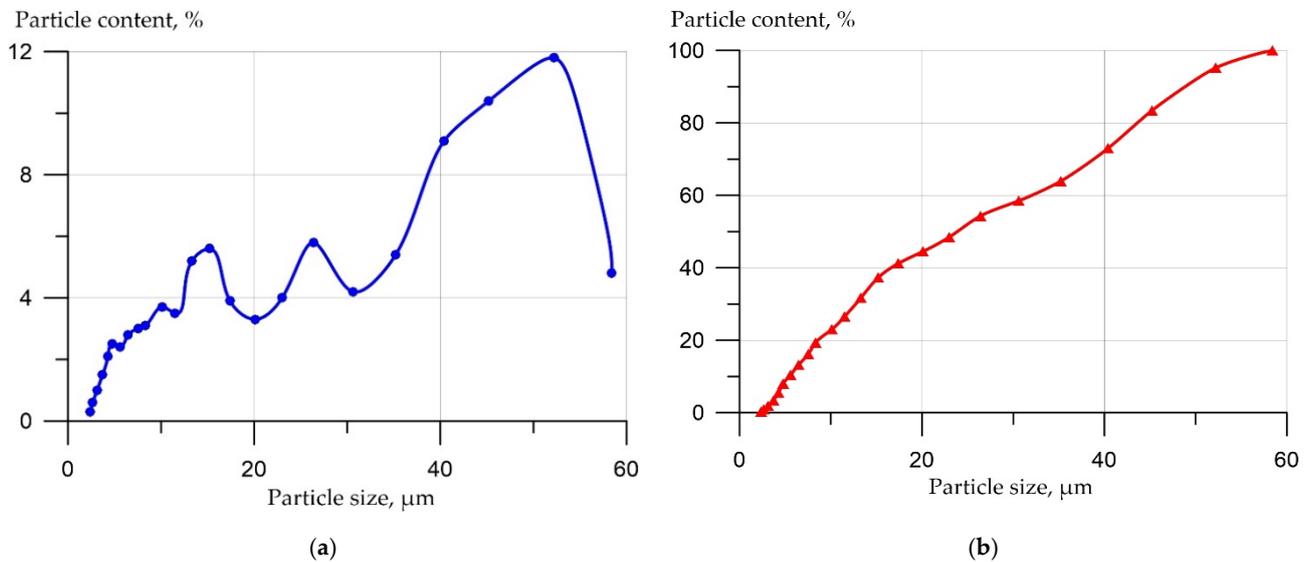


Figure 2. River snail shell powder particle size distribution curve: (a) particle distribution; (b) cumulative curve.

Table 3. Dosage of the nanomodifying additive.

Num	PC, %	RSSP, %	Sand, %	Crushed Stone, %	Water, %
1	100	0	100	100	100
2	98	2	100	100	100
3	96	4	100	100	100
4	94	6	100	100	100
5	92	8	100	100	100
6	90	10	100	100	100
7	88	12	100	100	100

To analyze the size distribution of RSSP particles, a Microsizer 201C (OOO VA Install, St. Petersburg, Russia) was used. This is a fully automated instrument designed to measure particle size distribution in the range of 0.2–600 μm , the dosages of the components of which are presented in Table 4.

Table 4. Parameters of the composition of the concrete mixture.

Parameter Title	W/B	PC, kg/m^3	Water, L/m^3	Crushed Stone, kg/m^3	Sand, kg/m^3	ρ_{cm} , kg/m^3
Parameter value	0.5	375	190	1158	702	2425

The rest of the equipment was taken in accordance with [48–53].

The “mixing of the components of the concrete mixture was carried out in accordance with” [16].

The “mixing of the components of the concrete mixture was carried out in the following sequence: first, cement and sand were poured, then they were mixed until a homogeneous mixture was obtained. After that, a pre-prepared powder of snail shells was added and mixed with other dry ingredients. At the next stage, mixing water was introduced, and then coarse aggregate was added to the resulting mortar mixture. The concrete mixture was mixed until a homogeneous consistency was obtained. After the end of the mixing process, the finished concrete mixture was poured into metal molds of JSC Smolensk SKTB SPU (Smolensk, Russia) and vibrated on the laboratory vibrating platform SMZh-539-220A

OOO IMASH (Armavir, Russia)”. When compacting the concrete mixture, the form with the concrete mixture laid and compacted by bayonet was rigidly fixed on a laboratory vibration platform and vibrated until complete compaction, characterized by the cessation of concrete mixture settling, leveling its surface, and the appearance of a thin layer of cement paste on it. After the completion of the laying and compaction of the concrete mixture in the form, the upper surface of the sample was smoothed with a trowel or a plate. Immediately after their manufacture, the samples were marked with a marking identifying the sample’s ownership and the date of its manufacture.

Then the “molds filled with concrete mixture were placed in the normal hardening chamber of RNPO RusPribor LLC (St. Petersburg, Russia) and kept there for 24 h”. When determining the compressive strength of concrete, the samples were stripped after 24 h, the tensile strength was measured after 72 h, and then the samples were kept in the chamber for another 27 days. After 28 days of hardening, the samples were tested [16].

Before testing, the samples were subjected to visual inspection, establishing the presence of defects in the form of cracks around the ribs and shells and foreign inclusions. Concrete sags on the ribs of the supporting surfaces of the samples were removed with an abrasive stone. On the samples, the reference faces were selected and marked as to which forces should be applied during loading. The supporting faces of the molded cubes intended for compressive testing were chosen so that the compressive force during the test was directed parallel to the layers placing the concrete mixture into the molds. The linear dimensions of the samples were measured with an error of no more than 1%.

The types and number of samples made and tested in this study are shown in Figure 3.

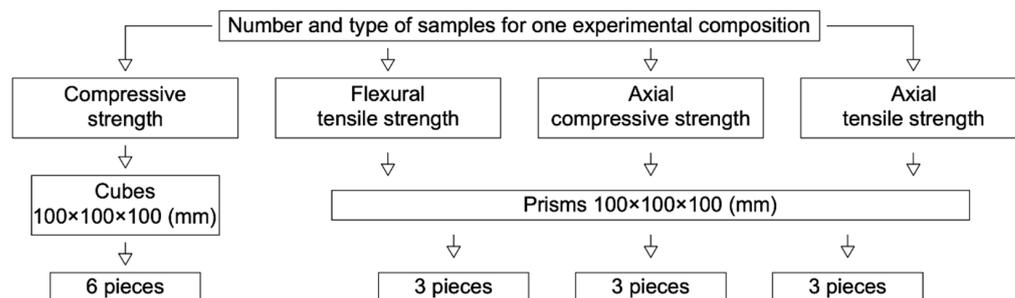


Figure 3. Program of the experiment.

Compressive strength, bending tensile strength, and axial tensile strength were determined under the requirements of GOST 10180 “Concretes. Methods for strength determination using reference specimens”.

All samples of one series were tested at the estimated age for 1 h. The loading of the samples was carried out continuously at a constant rate of load increase until its destruction. In this case, the loading time of the sample until its destruction was 30 s. During the compression test, the sample cubes were installed with one of the selected faces on the lower support plate of the press centrally relative to its longitudinal axis, using the marks applied to the press plate.

