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# Cement compositions with the chitosan additive

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**Abstract**

The article deals with the results of the studies of the pore structure, strength properties, biocidal properties and frost resistance of the cement composition samples with the additives of a synthetic water repellent polyethylhydrosiloxane and a natural aminopolysaccharide 2-amino-2-deoxy-β-D-glucan – chitosan. It is shown that an application of the chitosan additive does not reduce strength characteristics of the cement compositions in comparison with a synthetic polymer additive on the basis of polyethylhydrosiloxane. An introduction of the chitosan into the cement compositions allows to reduce total pore volume and has a positive effect over the character of their distribution, and also increases frost resistance and biostability.

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*Keywords:* Portlandcement; cement composition; mortar; additive; polyethilhydrosiloxane; chitosan; aminopolysaccharide 2-amino-2-deoxy-β-D-glucan; pore structure; compresive strength; frost resistance; biocidal properties.

## 1. Introduction

A problem of the synthetic polymer additive replacing by the biodegradable natural polymeric compounds is particularly relevant on the environmental requirement background. Therefore, this article investigates the effect of synthetic water repellent polyethylhydrosiloxane (PEGS) and natural aminopolysaccharide 2-amino-2-deoxy-β-D-glucan – chitosan – over the properties of cement compositions.

Chitosan is a product of chitin de-acetylation. Chitin is the second (after cellulose) on the prevalence of natural biopolymer extracted from fully renewable natural raw materials. It goes to the composition of the supporting tissue and the external skeleton of arthropods (crustaceans, arachnids, insects), cell walls of microorganisms and fungi

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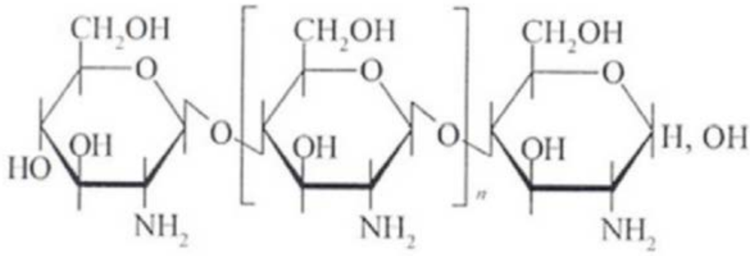
where chitin is complexed with proteins and mineral salts. Annually living organisms produce tens of billions of tons of chitin.

Chitosan is obtained in toughest conditions by processing chitin with a 40-49% sodium hydroxide aqueous solution under the temperature of 110-140°C within 4-6 hours. This results to the compound corresponding to the following structural formula [1]:




Due to the biocompatibility with living tissues, ability to biodegradation, high adhesion, non-toxicity and other properties, chitosan is widely used in medicine, agriculture, crops, veterinary, food, cosmetic, paper, textile and other industries.

## 2. Methods

To study the pore structure, compressive strength and biocidal properties the samples have been produced on the basis of a cement-sand mortar of 1:3 by weight with the additives (wt. %): chitosan – 1.0; PEGS – 0.1; chitosan – 1.0 + PEGS – 0.1; chitosan – 1.0 + PEGS – 0.5.

The pore structure investigations have been carried out by the reference method of the pore structure measurement. The method is based on a measurement of the relative moisture content curve with the evaporation of the measuring liquid (decane) and comparing it with the independently obtained equilibrium curve of relative moisture content standards. The reference method of the pore structure measurement has a number of significant advantages over the existing ones:

- Wide measuring range of pores from 10 Å to 106 Å
- Elimination of measurement error associated with the deformation patterns of the specimen, typical of this popular method, like mercury pore measurement.
- An opportunity to explore the structure of porous bodies of any chemical nature.

The investigations of the compressive strength and biostability have been carried out according to the Russian state standards GOST 5802-86. Mortars. Test Methods; GOST 9.048-89. Unified system of corrosion and ageing protection. Technical items. Methods of laboratory tests for mould resistance; GOST 9.049-91. Unified system of corrosion and ageing protection. Polymer materials and their components. Methods of laboratory tests for mould resistance.

