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RESEARCH OF STRUCTURE AND DURABILITY OF NATURAL POLYMER MODIFIED CLAYS

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Supervisor

Dr Olga KIZINIEVIČ (Vilnius Gediminas Technical University, Materials Engineering – T 008).

The Dissertation Defence Council of the Scientific Field of Materials Engineering of Vilnius Gediminas Technical University:

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Assoc. Prof. Dr Šarūnas SKUODIS (Vilnius Gediminas Technical University, Civil Engineering – T 002),

Prof. Dr Jiri ZACH (Brno University of Technology, Czech Republic, Materials Engineering – T 008).

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Address: Saulėtekio al. 11, LT-10223 Vilnius, Lithuania.
Tel.: +370 5 274 4956; fax +370 5 270 0112; e-mail: doktor@vilniustech.lt

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yahor.trambitski@vilniustech.lt

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Vadovas

dr. Olga KIZINIEVIČ (Vilniaus Gedimino technikos universitetas, medžiagų inžinerija – T 008).

Vilniaus Gedimino technikos universiteto medžiagų inžinerijos mokslo krypties disertacijos gynimo taryba:

Pirmininkas

dr. Viktor GRIBNIAK (Vilniaus Gedimino technikos universitetas, medžiagų inžinerija – T 008).

Nariai:

dr. Agnė KAIRYTĖ (Vilniaus Gedimino technikos universitetas, medžiagų inžinerija – T 008),

prof. habil. dr. Aivaras KAREIVA (Vilniaus universitetas, chemija – N 003),

doc. dr. Šarūnas SKUODIS (Vilniaus Gedimino technikos universitetas, statybos inžinerija – T 002),

prof. dr. Jiri ZACH (Brno technologijos universitetas, Čekija, medžiagų inžinerija – T 008).

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Adresas: Saulėtekio al. 11, LT-10223 Vilnius, Lietuva.
Tel.: (8 5) 274 4956; faksas (8 5) 270 0112; el. paštas doktor@vilniustech.lt

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Abstract

The issue of eco-friendly construction is highly relevant nowadays. Unfired clay materials represent a sustainable alternative to other building products, because of their extremely low carbon footprint. Nevertheless, a pressing need remains to enhance their physical, mechanical, and durability characteristics. To save the great ecological potential of unfired clay materials, the most rational way is to modify them with the help of different biopolymers. Therefore, the dissertation considers the possibilities of different biopolymers (polysaccharides – starch, alginate, and chitosan) to modify clay-based building materials. Different preparation technologies (biopolymers gelation and starch retrogradation processes) were used to evaluate the effect of the examined biopolymers on some properties, structure, and durability of clay materials. Biopolymers and their technological parameters were selected according to their origin, chemical structure, and ability to interact with water. The main principle of clay modification, implemented in this research is the complete replacement of water with a biopolymer solution during the manufacturing process of clay composites. The resulting clay composites with starch or alginate solutions exhibit not only improving mechanical properties but also durability, which could make them very attractive for a wide variety of applications from clay masonry units to plasters. The first chapter presents a comprehensive outlook on contemporary trends in the evolution of sustainable clay-based construction materials. Furthermore, it delves into an exploration of the biopolymers, their distinctive characteristics, and the potential avenues for modification. The second chapter is dedicated to the exploration of the raw materials, processing techniques, testing methodologies and equipment used to evaluate the impact of biopolymers on unfired clay composites. The discussion has also focused on the technology of producing gelated biopolymer aqueous solutions, and the possibilities to technologically modify specific biopolymers using the retrogradation process. Also, this chapter presents the methodology of clay composite testing. The third chapter presents the evaluation of the effect biopolymers have on the physical, mechanical, and hygroscopic properties and durability of clay-based composites, describing interaction mechanisms between clay and biopolymers, and the peculiarities of clay composite structure formation. Nine scientific papers were published on the topic of the dissertation: three papers in scientific journals included in the list of *Clarivate Analytics Web of Science* database with an impact factor, and four papers in conference proceedings included in the *Clarivate Analytics Web of Science* and *Scopus* databases, two – in other international databases. A Lithuanian patent based on the results of the dissertation has been granted, and seven reports were presented at national and international scientific conferences.