The specimen was fixed in a tensile testing machine and loaded to failure at a constant rate of load increase (0.05 ± 0.01) MPa/s.

The “determination of the axial compressive strength is carried out in accordance with the requirements of GOST 24452 Concretes. Methods of prismatic, compressive strength, modulus of elasticity and Poisson’s ratio determination” [16].

Before testing, the samples were kept in the laboratory for 2 h. Central lines were placed on the side surfaces of the specimens for the installation of instruments for testing deformations and centering the specimens along the axis of the press. The bases for measuring the deformations of the samples were marked along the central lines. Instruments for measuring the strains of specimens were installed along its four faces. To fasten the indicators, we used fixtures in the form of steel frames fixed on the sample with four stop screws—two on opposite sides of the sample—or support inserts glued onto the sample.

Before testing, the sample with the instruments was installed centrally according to the marking of the press plate and the alignment of the initial reading with the division of the instrument scale was checked. The initial compression force of the sample was no more than 2% of the expected breaking load.

3. Results

Table 5 presents the test results of concrete prototypes with the RSSP addition as a partial cement replacement in terms of “compressive strength” $R_{b.cubr}$, “axial compressive strength” R_b , “flexural tensile strength” R_{btb} , “axial tensile strength” R_{bt} , “ultimate axial compressive strain” ϵ_b , “ultimate axial tensile strain” ϵ_{bt} , and “elastic modulus” E .

Table 5. Strength and deformation characteristics.

Composition Number	$R_{b.cubr}$, %	R_b , %	R_{btb} , %	R_{bt} , %	ϵ_b , %	ϵ_{bt} , %	E , GPa
1	39.4	29.9	4.72	2.62	2.28	1.34	27.4
2	40.6	30.3	4.84	2.68	2.24	1.32	27.8
3	42.2	31.2	4.98	2.79	2.19	1.28	28.5
4	44.1	32.3	5.15	2.91	2.14	1.25	29.4
5	40.2	30.1	4.81	2.66	2.27	1.34	27.7
6	36.3	27.2	4.25	2.38	2.47	1.45	25.2
7	32.8	24.5	3.89	2.19	2.68	1.57	22.7

Figure 4 “shows the effect of the amount of snail shell powder on the compressive strength of concrete”.

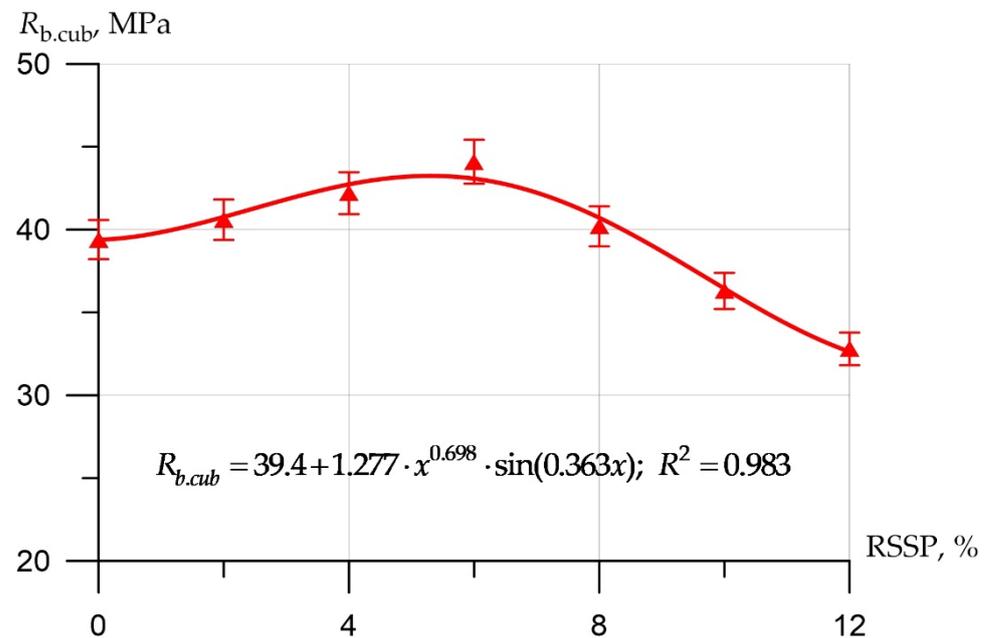


Figure 4. Compressive strength of snail shell powder concrete.

The influence of the nano-modifying additive on the mechanical properties of concrete is represented by dependencies based on the saturation function [15].

$$Y(x) = C_0 + Ax^b \sin(\omega x + \varphi) \tag{1}$$

Here $Y(x)$ is the mechanical characteristics; x is the amount of powder in the shells of river snails RSSP, %; C_0 is the value of mechanical characteristics without additives; b is the degree parameter; ω , φ are parameters of the frequency and phase angle, respectively.

The physical meaning of the saturation function is as follows. The function reflects two processes: quality improvement and a destructive process of quality reduction if this additive becomes too much. At the first stage, the nano-modifying additive “leads to an increase in the strength characteristics of concrete”. Then, its effect reaches a maximum and gradually decreases.

Figure 4 “shows that the compressive strength of concrete” when cement is replaced with snail shell powder in the amount of 6% has a maximum value—12% more than that of the composition without RSSP. At the same time, higher values of compressive strength than the composition without RSSP were observed at dosages of 2, 4 and 8% (from 2 to 7%). From 0 to 6%, the strength increased, while at a dosage of more than 6%, a sharp drop in the strength of concrete was observed (up to 17%).

The dependence of the compressive strength of concrete when cement is replaced by snail shell powder was approximated by the function with a coefficient of determination of 0.983.

$$R_{b.cub} = 39.4 + 1.277 \cdot x^{0.698} \cdot \sin(0.363x); \quad R^2 = 0.983 \quad (2)$$

Figure 5 “shows the effect of the amount of snail shell powder on the axial compressive strength of concrete”.

