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INFLUENCE OF POLYMERS ON THE PROPERTIES OF HIGH-STRENGTH PRESSED MINERAL-BINDING COMPOSITIONS

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One of the ways to improve the physical and mechanical properties of cement compositions is their modification with polymers. The article presents the results of the study of pressed cement-polymer compositions based on Portland cement modified with complex polymer additives. It is shown that with the simultaneous application of pressure and temperature, the final product has a denser defect-free structure due to the reduction of porosity and the formation of hydration products with higher density, and the replacement of part of pure clinker Portland cements with polycomponent mineral additives reduces CO_2 emissions. A set of complex polymer additives has been developed that provide an increase in bending strength by 1.5–2 times compared to single-component additives.

Keywords: hot pressing, polymer modifiers, pressed polymer-cement compositions, multicomponent mineral additives, low-carbon mineral materials.

Introduction

Modern construction requires materials with high performance characteristics: strength, frost resistance, durability and stable structure. Traditional cement systems have a few disadvantages: high porosity, cracking during hardening and limited durability. The binding properties of Portland cement, mortars and concrete during their compaction and shaping by traditional methods are not fully used. One of the ways to improve these properties is to modify cement compositions with polymer additives by pressing. This makes it possible to combine the benefits of densification during pressing with the effects of polymer micro-reinforcement (Goyda G. R. et al., 2005).

Pressed cement compositions make it possible to obtain materials with maximum density and low porosity. The strength of pressed compositions exceeds the cement class by 10 times. During the pressing process, high pressures are created in the sample, and the formation of a new structure occurs under conditions different from the usual hardening of cement compositions. Cement pressing methods have found wide application in the production of small-sized construction products.

The construction industry is one of the key drivers of the economy and at the same time one of the largest sources of greenhouse gas emissions. The construction and construction materials sector accounts for more than 35 % of global energy consumption and about 40 % of CO_2 emissions. In the context of the implementation of the European Green Deal (Green Deal. COM, 2019), the Paris Climate Agreement and the global trend towards decarbonization, construction itself should become a space for the introduction of low-carbon technologies and materials. To reduce CO_2 emissions, part of the pure clinker Portland cement of type CEM I in polymer–cement composites is intended to be replaced with multicomponent mineral additives, representing a promising approach toward sustainable development in the construction industry (De Grazia M. T. et al., 2023).

The modern model of construction development is based on the principles of sustainability, energy efficiency and resource conservation. The main requirements for the industry are:

– energy efficiency and thermal standards for buildings (NZEB) (State Building Standards of Ukraine, 2022);

– reduction of the carbon footprint at all stages of the life cycle (CEMBUREAU, 2020);

– circular economy, recycling of materials (Kirchherr, Julian, 2023);

– environmental certification (LEED, BREEAM, DGNB) (Whole Building Design Guide, 2023).

For Ukraine, adaptation to these requirements is part of the implementation of European legislation (CEMBUREAU, 2020).

Research on pressed binder systems indicates the effectiveness of using polymer and technogenic additives to improve the physical and mechanical properties of materials. The use of lignosulfonate, redispersal polymers and carbon nanoparticles contributes to increasing strength, reducing shrinkage cracks and improving the structural uniformity of pressed compositions.

The strength of cement products and materials in the general case is limited by the value of capillary porosity. Theoretical and experimental studies by D. M. Roy, G. R. Gowdy et al. (Goyda G. R. et al., 2005) established the possibility of obtaining high-strength hardened cement paste by pressing. The authors established the influence of high pressure (up to 690 MPa) and temperature (up to 300 °C) on the physical and mechanical properties of hardened cement paste. However, significant pressing parameters are difficult for technical applications. Based on mineral binder systems, composites called chemically bonded ceramics (CBC) and cement materials with a defect-free structure (MDF) were obtained. The use of polymer modifiers made it possible to create high-strength and chemically resistant polymer-cement compositions. They began to successfully compete with aluminum, cast iron, steel and plastics in their characteristics.

Currently, important studies aimed at optimizing mechanical properties, increasing environmental safety and improving technological processes for the manufacture of polymer-modified pressed materials (Min Li et al., 2023; Sanytsky M. et al., 2024). It has been established that the properties of such materials can be significantly improved by changing the types of polymers and their concentrations in the composition, which makes them universal in application.

