Organic Polymers Reinforced Inorganic Polymers - An Overview

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Abstract. Nowadays hybrid materials started to be more and more popular. The main attention is focused on materials containing organic–inorganic components. Different combinations of organic and inorganic components allow the achievement of exceptional properties, such as electrical, catalytic, antibacterial, radiation-resistant, optical, excellent thermal, and mechanical properties. It gives a potential application for these materials in completely new fields. The main objective of the article is to analyse challenges and future trends for new composites - inorganic-organic polymers as well as shows the results of preliminary research. The article based on: critical analysis of literature sources and laboratory research: visual assessment and compressive strength test.

1. Introduction

Inorganic polymers called also as geopolymers are chemically alkaline aluminosilicates [1,2]. They are obtained in the reaction of polycondensation of ortosilicans (comprising Si and Al atoms in their structure) with activated NaOH or KOH. Structurally, the obtained materials are all aluminosilicates made from Si and Al tetrahedra linked alternately by the oxygen atoms. In this network, there are also present positive ions (Na +, K +, Li +, etc.) that balance the electrical charge of aluminium, which is in tetrahedral coordination. Cross-linked in this way, silicates consist of chains which may include such entities as: sialan, silokso-sialan, or disilokso-sialan [3]. Geopolymers are attractive for industrial application taking into consideration several perspectives [1,4]: environmental (CO2 emission and energy efficiency during the production process) [5,6], effectiveness of the manufacturing process [4,7], simplicity of application: low shrinkage and adherence to such materials as: concrete, steel, glass, ceramics [8,9], attractive mechanical properties [1,10], possibilities of application in different conditions because their chemical resistant to atmospheric conditions and a variety of acids [11] and salts [12, 13] and fire resistant [1,14].

The one of the most important limitations of geopolymers is brittle behavior. They have relatively low tensile and flexural strength. To improve this mechanical properties it is possible to introduce to the matrix some additives [1,6]. The best results are achieved through the mixed organic and inorganic polymers. Because of that the effect of polymer admixtures on geopolymers is one of the up-to-date research topic on the optimization of the mechanical properties [5,15].
Recently, the research in this area are focused on the development of mechanical properties, especially brittleness reduction [5, 16]. A lot of research on reinforcement for geopolymers matrix such as fibres has been made [4,7]. Incorporation such kind of additives provide the control of cracking by bridging action during both micro and macrocracking of the matrix thus increasing the fracture toughness [16, 17]. Nowadays hybrid materials started to be more and more popular. The main attention is focused on materials containing organic–inorganic components. They have gained increased interest due to their exceptional multifunctional properties [18, 19]. Different combinations of organic and inorganic components allow the achievement of exceptional properties, such as electrical, catalytic, antibacterial, radiation-resistant, optical, excellent thermal, and mechanical properties. It gives a potential application for this materials in completely new fields [5, 17].

Synthesis of organic–inorganic components together could change the chemical composition of the components, it is feasible to realize different kinds of materials, with different properties, whose applications depend on the ratio between organic and inorganic phases [18].

The literature review shows that attempt with some different materials have been made, especially with: polyvinyl acetate [5], polyacrylic acid (PAA) [20], sodium polyacrylate (PANa) [20], polyethylene glycol (PEG) [20, 21], polyvinyl alcohol (PVA) [5, 20], polyacrylamide (PAAM) [20], Polydimethylsiloxane (PDMS) [22], and different kind of resins, including melamine resins [5, 23]. The investigations show different influence additives on geopolymers properties. Exemplary, the mechanical properties of geopolymers can be improve by admixture of polyacrylic acid (PAA) and sodium polyacrylate (PANa) and they can be decreasing by admixture of polyacrylamide (PAm) and polyvinyl alcohol (PVA) [20]. However, additive of PAm and PVA have negative influence for results of the compressive strength tests in the same time it is beneficial for other material properties. By proper composition two or more organic polymers used together, it is possible to improve simultaneously the mechanical property, water-resistant property and the specific strength [20]. The promising results are given by epoxy resins, such as melamine resins makes the novel materials, thanks to isolating properties, are very attractive for the manufacturing thermo-resistant and thermo-insulating panels [5]. The results of the research show that incorporating content of 1 % by mass resin to geopolymer composites increasing significantly mechanical properties thorough the limitation of microcracks on the surface of geopolymers, The admixture prevent the cracking growth through filling effect, immobilizing water molecules and effectively postpone the water evaporation [23, 24].

This novel modification by organic polymers for inorganic polymers are required. The composition of several organic polymers is supposed to be suitable for wide range of geopolymer based on alkali activated materials, such as: kaolinite-based, fly ash-based, slag-based and waste-based geopolymers, because there is only minor difference between the chemical reactions of these systems [20].