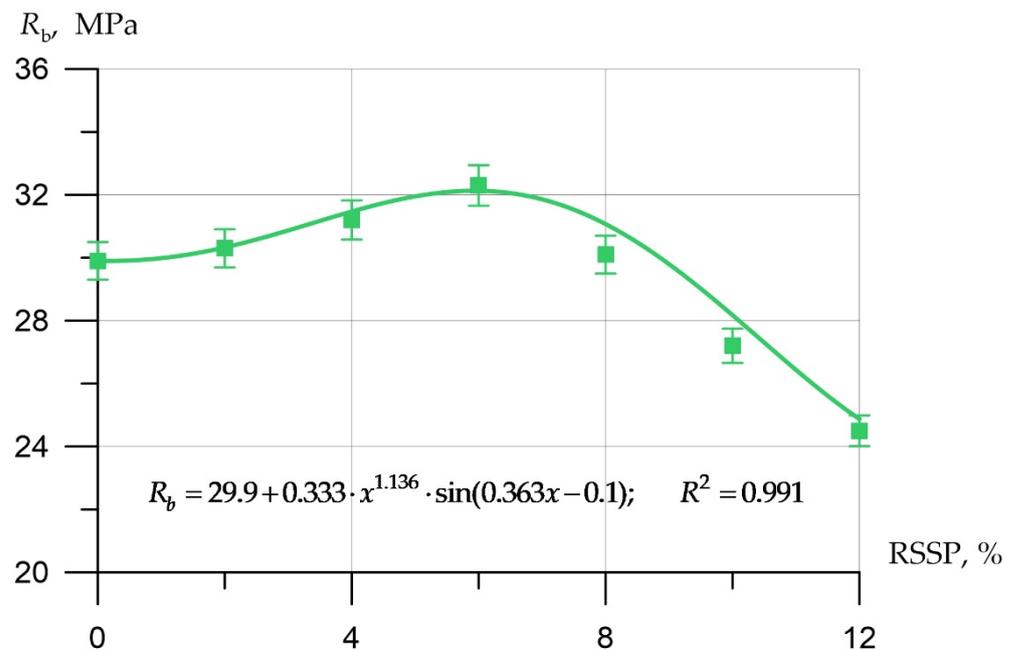


Figure 5. Axial compressive strength of snail shell powder concrete.

The dependence of the axial compressive strength of concrete on the amount of powder of snail shells RSSP was approximated by the function with a coefficient of determination of 0.991.

$$R_b = 29.9 + 0.333 \cdot x^{1.136} \cdot \sin(0.363x - 0.1); \quad R^2 = 0.991 \quad (3)$$

Based on the data in Figure 5, the highest axial compressive strength was observed in concrete with a dosage of RSSP of 6–8% more than that of a composition without RSSP. The trend of increase and decrease in strength at other considered dosages of the additive instead of part of the cement is the same as in Figure 4 for compressive strength. The increase in the axial compressive strength at doses of RSSP 2, 4, and 8% ranged from 0.6 to 4.4%, and the decrease in strength at nanomodifier doses of 10 and 12% reached 18%.

Figure 6 “shows the effect of the amount of snail shell powder on the tensile strength in bending of concrete”.

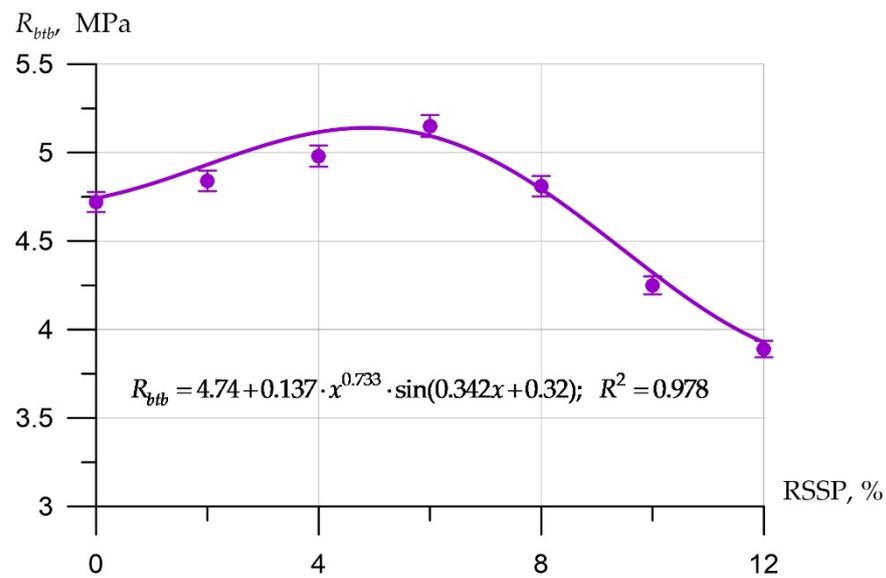


Figure 6. Tensile strength in bending of snail shell powder concrete.

The “dependence of the tensile strength in bending of concrete on the amount of snail shell powder was approximated by a function with a determination coefficient” of 0.978.

$$R_{btb} = 4.74 + 0.137 \cdot x^{0.733} \cdot \sin(0.342x + 0.32); R^2 = 0.978 \quad (4)$$

The data presented in Figure 6 confirm the effectiveness of the 6% RSSP dosage: the flexural tensile strength increased by up to 9% compared to the 0% RSSP control formulation. At the same time, the behavior of the dependence curve of R_{btb} on the amount of RSSP is approximately similar to the dependence curves in Figures 4 and 5, that is, a smooth increase in tensile strength in bending was observed with an increase in the dosage of RSSP from 0 to 6% (from 2 to 9% in comparison with the control composition); at 6% a peak (9%) was observed, followed by a sharper decrease in strength at dosages of 8, 10 and 12% (up to 17.6%).

Figure 7 “shows the effect of the amount of snail shell powder on the axial tensile strength of concrete”.

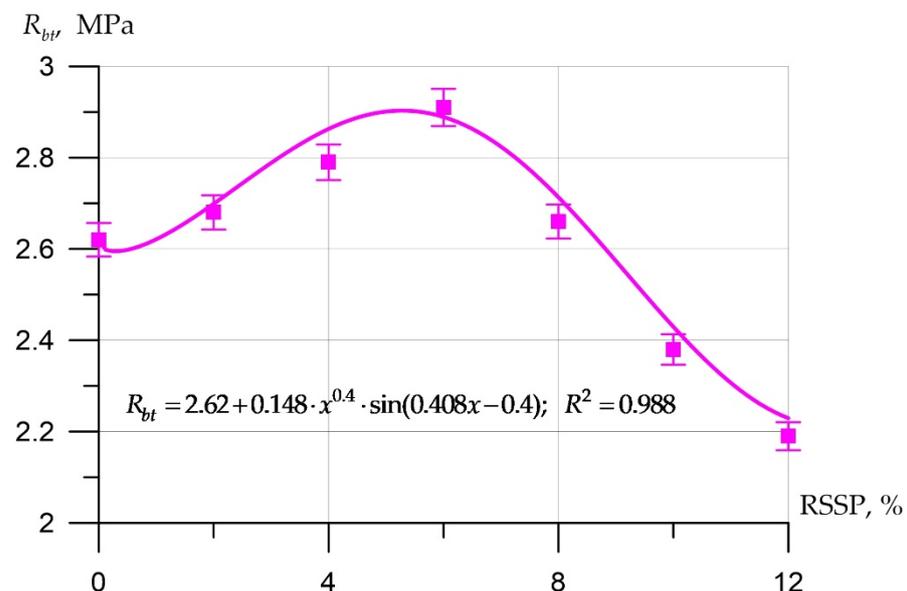


Figure 7. Axial tensile strength of snail shell powder concrete.