Thus, there is a trend towards an integrated approach: the combination of polymer and technogenic additives, pressing under pressure and control of technological parameters allows obtaining high-quality pressed binding materials with improved operational and performance characteristics. At the same time, modern requirements for the construction industry determine the need to transition from traditional production models to low-carbon practices. The challenges facing Ukraine are at the same time opportunities for modernization of production and the introduction of innovations.

Low-carbon construction is not only a tool for environmental transformation, but also a condition for ensuring the competitiveness of the Ukrainian economy. Such construction encompasses a set of solutions aimed at minimizing CO_2 emissions in the life cycle of structures. Key areas include low-carbon cement and polymer-cement compositions (WCA, 2021).

The study aims to substantiate the efficiency of using polymer modifiers in pressed mineral binder compositions to produce high-strength and durable low-carbon construction composites

Materials and methods

The following types of Portland cements were used as binders: CEM I 42.5 R.

As polymers with simple and complex ester groups, polyisocyanates, Laprol-502, Laproxide were used; as well as oligoheteroacrylate and glycerin.

Production technology: cold and hot pressing under simultaneous pressure and temperature; molding into standard samples for testing.

The curing processes of the binders were carried out by cold pressing with subsequent steam curing or hot pressing. The semi-dried mixtures (water / solid ratio was 0.1) were compacted by double-sided pressing at a specific pressing pressure of 50 MPa. The samples were compacted by this pressure for 1 minute. These parameters were obtained by operating the compacting equipment. After that, the samples were pressed and hardened with steam environment at a temperature of 85 °C in the mode of 3 + 6 + 2 hours. After steam treatment, the samples were removed from the mold and tested for compressive and bending strength. The hot-pressing temperature was 150 °C. The temperature increased using resistive heaters located around the perimeter of the pressing mold. The temperature of the samples was regulated by a thermocouple and a potentiometer. The temperature increase rate was 10 °C per minute. The total pressing time with the inclusion of heating and isothermal hardening was 30–45 minutes.

The properties were controlled according to standard methods for determining bending strength, density and porosity according of DSTU B V.2.7-187, DSTU B V.2.7-185, DSTU B V.2.7-202, DSTU EN 197-1.

The research methods also included microstructural analysis to assess the homogeneity and defects of the structure using an X-ray phase microscope.

Results and discussions

Hot-pressing technology was found to accelerate the hardening of hardened cement paste, resulting in high strength in a short period. Hot pressing technology provided a reduction in the content of polymer additives in comparison with traditional methods of pressing samples.

The bending strength of samples based on Portland cement with additives containing polyester groups and polyisocyanates in an amount of 0.1+5 wt. % was determined. It was found that the introduction of a single-component additive to a polymer containing an ether or ester group cannot provide an improvement in physical and mechanical properties. The simultaneous addition of polyester-containing polymers – Laprol (2 mass. %) with polyisocyanate (2 mass. %) and Laproxide (2 mass. %) with polyisocyanate (0.6 mass. %) provided an increase in the bending strength to values equal to 46.27 MPa and 48.34 MPa, respectively while for the traditional composition the strength is achieved at the level of 5–7 MPa, and after steaming – 29.30 MPa (Fig. 1). It follows that complex polymer additives provide an increase in bending strength by 1.5–2 times compared to single-component systems. Steam-cured cold-pressed samples from a mixture of polyisocyanates and polyesters show a bending strength of 48 MPa, which is 1.5 times higher than the strength of samples without additives