To study a frost resistance of the cement compositions with the chitosan additive the samples have been produced on the basis of a cement-sand mortar of 1:3 by weight with the various amounts of the chitosan additive from 0.2 to 2.0 percent. The investigations have been carried out according to the GOST 5802-86. Mortars. Test Methods.

## 3. Results and Discussion

The permeability of cement concretes and mortars is largely dependent on volume, distribution and structure of pores. Concretes and mortars are capillary-porous materials, like full with subtle mesh of pores and capillaries of various sizes. Fine pores and capillaries (micropores) smaller than $10^{-5}$ cm, which include, in particular, the pores of the cement gel, is virtually impermeable to the water and microorganisms. The micropores and capillaries larger than

$10^{-5}$ cm are available for the filtration of the water and aggressive substances and for the penetration of microorganisms [2, 3]. Therefore, the reduction of section size of pores, tortuosity and length is the way to improve the impermeability of cement concrete and mortar for microorganisms and water.

In this regard, we have studied the effect of PEGS and chitosan additives on the volume of the cement composition pore space. The results of the pore structure investigation are given in Fig. 1 and Fig. 2.

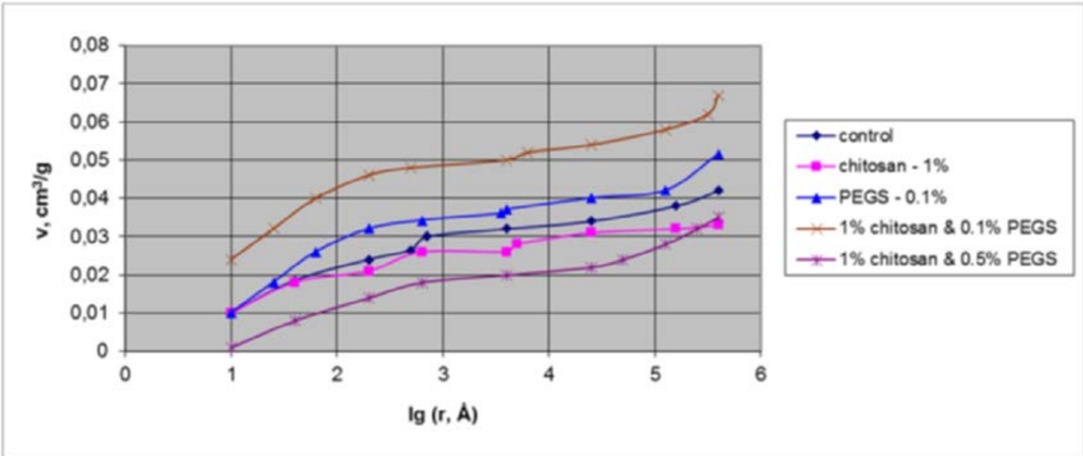



Fig. 1. The average porogrammes of the cement mortars with PEGS and chitosan additives