The “dependence of the axial tensile strength of concrete on the amount of snail shell powder is approximated by a formula with a determination coefficient” of 0.988.

$$R_{bt} = 2.62 + 0.148 \cdot x^{0.4} \cdot \sin(0.408x - 0.4); \quad R^2 = 0.988 \quad (5)$$

The axial tensile strength of concrete when 6% cement was replaced with snail shell powder was 2.91 MPa, which is 11% higher than that of the control composition without replacing cement with a nanomodifying additive. When replacing 2, 4 and 8% cement, R_{bt} increased from 1.5 to 6.5%. At dosages of the nanomodifying additive of more than 6 to 12%, a drop in axial tensile strength to 16.5% was observed. Thus, the dependence considered in Figure 7 only confirmed the previously considered dependences in Figures 4–6 in terms of the nature of the change in the strength characteristics and effective dosages of the nanomodifying additive in the form of a powder of snail shells.

Figure 8 the effect of the amount of snail shell powder on the modulus of elasticity of concrete is shown.

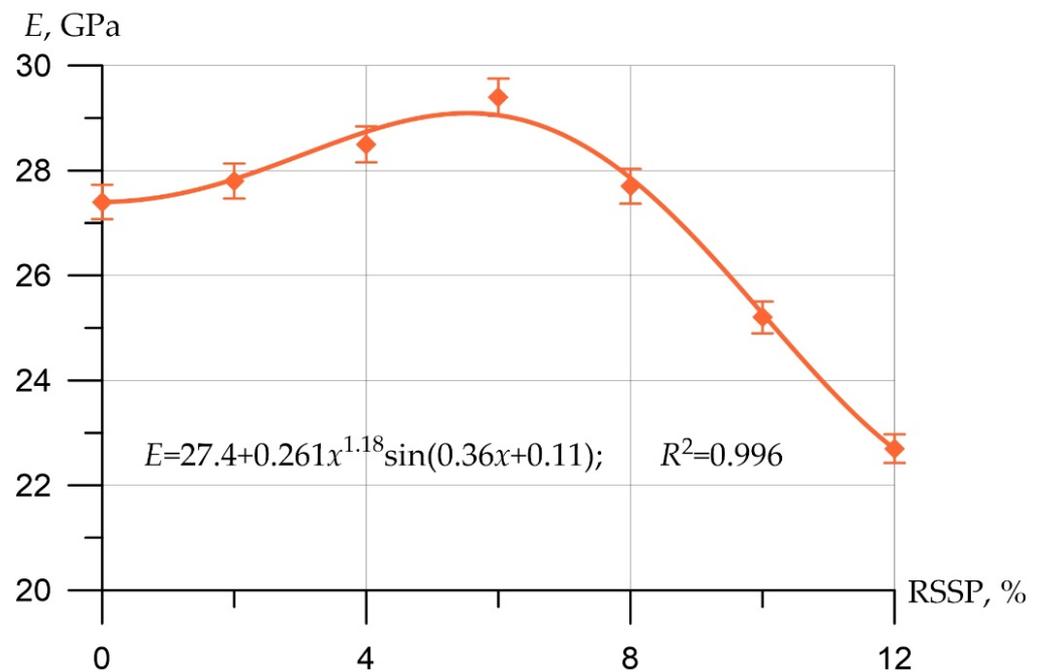


Figure 8. Modulus of elasticity of river snail shell powder concrete.

The “dependence of the modulus of elasticity of concrete on the amount of snail shell powder is approximated by a formula with a determination coefficient” of 0.996.

$$E = 27.4 + 0.261 \cdot x^{1.18} \cdot \sin(0.36x + 0.11); \quad R^2 = 0.996 \quad (6)$$

The maximum value of the E was recorded when replacing 6% of the cement with the RSSP nanomodifying additive. The values of the elasticity modulus increased with an increase in the dosage of the nanomodifying additive from 0 to 6%, and when the cement was replaced by more than 6%, a drop in the elasticity modulus was observed.

The “effect of the dosage of snail shell powder on the strain characteristics of concrete is shown in Figure 9”.

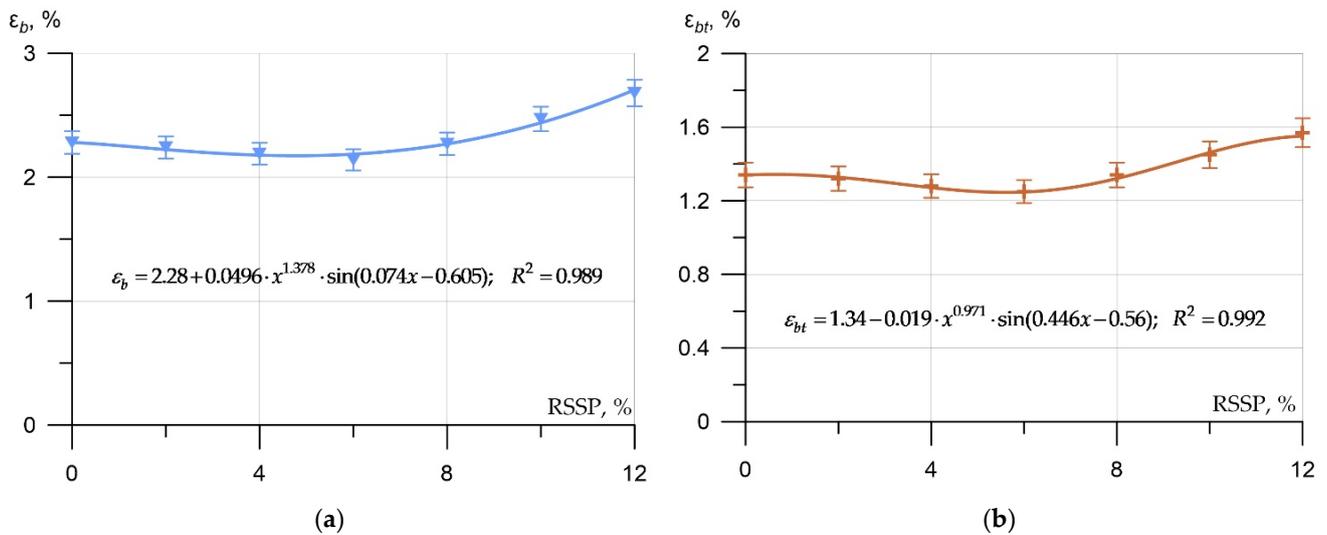


Figure 9. Strain characteristics of snail shell powder concrete: (a) under compression; (b) in tension.

The dependences of the strain characteristics of concrete on the dosage of snail shell powder are approximated by formulas with determination coefficients of 0.989 and 0.992.

$$\epsilon_b = 2.28 + 0.0496 \cdot x^{1.378} \cdot \sin(0.074x - 0.605); \quad R^2 = 0.989 \quad (7)$$

$$\epsilon_{bt} = 1.34 - 0.019 \cdot x^{0.971} \cdot \sin(0.446x - 0.56); \quad R^2 = 0.992 \quad (8)$$

The influence of the dosage of snail shell powder on the deformation characteristics of concretes was also evaluated by plotting compression diagrams “ $\epsilon_b - \sigma_b$ ” and tension “ $\epsilon_{bt} - \sigma_{bt}$ ”.

Stress–strain diagrams are shown in Figures 10 and 11.