2. Experimental procedure

Specimens based on geopolymer matrix with 5, 10 and 15% of different organic polymers were investigated. The variables include: different materials and different amount of additions as well as two ways of samples preparation. The composites in series I – the organic polymers were added as dry material and preliminary mixing with fly ash, then the alkaline solution was added. In series II – the organic polymers were prepared as water solution and then added during the mixing process together with the alkaline solution.

2.1. Materials and methods

2.1.1. Inorganic polymer. The base for inorganic polymers was fly ash form CHP plant in Skawina, Poland, which is rich in oxides such as SiO₂ – 55.89% by mass and Al₂O₃ – 23.49% by mass. The morphology of the particles of fly ash is typical for by-products of coal combustion. The process of alkali activation has been made by 8M sodium hydroxide solution combined with the sodium silicate solution.
2.1.2. Organic polymers. The seven different organic polymers have been chosen to preliminary research: polyvinyl alcohol - PVA, starch (amylum), chitosan, gelatin (gelatine), polyvinylpyrrolidone - PVP, polyethylene glycol - PEG, and gum Arabic (also known as acacia gum). The polymers was chosen based on literature review, exemplary PEG and PVA and taking under consideration also lack of information about investigation with particular composition, exemplary chitosan.

PVA (polyvinyl alcohol) is a water-soluble synthetic polymer, made from polyvinyl acetate through hydrolysis. It has been used during the first half of the 20th century worldwide. PVA is easily degradable by biological organisms and it is a solubilized crystalline structure polymer in water. It is used in papermaking, textiles, food packing, and a variety of coatings, including surgical threads [25, 26].

Starch (amylum) is a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store. It has some application in the food industry, especially after chemical modification [27].

Chitosan is a linear polysaccharide composed made by treating the chitin (usually shells of shrimp) with an alkaline substance, exemplary sodium hydroxide. It has commercial application in biomedical area, agriculture (including winemaking) and as a component of coatings [28].

Gelatin (gelatine) is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from various animal body parts. It is applied in food and pharmaceutical industry as well as for cosmetic manufacturing.

PVP (polyvinylpyrrolidone) is a water-soluble polymer. It is PVP is used in wide range of medical and in many technical applications and also in cosmetic and food industry [29].

PEG (polyethylene glycol) produced by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. It is also known as polyethylene oxide (PEO) or polyoxyethylene (POE), depending on its molecular weight. It has numerous of applications including: medicine, chemistry, biological laboratories, in industry [30, 31].

Gum Arabic, also known as acacia gum [32] is an edible biopolymer obtained from trees of *Acacia senegal* and *Acacia seyal* which grow principally in the Africa. Chemically, it is a complex mixture of macromolecules of different size and composition, mainly carbohydrates and proteins. It is applied in many industrial sectors such as: textiles, ceramics, cosmetics and pharmaceuticals, food [32, 33].

2.2. Specimens

The samples were prepared using sodium promoter, fly ash and additives of various organic polymers (5%, 10% and 15% by mass). The process of alkali activation has been made by 8M sodium hydroxide solution combined with the sodium silicate solution (liquid glass at a ratio of 1:2.5). To produce geopolymers flakes of technical sodium hydroxide were used and an aqueous solution of sodium silicate (R-145) whose molar module was 2.5 and density was about 1.45 g/cm³. The tap water was used instead of the distilled one. The alkaline solution was prepared by means of pouring the aqueous solution of sodium silicate over the solid sodium hydroxide. The fly ash, alkaline solution and organic polymer (series I – organic polymer as dry material, and series II - organic polymer as water solution) were mixed about 15 minutes. The homogeneous dispersion of the organic particles was obtained just by hand mixing. Next, it was poured into sets of plastic moulds for compressive strength test. Tightly closed molds were cured in ambient temperature (20°C) trough 28 days. Then, the samples were unmoulded.

2.3. Analytical procedure

Compressive strength tests were carried out according to the methodology described in the standard EN 12390-3 ‘Testing hardened concrete. Compressive strength of test specimens’, because of the lack of separate standards for geopolymer materials. The tests involved at least 3 samples. Samples used to the compressive strength test had cylindrical shape with dimensions: \( \Phi = 36.5 \text{ mm} \) and \( h = 70 \text{ mm} \). Test was made on the concrete press - MATEST 3000kN).