Reziumė

Ekologiškos statybos klausimas šiais laikais itin aktualus. Nedegto molio medžiagos yra tvari alternatyva kitiems statybos produktams, nes jų anglies pėdsakas yra labai mažas. Tačiau vis dar išlieka poreikis pagerinti tokių medžiagų fizines, mechanines savybes ir ilgaamžiškumą. Norint išsaugoti didelį nedegto molio medžiagų ekologinį potencialą, racionaliausias būdas yra jas stabilizuoti naudojant biopolimerus. Todėl disertacijoje nagrinėjamos biopolimerų (polisacharidų – krakmolo, alginato, chitozano) panaudojimo, modifikuojant statybines molio medžiagas, galimybės. Siekiant įvertinti tirtų biopolimerų poveikį molio medžiagų struktūrai, savybėms ir ilgaamžiškumui, buvo naudojamos skirtingos jų paruošimo technologijos (biopolimerų geliavimo ir krakmolo retrogradacijos procesai). Biopolimerai ir jų paruošimo technologiniai parametrai parinkti atsižvelgiant į biopolimerų kilmę, cheminę struktūrą bei gebėjimą sąveikauti su vandeniu. Pagrindinis šiame darbe molio modifikavimo principas yra visiškas vandens pakeitimas biopolimeriniais tirpalais molio kompozitų gamybos metu. Gauti molio kompozitai su krakmolo arba alginato tirpalais pasižymi ne tik pagerintomis mechaninėmis savybėmis, bet ir ilgaamžiškumu. Toks molio medžiagų modifikavimo būdas yra labai patrauklus ir gali būti taikomas gaminant įvairius statybos produktus molio pagrindu (pvz., molio mūro gaminiai, molio tinkai ir kt.). Pirmajame skyriuje pateikiama išsami šiuolaikinių tvarių molio pagrindu pagamintų statybinių medžiagų gamybos tendencijų apžvalga. Taip pat analizuojami įvairių biopolimerų modifikavimo būdai, jų savybės bei biopolimerų poveikis molio gaminių savybėms. Antrajame skyriuje aptartos biopolimerų paruošimo technologijos, želatinizuotų biopolimerų vandeninių tirpalų gamybos technologijos bei biopolimero (krakmolo) modifikavimo retrogradacijos būdu galimybės. Taip pat šiame skyriuje pateiktos molio kompozito tyrimo metodikos. Trečiajame skyriuje analizuojamas biopolimerų, panaudojant skirtingas paruošimo technologijas (biopolimerų geliavimo ir krakmolo retrogradacijos procesai), poveikis molio kompozitų fizikinėms ir mechaninėms, higroskopinėms savybėms, taip pat įvertinta jų struktūra bei ilgaamžiškumas. Apibūdinami molio ir biopolimerų sąveikos mechanizmai, kompozitinės struktūros formavomosi ypatumai. Disertacijos tema buvo paskelbti devyni moksliniai straipsniai: trys straipsniai mokslo žurnaluose, įtrauktuose į *Clarivate Analytics Web of Science* leidinių sąrašą ir turinčiuose citavimo indeksą, keturi straipsniai *Clarivate Analytics Web of Science* duomenų bazės *Conference Proceedings*, du straipsniai kitų tarptautinių duomenų bazių leidiniuose. Remiantis disertacijos rezultatais, išduotas Lietuvos patentas. Darbas buvo pristatytas septyniuose pranešimuose nacionalinėse ir tarptautinėse mokslinėse konferencijose.