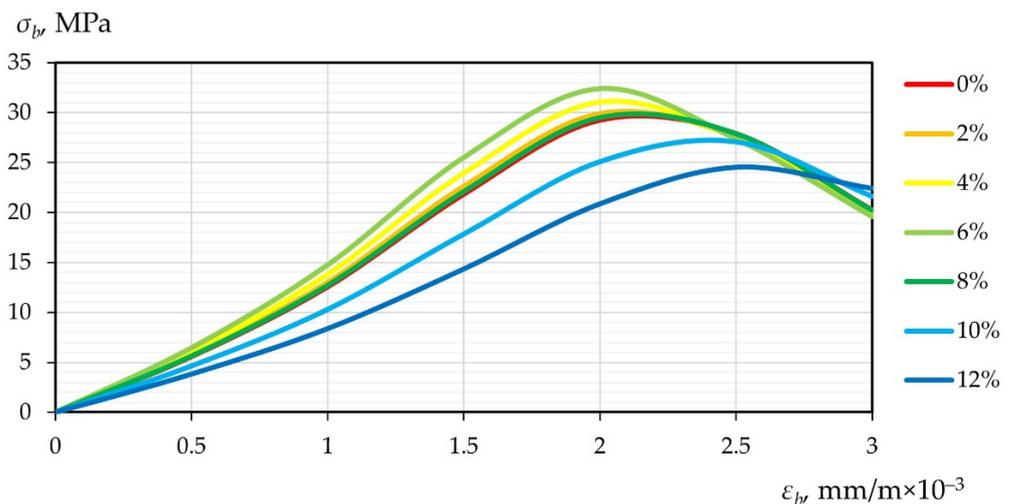


Figure 10. Stress–strain diagram in compression.

Analyzing the “stress–strain” diagrams during compression in Figure 9, we can conclude that the best properties are characteristic of concrete nanomodified with snail shell powder in the amount of 6%. The “peak of its diagram is shifted upwards and to the left relative to other diagrams, which indicates its high strength and low deformation characteristics”. Concrete has the worst deformation characteristics, “in which 12% of the cement was replaced by the powder of snail shells”. This is due to the oversaturation of concrete with a nanomodifying additive in excess of its rational amount. Thus, the peak of the stress–strain diagram at a dosage of 12% RSSP is shifted to the right and down relative to other

diagrams corresponding to lower dosages of RSSP. The peaks of the charts corresponding to dosages of RSSP 0, 2, 4, 8 and 10% are between the above charts with the best and worst dosages of RSSP. The above analysis of stress–strain diagrams in compression is also applicable to diagrams in tension. Therefore, with regard to deformability, the composition of concrete with a 6% replacement of cement with a nanomodifying additive in the form of RSSP also turned out to be the most effective and confirmed the dependencies previously obtained in Figures 5–8 and, accordingly, a certain rational composition of concrete.

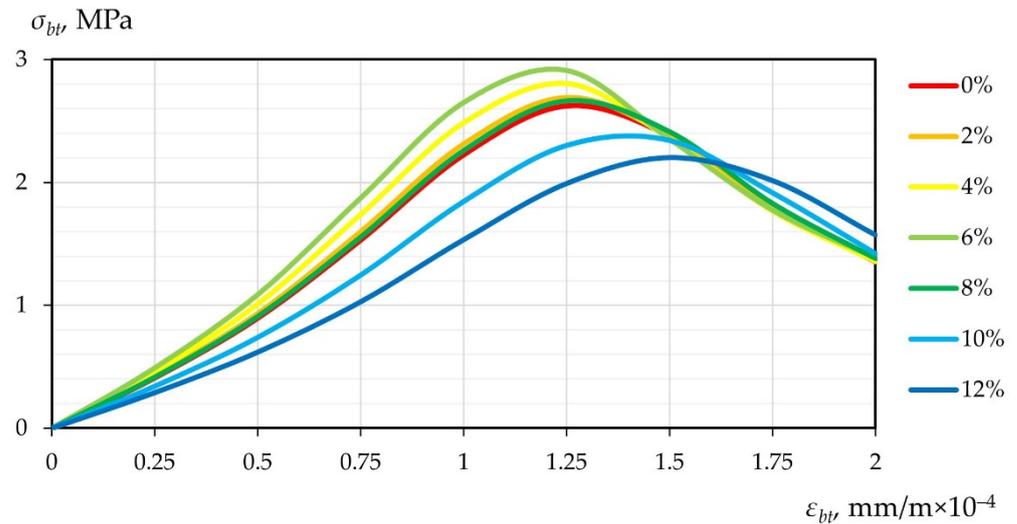


Figure 11. Stress–strain diagram in tension.

Photographs of “the microstructure of cement stone with different dosages of snail shell powder are shown in Figures 12–17”.

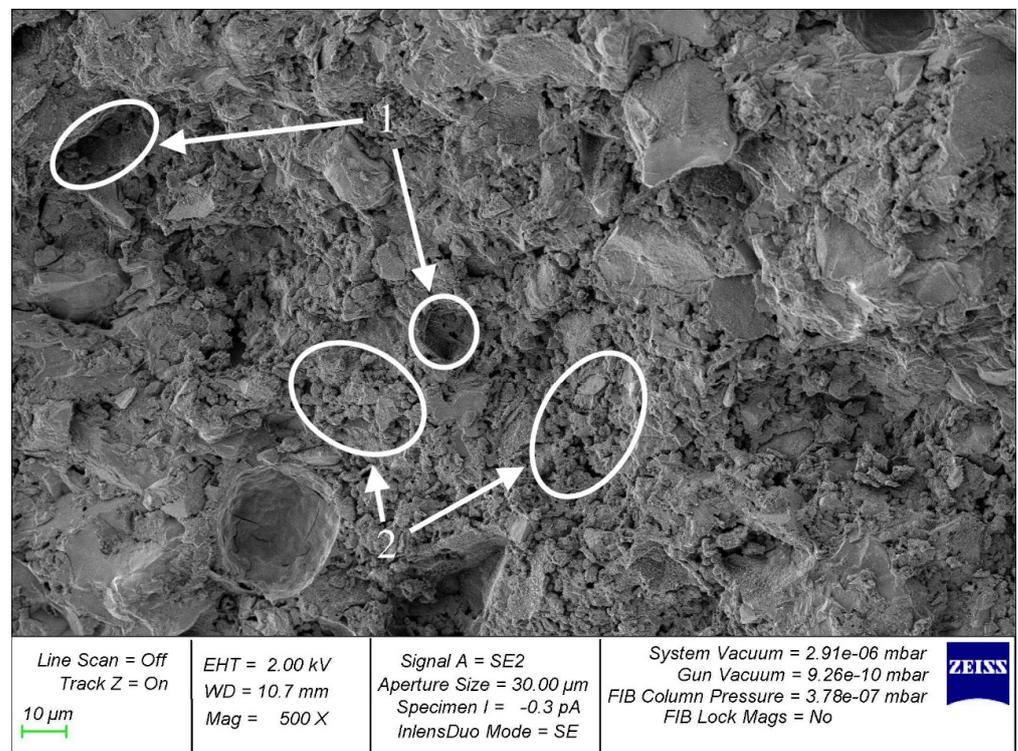


Figure 12. Sample with snail shell powder dosed at 2% (1—porosity, 2—binder phase).