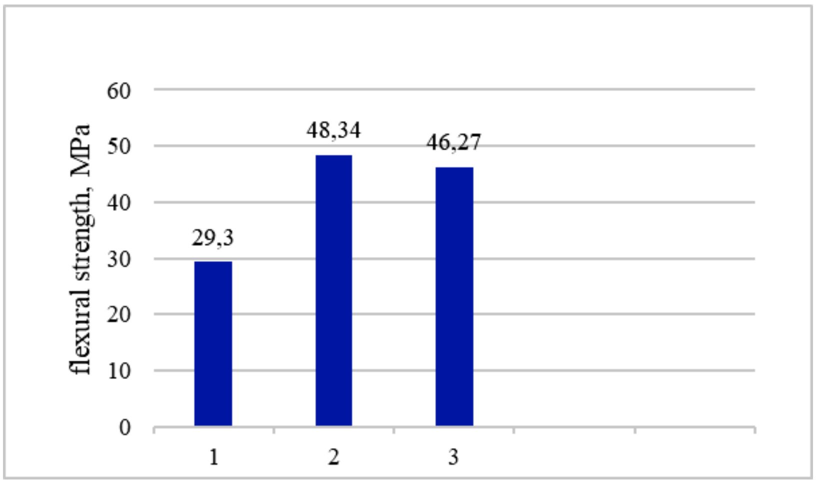

Fig. 1. The effect of complex polymer additives on the bending strength of hardened cement paste: 1 – portland cement CEM I 42.5 R; 2 – portland cement modified with polyisocyanate (0.6 %) and Laprol (2 %); 3 – portland cement modified with polyisocyanate (2 %) and Laprol (2 %)

Microstructural analysis confirmed the reduced porosity and denser structure of the pressed compositions, which explains the increased strength.

Fig. 2 shows the effect of the glycerin additive in the composition in the amount of 0.1–1 %. The optimal amount of the additive is 0.2 %, which provides an increase in bending strength of hardened cement paste to 52.48 MPa. Increasing the amount of glycerin additive to 1 % and more percent provided a change in the structure of the hydrated polymer films, which slows down the diffusion process of adsorbed water deep into the cement particle and induces inhibition of the hardening process of the cement material. The addition of glycerin plasticized the cement system, which allowed to create a more compacted structure of the hardened cement paste.

Hot pressing of compositions based on Portland cement with polyisocyanate and oligoether acrylate (Fig. 3) allows to create the maximum bending strength of samples – 65.5 MPa, which is 32 % higher than the strength of samples manufactured using traditional technology. The CO_2 intensity of such compositions is 13.2 kg CO_2 / (t·MPa). This indicates that the use of high-strength pressed mineral-binder compositions creates a real opportunity to reduce the carbon footprint of construction products.

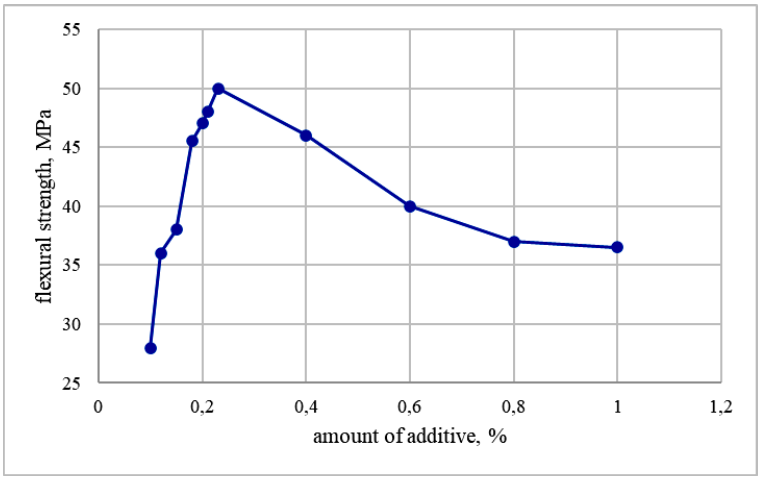

Fig. 2. Effect of the amount of glycerin additive on the strength of the polymer-cement composition

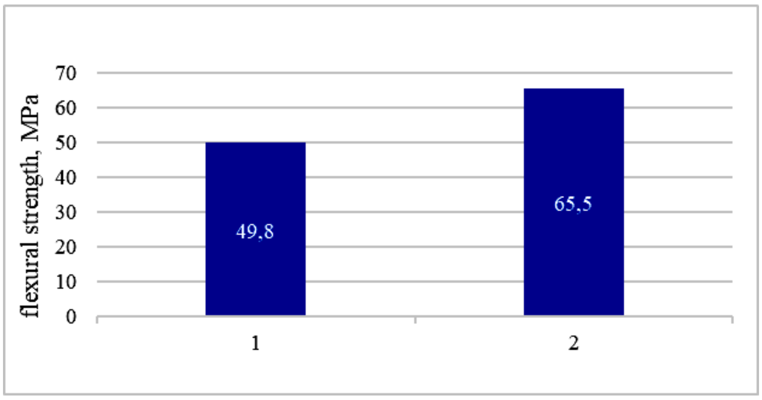

Fig. 3. The effect of complex polymer additives (indicate which ones and mark them in the figure) on the strength of the compositions:1 – portland cement CEM I 42.5 R; 2 – portland cement modified with polyisocyanate (2 %) and oligoether acrylate (0.6 %)