Notations

Abbreviations

3D – three-dimensional (liet. *trimatis*);
AC – alginate-clay composite (liet. *alginate-molio kompozitas*);
BD – bulk density (liet. *tūrinis tankis*);
BS – bending strength (liet. *lenkimo stipris*);
CC – chitosan-clay composite (liet. *chitozano-molio kompozitas*);
CD – compaction density (liet. *tankis po tankinimo*);
CEB – compressed earth bricks (liet. *suspaustos žemės plytos*);
CS – compressive strength (liet. *gniuždymo stipris*);
EM – elastic modulus (liet. *tamprumo modulis*);
EMC – equilibrium moisture content (liet. *pusiausvyros drėgmės kiekis*);
GSS – gelling starch solution (liet. *gelio krakmolo tirpalas*);
GAS – gelling alginate solution (liet. *gelio alginato tirpalas*);
GCS – gelling chitosan solution (liet. *gelio chitozano tirpalas*);
LCA – life cycle assessment (liet. *gyvavimo ciklo vertinimas*);
MS – microstructure (liet. *mikrostruktūra*);
OWC – optimal water content (liet. *optimalus vandens kiekis*);
PS – polysaccharide (liet. *polisacharidas*);

RH – relative humidity (liet. *santykinė drėgmė*);
RSH – retrograded starch hydrogel (liet. *retrograduoto krakmolo hidrogelis*);
SBS – sick building syndrome (liet. *sergančio pastato sindromas*);
SC – starch-clay composite (liet. *krakmolo-molio kompozitas*);
SCT – special curing time (liet. *tam tikras kietėjimo laikas*);
SEM – scanning electron microscopy (liet. *skenuojančioji elektroninė mikroskopija*);
SWT – special water content (liet. *tam tikras vandens kiekis*);
SHR – shrinkage (liet. *susitraukimas*);
SS – split strength (liet. *stipris atplėšiant*);
TS – tensile strength (liet. *tempimo stipris*);
UPV – ultrasonic pulse velocity (liet. *ultragarso impulse greitis*);
VOCs – volatile organic compounds (liet. *lakieji organiniai junginiai*);
XCT – X-ray computed tomography (liet. *rentgeno kompiuterinė tomografija*);
XRD – X-ray diffraction (liet. *rentgeno spindulių difrakcija*);
XRF – X-ray fluorescence (liet. *rentgeno spindulių fluorescencija*).

Terms and definitions

Clay composite – the combination of mica-clay and biopolymers (polysaccharides – starch, alginate and chitosan) resulting in sustainable building material with synergistically enhanced performance characteristics (liet. *Molio kompozitas – žėručio-molio ir biopolimerų (polisacharidų – krakmolo, alginato ir chitozano) derinys, sukuriantis tvarią statybinę medžiagą su sinergiškai patobulintomis eksploatacinėmis charakteristikomis*).

Polysaccharides – a class of biopolymers, representing complex carbohydrates consisting of long chains of sugar molecules (monosaccharides) linked together. Polysaccharides serve as energy-storage molecules or structural components in various living organisms (Maji, 2019) (liet. *Polisacharidai – biopolimerų klasė, atstovaujanti sudėtingiems angliavandeniams, sudarytiems iš ilgų cukraus molekulių (monosacharidų), sujungtų tarpusavyje. Polisacharidai tarnauja kaip energiją kaupiančios molekulės arba struktūriniai komponentai įvairiuose gyvuose organizmuose (Maji, 2019)*).

Mica clay – 2:1 clay mineral with a layered structure composed of repeating T-O-T units, where one octahedral sheet (O) intercalates between two tetrahedral sheets (T) (Brigatti et al., 2013) (liet. *Žėručio molis – 2:1 molio mineralas, kurio sluoksnių struktūra susideda iš pasikartojančių T-O-T vienetų, kur vienas oktaedrinis lakštas (O) įsiterpia tarp dviejų tetraedrinių lakštų (T) (Brigatti ir kt., 2013)*).