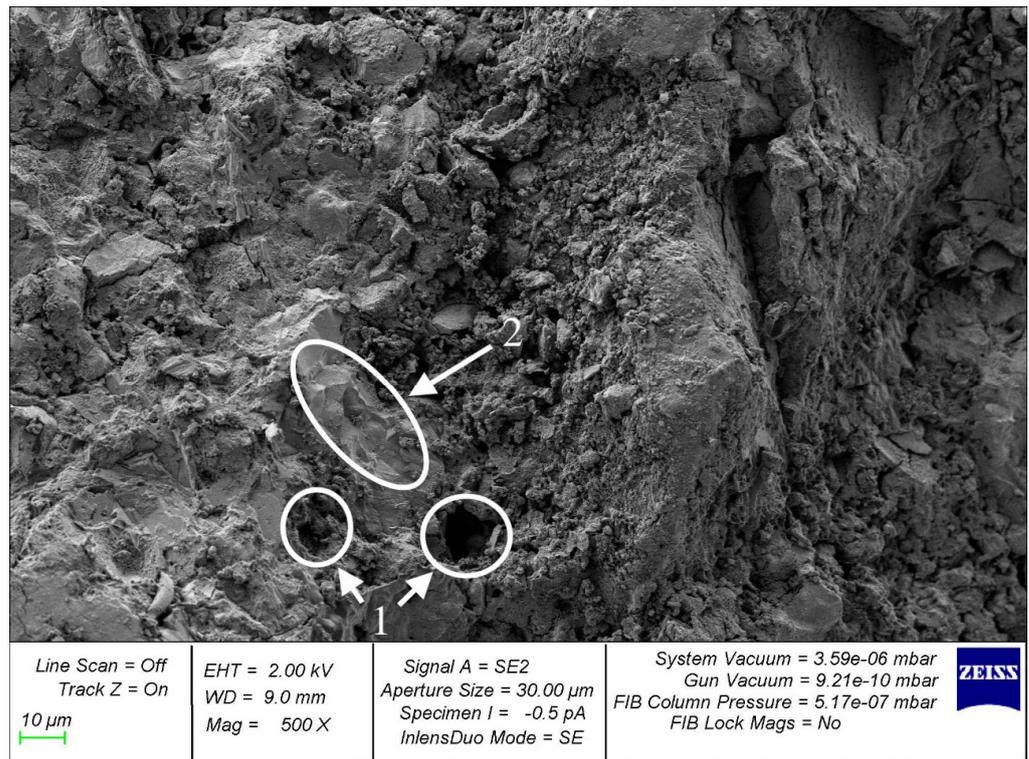


Figure 13. Sample with 4% snail shell powder dosage (1—porosity, 2—binder phase).

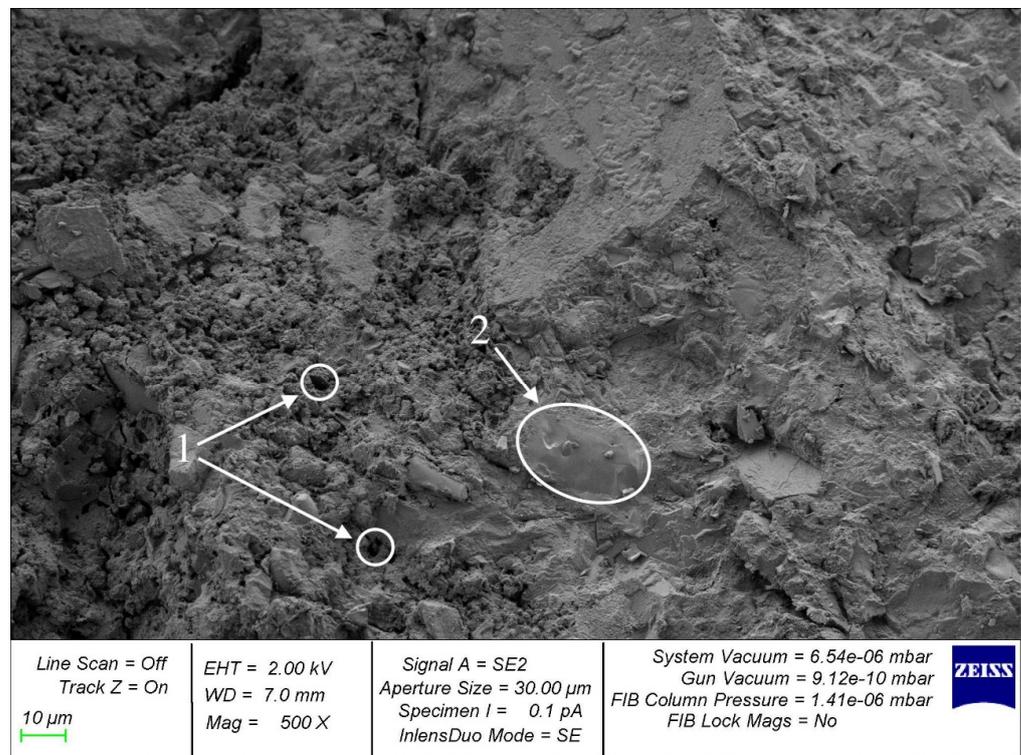


Figure 14. Sample with 6% snail shell powder dosage (1—porosity, 2—binder phase).