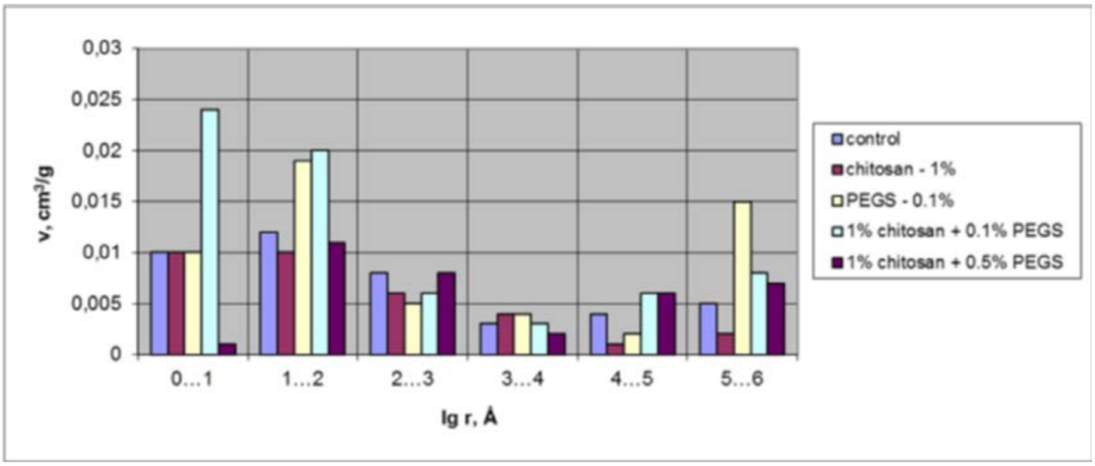



Fig. 2. The content of pores in the cement mortar with PEGS and chitosan additives.

The porograms show that the pore structure of the samples changes under the introduction of PEGS additive in an amount of 0.1% and 0.5% by cement's weight and chitosan in an amount of 1% by cement's weight. The additives affect total pore volume and the nature of their distribution.

As it can be seen from Fig. 1 and Fig. 2, in the samples of cement mortar, which includes an additive based on PEGS in an amount of 0.1% by weight of cement, the volume of gel pores with a radius of $10...10^2$ Å significantly increases and a contraction pore volume with a radius of $10^4…10^3$ Å decreases. However, the volume of capillary pores with a radius of more than $10^4$ Å rises in 3 times in comparison with the composition without additives that will contribute to the development of destructive processes in the future.

The results of studies of pore structure of modified cement mortars showed that in the samples of cement mortar, which includes a chitosan additive in an amount of 1% by cement's weight total pore volume slightly decreases in comparison with the control sample without additives. However, the nature of pore distribution changes. Gel pores occupy 19...20% of the volume of material and the total volume of contraction and capillary pores does not exceed 5%.

The introduction of complex additives on the basis of PEGS – 0.1% by weight of cement and chitosan – 1% by weight of cement leads to a sharp increase in the total pore volume (Fig. 1). Therefore, we can assume that in long-term operation (for example, at industrial enterprises) the cement concretes and mortars, which include such additive, will be subjected to the migration of the moisture, corrosive substances and microorganisms.

An application of complex additive on the basis of PEGS – 0.5% by weight of cement and chitosan – 1% by weight of cement is the most effective way to reduce the volume of the pore space of cement compositions.

However, the test results of the samples of the modified cement compositions in compression have shown that a cement composition with the additive on the basis of chitosan in an amount of 2.0% by mass has a maximum strength, and a composition with the additive on the basis of PEGS and chitosan in an amount of 0.5% and 1.0% by mass respectively has a minimum strength (see Table 1).

Table 1. The results of the compressive strength tests.

| Additive | Additive content, % | The tensile of compressive strength, MPa |
|---|---|---|
| Control | 0 | 55.24 |
| PEGS | 0.1 | 49.10 |
| Chitosan | 0.4 | 55.58 |
| Chitosan | 1.0 | 55.98 |
| Chitosan | 2.0 | 57.43 |
| Chitosan + PEGS | 1.0 + 0.1 | 48.89 |
| Chitosan + PEGS | 1.0 + 0.5 | 48.54 |

The results of the tests of biostability have shown that the hardened cement mortar, both in pure form and with different additives (chitosan, PEGS, and the mixture PEGS+chitosan), is not a food source for fungi and can be considered as fungi resistant. In addition, these cement compositions possess strong fungistatic properties.

In the initial period cement mortars and concretes have antibacterial properties due to the alkaline environment of the pore fluid of a cement paste. But over time they are subjected to carbonization and lose their antibacterial properties.

We can expect that the introduction of chitosan into the cement composition is accompanied by changes in the structure both of the original matrix of the binder, and of the biopolymer, which naturally reduces the availability of the attack of fungi of this modified material. Another likely reason for the fungicidal activity of chitosan may be the inhibition of the enzymatic activity.

The following Table 2 covers the data of the study of bactericidal (fungicidal) activity of the chitosan and PEGS.