X-ray diffraction (XRD) analysis revealed that, during the hot-pressing process, various types of poorly crystallized calcium hydrosilicates are formed within the cement matrix. In additive-free compositions, hydrosilicates of the CSH (II) type (*d* = 0.428, 0.278, 0.182, and 0.176 nm) and gyrolite $C_3S_6H_6$ (*d* = 0.468, 0.334, 0.264, and 0.293 nm) were identified. Minor phase differences were recorded when polymer additives were introduced. In polymer hardened cement paste, CSH (II) is also fixed and additionally afvillet $C_3S_2H_3$ (*d* = 0.305; 0.262; 0.220; 0.193 nm) and ockenite $C_3S_6H_6$ (0.427; 0.305; 0.277; 0.230 nm).

One of the reasons for the change in phase composition is a change in hydration kinetics. At the initial stage, retention of part of the mixing water by the polymer is fixed, its gradual release and binding by hydrosilicate phases at later stages of hardening. In compositions that do not contain additives, the redistribution of bound water occurs only between different hydrosilicate phases, due to their different thermodynamic stability at certain stages of hardening.

A distinctive feature of the differential thermal analysis (DTA) curves with a complex polymer additive of polyisocyanate and oligoether acrylate is the presence of a significant exoeffect in the region of 445 °C. This effect is due to the destruction of the polymer component of the hardened cement paste. On the differential thermogravimetry (DTG) curves, a shift of the first endoeffect in the region of 90 °C to 140 °C (hydrosilicate phases) is recorded. The obtained data indicates a modification of the structure of hydrosilicates by the polymer, a change in their pore structure and an increase in the binding energy of water in hydrates.

The results of IR spectroscopy showed that the introduction of polymers increases the degree of hydroxylation of the surface of hydrates by OH groups bound by hydrogen bonds (absorption band in the region of 3400 cm^{-1}). The absorption bands at 1610 and 1300–1500 cm^{-1} correspond to the NH and C–O stretching vibrations of disubstituted urea, formed during the reaction between polyisocyanate and polyester. In addition, the formation of these bonds indicates the destruction of hydrogen bonds and the formation of free C-O and NH-groups, which is explained by the destruction of cyclic associates of urea in an alkaline environment. NHCO-groups form mosaic coating on the surface of hydrate particles with additives with the formation of fibrillar-type structures in the pores.

Electron microscopic studies of polymer-cement compositions indicate that hydration products at low W/C appear in the form of the smallest particles, the size of which does not exceed 2–3 microns, which determines the high strength of the bonds. At the same time, there is an increase in the number of weakly crystallized aggregates along the grain boundary. In polymer-modified of the hardened cement paste, the images show predominantly rounded particles and aggregates with a denser and monolithic structure with a complete absence of cement gel fibres, and virtually no pores are observed.

Studies of cement samples moulded by vibration have shown that the elements of their structure are distant from each other, this is due to high water mixing. The structure of the hardened cement paste is significantly loosened, there is no monolithicity of new formations. As a result, increased porosity and insignificant strength of the samples are recorded. Based on the data of X-ray diffraction, DTA and IR spectroscopy, it can be concluded that the structure of the hardened cement paste is modified by polymers: the phase composition of new formations, the degree of hydroxylation of the surface of hydrates, the binding energy of water in new formations partially changes. In pressed polymer-cement compositions, which are characterized by 5–10 times reduced total porosity and the practical absence of pores larger than 10 μm, polymer layers, due to their smaller thickness, will have more uniform properties compared to layers in compositions obtained by vibration. As a result of pressing, compressed conditions are formed in the samples, and the formation of new formations occurs much faster compared to samples obtained by traditional technology.

To achieve maximum mechanical properties, the structure of polymer cement matrix should consist of small, hydrated neoplasms covered with a thin film of polymer layers. As a result, the polymer layer will prevent the formation of a fracture crack in the brittle phase of the hardened cement paste. The simultaneous action of pressure and temperature allows, within a short period (0.2–1.0 h), to obtain the hardened cement paste, the strength of which increases by 8–10 times. The increase in strength and decrease in poverty is explained by the complication of hydration products and the compaction of the structure during the simultaneous action of pressure and temperature. Complex polymer additives demonstrate a synergistic effect compared to single-component ones, which confirms the feasibility of their use for the manufacture of high-strength pressed materials.