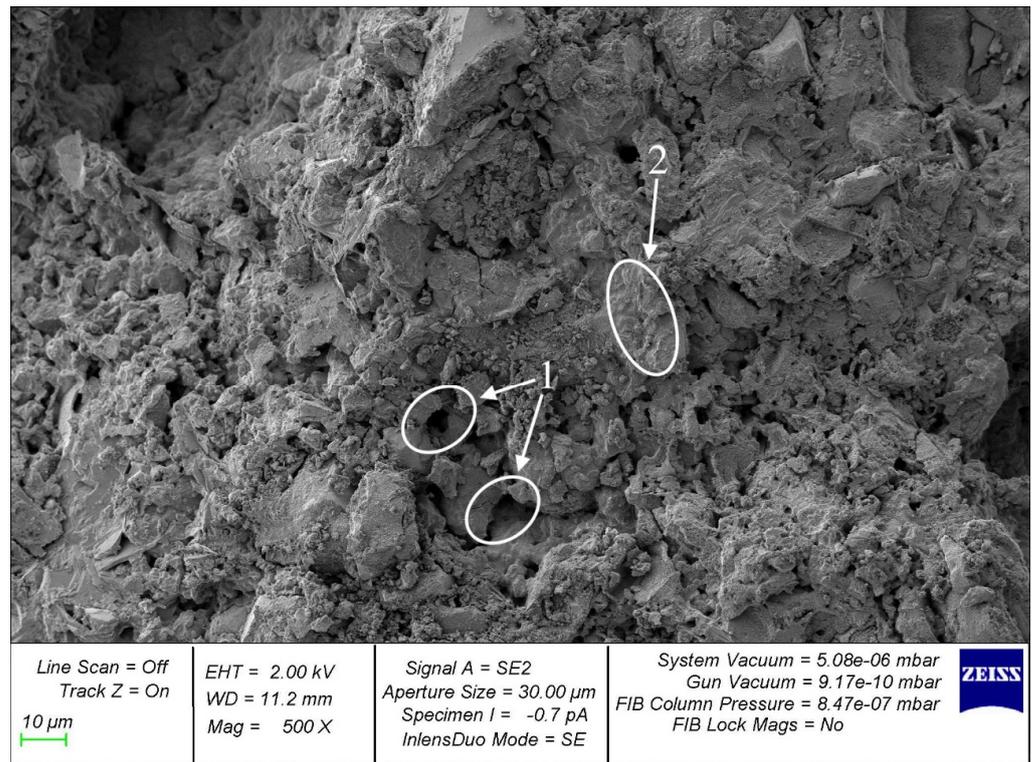


Figure 15. Sample with 8% snail shell powder dosage (1—porosity, 2—binder phase).

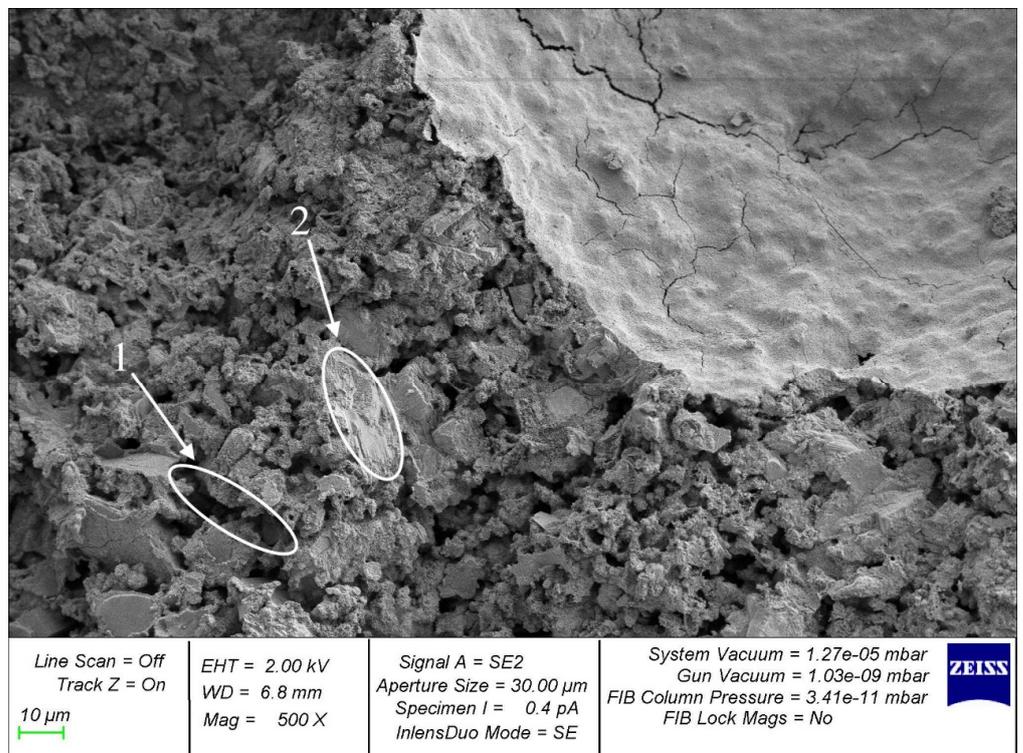


Figure 16. Sample with 10% snail shell powder dosage (1—porosity, 2—binder phase).

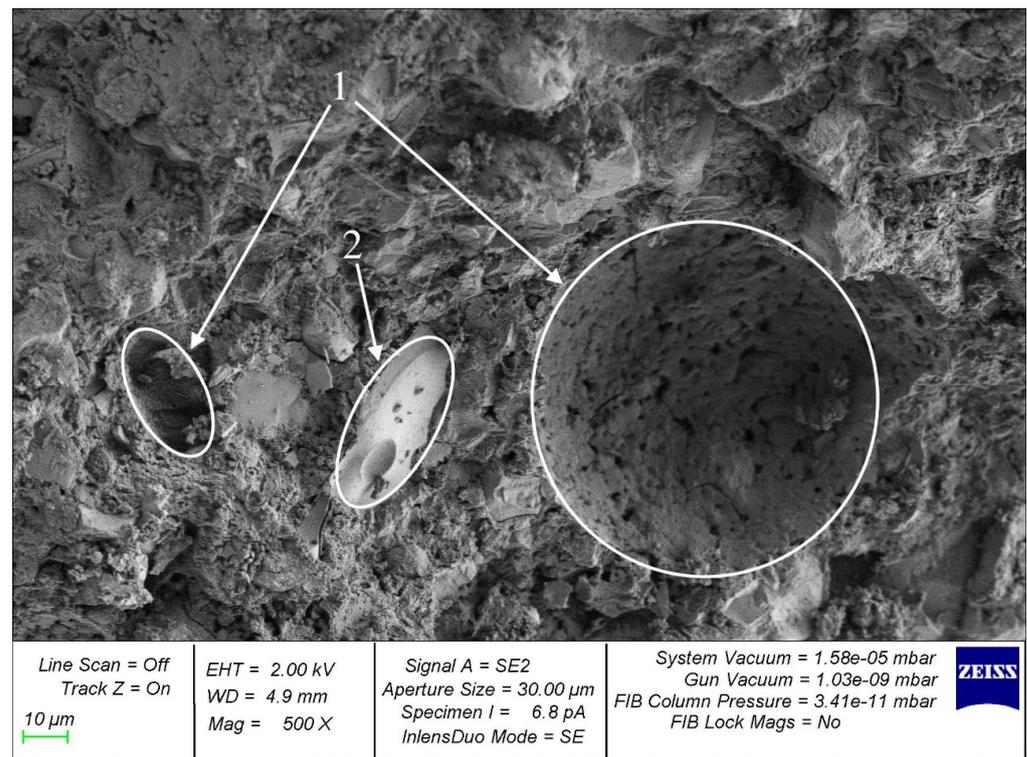


Figure 17. Sample with 12% snail shell powder dosage (1—porosity, 2—binder phase).

Samples with a dosage of 6% RSSP have the highest integrity of the microstructure, without voids and cracks in comparison with other samples (Figures 11, 12 and 14–16). That is, replacing part of the cement with 6% snail shell powder contributes to the formation of a denser microstructure by improving the interaction between the phases of various concrete components. The shells of river snails contain a lot of calcium, which, when interacting with the cement system, forms a larger network of calcium silicate hydrate (CS–H) minerals. An increase in the proportion of C–S–H gel in the microstructure leads to compaction and, accordingly, an increase in its strength (Figures 11–13). When replacing more than 6% of the cement (Figures 14–16), a large number of voids were formed, and cracking occurred inside the structure due to the solubility of the carbonate compound when it interacted with water during the hardening process. This, probably, led to a decrease in the strength characteristics of concrete mixes with RSSP dosages of 8, 10, and 12% [16,40].