Table 2. The results of the inhibitory effect on fungi of the chitosan and PEGS.

| Species of fungi | The inhibitory effect on fungi, % | | | |
|---|---|---|---|---|
| | Chitosan | | PEGS | |
| | 1st week | 2nd week | 1st week | 2nd week |
| Aspergillus niger | 65 | 37 | 11 | 7 |
| Aureobasidium pullulans | 64 | 62 | (+)3 | (+)2 |
| Penicillium chrysogenum | 43 | 6 | (+)38 | (+)54 |
| P.cyclopium | 62 | 35 | 0 | (+)6 |
| P.funiculosum | 59 | 38 | 9 | 1 |

| | | | | |
|---|---|---|---|---|
| P.ochro-cloron | 39 | 35 | (+)7 | (+)4 |
| Paecilomyces varioti | 100 | 100 | 1 | (+)1 |
| Trichoderma viride | 82 | — | 0 | — |

As it can be seen from the Table 2, by the end of the 1st week chitosan has a significant inhibitory effect. The degree of suppression of fungal growth exceeds 40%. This figure is more than 60% for the five species of fungi, and it reaches 100% for Paecilomyces varioti. By the end of the 2nd week the action of chitosan slackens for most species that is probably due to the natural slowdown in the growth of the fungi themselves. However, this figure still equals 100% for Paecilomyces varioti. Thus, it is possible to speak about clearly marked fungistatic and even fungicidal action of chitosan.

Polyethylhydrosiloxane has showed almost complete absence of biocidal properties. The degree of suppression of growth of fungi ranges from 0 to 11%, and sometimes even has a stimulating effect. Therefore, we can assume that cement mortars and concretes, modified by PEGS, will be subject to the destruction under the influence of biologically active substances in an urban environment.

Thus, from a technological point of view and from the point of view of physical-mechanical indicators a preference should be given to the chitosan additive for the modification of the cement compositions studied in our work.

The normal conditions of hardening of mortars corresponds to the temperature of 15-20 °C. At lower temperatures the hardening process slows down. To maintain normal conditions of hardening in the solutions antifreeze additives are used to be added to the mortars. These additives put the water in a bound state and participate in further hydration processes of a binder. In the presence of water, chitosan swells and actively calmative pores, increasing the density of a cement stone. Therefore, the studies of the frost resistance of the cement compositions with the chitosan additive have been conducted. The results are represented in the Table 3.

Table 3. The results of the frost resistance tests.

| Chitosan content, % | The tensile strength in bending, MPa | | The tensile of compressive strength, MPa | | Loss of strength, % |
|---|---|---|---|---|---|
| | before exposure | after exposure | before exposure | after exposure | |
| 0 | 7.12 | 3.46 | 55.24 | 19.20 | 65.20 |
| 0.2 | 7.26 | 5.31 | 55.42 | 32.47 | 41.40 |
| 0.6 | 7.49 | 6.53 | 55.72 | 42.04 | 24.50 |
| 1.0 | 7.59 | 6.47 | 55.98 | 42.58 | 24.00 |
| 2.0 | 7.12 | 5.54 | 57.93 | 38.69 | 33.80 |

The tests carried out in the mode of alternate freezing and thawing of water-saturated cement samples have showed that the percentage loss of strength of samples in compression with the content of chitosan from 0.6 to 1.0% by weight of cement does not exceed the permissible limit values of 25%. The control samples correspond to the Marche F50, the samples with the chitosan additive correspond to the Marche F100.

## 4. Conclusions

1. The introduction of the additive based on a natural polymer – chitosan – in the cement compositions allows to reduce the total volume of pores and has a positive effect on the nature of their distribution.
2. It is shown that the addition of chitosan does not reduce the strength characteristics of the cement compositions in comparison with synthetic polymer additives on the polyethylhydrosiloxane basis.
3. The optimum amount of the chitosan additive, which allows to increase the resistance of the cement compositions to the alternate freezing and thawing, is of 0.6-1.0% from cement mass.

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