3. Experimental results and discussion

The results of the compressive strength test are shown in the table 1.
Table 1. The results of the compressive strength test - series I (samples preparing without solvent).

| Sample                                | Compressive strength [MPa] | Standard deviation |
|---------------------------------------|----------------------------|--------------------|
| Inorganic polymer                     | 11.396                     | 1.293              |
| Inorganic polymer with chitosan (5%)  | 7.586                      | 1.161              |
| Inorganic polymer with chitosan (10%) | 6.111                      | 1.122              |
| Inorganic polymer with chitosan (15%) | 3.539                      | 0.314              |
| Inorganic polymer with gelatine (5%)  | 4.835                      | 0.385              |
| Inorganic polymer with gelatine (10%) | 5.373                      | 0.113              |
| Inorganic polymer with gelatine (15%) | 3.722                      | 0.462              |
| Inorganic polymer with gum Arabic (5%)| 8.085                      | 1.149              |
| Inorganic polymer with gum Arabic (10%)| 5.716                     | 0.939              |
| Inorganic polymer with gum Arabic (15%)| 4.009                     | 0.791              |
| Inorganic polymer with PEG (5%)       | 6.411                      | 0.380              |
| Inorganic polymer with PEG (10%)      | 4.944                      | 0.991              |
| Inorganic polymer with PEG (15%)      | 4.580                      | 0.502              |
| Inorganic polymer with PVA (5%)       | 7.034                      | 1.195              |
| Inorganic polymer with PVA (10%)      | 3.056                      | 0.743              |
| Inorganic polymer with PVA (15%)      | 1.777                      | 0.372              |
| Inorganic polymer with PVA (15%)      | 6.499                      | 1.876              |
| Inorganic polymer with PVP (5%)       | 8.397                      | 2.688              |
| Inorganic polymer with PVP (10%)      | 7.759                      | 0.748              |
| Inorganic polymer with PVP (15%)      | 6.964                      | 1.896              |
| Inorganic polymer with starch (10%)   | 7.171                      | 1.262              |
| Inorganic polymer with starch (15%)   | 5.959                      | 1.291              |

The best results were achieved for the matrix without reinforcement. The additives of organic polymers decreased the compressive strength results. The relatively good results were achieved for 10% PVP, 5% Arabic gum and 5% chitosan.

Table 2. The results of the compressive strength test - series II (samples preparing with solvent).

| Sample                                | Compressive strength [MPa] | Standard deviation |
|---------------------------------------|----------------------------|--------------------|
| Inorganic polymer                     | 11.396                     | 1.293              |
| Inorganic polymer with chitosan (5%)  | 8.147                      | 2.738              |
| Inorganic polymer with chitosan (10%) | 10.074                     | 1.813              |
| Inorganic polymer with chitosan (15%) | 6.352                      | 2.167              |
| Inorganic polymer with gelatine (5%)  | 8.195                      | 1.481              |
| Inorganic polymer with gelatine (10%) | 5.458                      | 1.471              |
| Inorganic polymer with gelatine (15%) | 3.515                      | 0.680              |
| Inorganic polymer with gum Arabic (5%)| 8.366                      | 2.410              |
| Inorganic polymer with gum Arabic (10%)| 8.053                      | 1.938              |
| Inorganic polymer with gum Arabic (15%)| 6.310                      | 0.116              |
| Inorganic polymer with PEG (5%)       | 8.136                      | 1.209              |
| Inorganic polymer with PEG (10%)      | 7.245                      | 1.397              |
| Inorganic polymer with PEG (15%)      | 6.961                      | 1.326              |
| Inorganic polymer with PVA (5%)       | 8.318                      | 0.340              |
| Inorganic polymer with PVA (10%)      | 4.892                      | 0.822              |
| Inorganic polymer with PVA (15%)      | 3.872                      | 0.152              |
Inorganic polymer with PVP (5%) 10.562 2.543
Inorganic polymer with PVP (10%) 9.640 1.036
Inorganic polymer with PVP (15%) 7.129 0.419
Inorganic polymer with starch (5%) 8.638 2.205
Inorganic polymer with starch (10%) 7.493 0.840
Inorganic polymer with starch (15%) 6.230 0.640

The samples preparing with solvent give better results that the samples in series I (samples preparing without solvent). The best results were archived for 10% of chitosan addition and 5% of PVP addition. The manufacturing process have a significant influence for final properties of the material.

4. Conclusions
The literature research as well as the conducted preliminary research show that inorganic-organic composites can be interesting material for different applications. However the compressive strength decreased, the other properties have been changed, especially samples surface. It can happened increasing of resistant of the material, but it required future research.

The planned further research should also include the method of manufacturing. The application the same amount of organic polymers to inorganic matrix by using different processing methods gives significantly changes with the results of compressive strength test.

5. References
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Acknowledgments

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