The obtained applied advantages of the new nanomodified concrete are substantiated by structural–chemical and structural–physical aspects. Figures 12–17 clearly confirm the interactions that have occurred at the micro- and macrolevels and represent a graphical basis for immersing the reader in the process of controlling the applied properties of new concretes by interfering with the fundamental process of structure formation. Such studies have not been previously carried out in the considered works [2,38–40].

The effect obtained, expressed in the increase in the characteristics of concrete nanomodified by RSSP, can be explained as follows. First, from the point of view of the process of structure formation, it should be noted that the powder is well compatible with other components of concrete. Its introduction in a rational amount does not interfere with the main processes and, first of all, hydration, but, on the contrary, contributes to a more developed course of this process. This is confirmed by the chemical composition of the powder and its good correlation with other components and their chemical composition. In addition to structural–chemical interactions, the effect obtained is also explained by the structural–physical aspect. The introduction of a nanomodifying powder contributes to a denser packing of particles at the micro- and macrolevels, and the emergence of a developed structure of compacted and strengthened concrete.

It has been experimentally established and proven empirically that a dosage of RSSP in an amount of 6% leads to the best interactions from a structural–chemical point of view and the most developed structure of concrete from a structural–physical point of view. This is confirmed by the highest physical and mechanical indicators.

4. Discussion

To obtain a more accurate picture of the change in the characteristics of concrete, depending on the amount of RSSP additive introduced to replace part of the cement, we present them as a percentage in Table 6.

Table 6. Changes in characteristics of concrete depending on the dosage of snail shell powder (Δ).

Concrete Characteristics	Δ , %, When the Content of the Powder of the Shells of River Snails in the Amount						
	0	2	4	6	8	10	12
$R_{b.cub}$, MPa	0	+3	+7.1	+11.9	+2.0	−7.9	−16.8
R_b , MPa	0	+1.3	+4.3	+8.0	+0.7	−9.0	−18.1
R_{btb} , MPa	0	+2.5	+5.5	+9.1	+1.9	−10.0	−17.6
R_{bt} , MPa	0	+2.3	+6.5	+11.1	+1.5	−9.1	−16.4
ε_{bR} , mm/m $\times 10^{-3}$	0	−1.8	−3.9	−6.1	−0.4	+8.3	+14.9
ε_{btR} , mm/m $\times 10^{-4}$	0	−1.5	−4.5	−6.7	0	+8.2	+17.2
E , GPa	0	+1.5	+4.0	+7.3	+1.1	−8.0	−17.1

From Table 5 it can be seen that the most optimal amount of cement to be replaced by the powder of snail shells is 6%. Such an amount of the nanomodifying additive makes it possible to increase the strength characteristics by up to 12% and reduce the deformations by up to 7%. In this case, the elastic modulus increased up to 8%. At the same time, replacing cement with the nanomodifier RSSP, from 0 to 6%, there is a smooth increase in strength characteristics and a decrease in the deformation properties of concrete in comparison with the control composition. It can also be seen that after a further increase in the dosage of RSSP instead of part of the cement from 6 to 12%, there is a sharper decrease in the strength characteristics (up to 18%) and an increase in the deformation properties (up to 17%) of nanomodified concrete compared to conventional concrete. The modulus of elasticity is reduced to 17% at 12% RSSP.

The obtained optimal dosage of the nanomodifying additive in the form of a powder of snail shells of 6% is in good agreement with the results of other studies [2,38–40], in which the most effective dosages of shell powder were 4% [38], 5% [39,40] and to a lesser degree at 10% [40]. However, at the same time, in [39], an increase in the compressive strength after 28 days of concrete hardening was achieved up to 7.5%, and the axial tensile strength up to 3.5%. The study [2] summarizes the feasibility of using various aquaculture wastes in concrete as a partial replacement for cement. However, it is noted that it is necessary to dose the obtained powder from the waste in a small amount, in which the compressive strength of concrete is only slightly below the strength of the control samples from ordinary concrete, in contrast to high percentages of cement replacement, in which the strength is much lower. Only a slight increase in flexural tensile strength and elastic modulus was observed due to the development of a good bond between the binder matrix and aggregates [2]. In [38], the optimal dosage of powdered ground shells, equal to 4%, did not lead to an increase in the compressive strength of concrete and the elastic modulus. At the same time, the tensile strength in bending and axial tension were increased to 10 and 9%, respectively. In comparison with the other studies [2,38–40], it was possible to achieve a more impressive improvement in the strength and deformation characteristics of concrete due to its nanomodification with the powder of snail shells.

5. Conclusions

(1) Concrete was obtained using aquaculture waste in the form of a nanomodifying powder of snail shells, the properties of which are improved compared to conventional concrete. This confirms the efficiency of using the accumulated aquaculture waste in concrete without reducing the strength characteristics and deteriorating other properties of the composite.

(2) The replacement of part of the cement with snail shell powder in the amount of 6% turned out to be optimal.

(3) By the nanomodification of concrete with powdered shells of river snails, it was possible to achieve an increase in compressive strength up to 12%, axial compressive strength—up to 8%, tensile strength in bending—up to 9%, axial tensile strength—up to 11%, modulus of elasticity—up to 8%. In this case, a gradual increase in the strength characteristics and elastic modulus was observed with an increase in the dosage of RSSP from 0 to 6% and a sharper drop with a further increase in the amount of nanomodifier used.

(4) Concrete nanomodification with snail shell powder in the amount of 6% contributed to the reduction of deformations up to 7%. Increasing the amount of RSSP instead of part of the cement to 12% led to an increase in deformations to 17%.

(5) The study of the microstructure of concrete samples nanomodified with snail shell powder confirmed the obtained dependences of properties on the dosage of the nanomodifier and the most effective dosage of RSSP.

The study is planned to continue in the direction of studying the effect of the nanomodification of concrete with other types of aquaculture waste to improve the structure and characteristics of concrete and the state of the environment by finding effective ways to dispose of accumulated waste.

Author Contributions: Conceptualization, S.A.S., E.M.S., A.N.B. and N.D.; methodology, S.A.S., E.M.S. and M.K.; software, S.A.S., E.M.S., A.N.B. and N.B.; validation, N.D., S.A.S., E.M.S. and A.N.B.; formal analysis, N.D., S.A.S. and E.M.S.; investigation, N.B., L.R.M., S.A.S., E.M.S., A.N.B. and B.M.; resources, B.M.; data curation, S.A.S., E.M.S. and M.K.; writing—original draft preparation, S.A.S., E.M.S. and A.N.B.; writing—review and editing, S.A.S., E.M.S. and A.N.B.; visualization, S.A.S., E.M.S., A.N.B. and N.B.; supervision, L.R.M. and B.M.; project administration, L.R.M. and B.M.; funding acquisition, A.N.B. and B.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Acknowledgments: The authors would like to acknowledge the administration of Don State Technical University for their resources and financial support.

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

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