The obtained data indicate that polymer additives significantly increase the bending strength of hardened cement paste. Under the action of bending load on the samples in the zones of tensile forces, as a result of the fibrillation effect of polymer layers, the microstructure of hardened cement paste is self-reinforced by dispersed fibril aggregates oriented in the direction of force action, which is the main reason for the increase in bending strength. In addition, a significant contribution to the increase in bending strength is made by adhesion between the polymer layer and hydrated neoplasms of hardened cement paste.

Pressing cement composites in combination with polymer modification allows you to significantly improve their performance properties. Compaction of the material under high pressure contributes to an increase its density and mechanical strength, a decrease in porosity and an increase in water resistance. Polymer additives provide an additional increase in crack resistance, frost resistance and durability of the compositions, and reduce shrinkage and deformation during hardening. As a result of these technological approaches, it becomes possible to manufacture thin-walled and high-precision products with stable physical and mechanical characteristics, which is important for modern construction and industrial production.

Conclusions

1. The use of polymer components in pressed cement-polymer compositions significantly increases the bending strength and density of the material.
2. Complex polymer additives are more effective than single-component ones, as they provide a synergistic effect.
3. Cold and hot pressing under pressure allows you to obtain a homogeneous structure with minimal porosity.
4. Research results confirm the feasibility of using pressed cement-polymer materials in modern construction for high-strength structures.

Prospects for further research

In the future, it is planned to present a study of the influence of the clinker factor of the used cements and various types of modifiers on the performance indicators of building composites to obtain modern low-carbon materials. This will open opportunities for creating predictive models of operational properties and will facilitate the transfer of laboratory research results into construction practice. The expected results are consistent with international strategies for reducing greenhouse gas emissions and the UN Sustainable Development Goals (SDGs), contributing to the formation of innovative, resource-efficient and environmentally friendly building material.

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Асоціація ”УКРЦЕМЕНТ”

ВПЛИВ ПОЛІМЕРІВ НА ВЛАСТИВОСТІ ВИСОКОМІЦНИХ ПРЕСОВАНИХ МІНЕРАЛЬНО-В’ЯЖУЧИХ КОМПОЗИЦІЙ

Одним зі способів покращення фізико-механічних властивостей цементних композицій є їх модифікація полімерами (полімерцементний бетон, полімербетон тощо). У статті викладено результати дослідження пресованих цементно-полімерних композицій на основі портландцементу, модифікованого полімерними компонентами (полімерами, що містять прості та складні ефірні групи, поліізоціанати, гліцерин, етери полікарбоксилатів тощо). Показано, що за одночасного застосування тиску та температури під час формування полімерцементу кінцевий продукт є щільнішим та має бездефектну структуру завдяки зменшенню пористості та утворенню продуктів гідратації із вищою щільністю. Використання пресованих цементно-полімерних композицій дає змогу зменшити витрату модифікувальних добавок порівняно з виготовленими за традиційною технологією (ущільнення вібрацією) і впровадити низьковуглецеві технології та матеріали. Комплексні полімерні добавки демонструють синергічний ефект порівняно із однокомпонентними, що підтверджує доцільність їх використання для виготовлення високоміцних пресованих матеріалів. Розроблено комплексні полімерні добавки, що забезпечують збільшення міцності на згин у 1,5–2 рази порівняно із однокомпонентними добавками. Для досягнення максимальних механічних властивостей структура полімерцементного каменю повинна складатися із дрібних гідратних новоутворень, вкритих тонкою плівкою полімерних прошарків. У результаті полімерний прошарок перешкоджатиме утворенню наскрізної тріщини руйнування по крихкій фазі цементного каменю. Зразки композицій, отримані холодним пресуванням із подальшим пропарюванням й виготовлені із суміші поліізоціанатів та полікарбоксилатів, характеризуються міцністю на згин 48 МПа, що більш ніж у 1,5 раза перевищує показники зразків без добавок. Експлуатаційні та екологічні властивості композицій покращені.

Ключові слова: гаряче пресування, полімерні модифікатори, пресовані полімерцементні композиції, полікомпонентні мінеральні добавки, низьковуглецеві мінерально-в’яжучі матеріали.