Gelation – the process by which a biopolymer, undergoes a phase transition from a liquid to a gel or semi-solid state. During gelation, the biopolymer molecules form a three-dimensional network structure that traps water or other liquid components, creating a gel with distinct textural and rheological properties (Maji, 2019) (liet. *Geliacija – procesas, kurio metu biopolimeras pereina iš skystos būsenos į gelį arba pusiau kietą būseną. Geliacijos metu biopolimero molekulės sudaro trimatį tinklo struktūrą, kuri sulaiko vandenį ar kitus skystus komponentus, sukurdama gelį, pasižymintį skirtingomis tekstūrinėmis ir reologinėmis savybėmis (Maji, 2019)*).

Retrogradation – the process in which the gelatinized or partially dissolved starch molecules, which have been subjected to heating and cooling, undergo reassociation and recrystallization (Wang et al., 2015) (liet. *Retrogradacija – procesas, kurio metu geliatinizuotos arba iš dalies ištirpusios krakmolo molekulės, kurios buvo kaitinamos ir atšaldomos, reasociuojasi ir persikristalizuoja (Wang ir kt., 2015)*).

Syneresis – a phenomenon in which a gel-like substance contracts or releases liquid, typically water. This contraction or expulsion of liquid occurs over time and can lead to the formation of small amounts of liquid or "weeping" from the gel structure (Wang et al., 2015) (liet. *Sinerezė – reiškinys, kai į gelį panašios medžiagos susitraukia arba išskiria skystį, dažniausiai vandenį. Šis skysčio susitraukimas arba išstūmimas vyksta laikui bėgant ir gali sukelti nedidelio skysčio kiekio susidarymą arba „išsiskirimą" iš gelio struktūros (Wang ir kt., 2015)*).

Contents

Introduction

Problem formulation

Unfired clay materials offer a sustainable alternative to conventional building products; however, they require enhancement in their mechanical and performance properties. The improvement of these characteristics is most effectively achieved by adding ecological products to preserve the sustainability of unfired clay products (e.g., unfired clay masonry units and plasters). The practice of reinforcing clay with various fibre types is well-established and, contrasts with the less common use of biopolymers. It is necessary to investigate the “clay-biopolymer” interaction, and the effect biopolymers have on several properties, as well as the durability and structure of clay-based composites. Such interactions required more careful research for the effective application of the biopolymers in the building materials. Also, the use of biopolymers for building materials lacks a clear understanding of the type, quantity, or form of such additives. Using biopolymers without considering their unique properties (e.g., in dry or liquid form or pure or rough state) is impractical. There is a lack of research on the influence of biopolymers on the structure and durability of clay-based materials. There are many types of clay whose chemical, mineralogical, and granulometric properties play a significant role in shaping the properties of the final composite, as well as in the interaction with certain polysaccharides. The need for environmentally friendly building materials is evident at present and the application of different biopolymers enables the development of unfired clay composites with required properties, which could be easily recycled at the end of their lifecycle.

Relevance of the dissertation

The issue of ecological construction and the production of sustainable building materials is highly relevant today. Therefore, in recent years, there has been an upsurge of interest in clay-based materials, because of their undeniable environmental friendliness, non-toxic and easy-to-recycle properties. Among other analogues, unfired clay materials have the highest environmental potential and certificates, reflected in low energy and carbon costs during their production, exploitation and utilisation. Unfortunately, unfired clay materials are inferior in strength and durability when compared to more “contemporary” materials. When considering the durability of unfired clay materials, their water erosion resistance stands out as the most critical factor. Therefore, unfired clay critically requires additional modification to improve its physical and mechanical properties, as well as durability while preserving its environmental potential. This issue can be solved by introducing biopolymers that possess high environmental qualities similar to unfired clay itself. According to modern concepts, the modification of clays can be due to the adsorption of biopolymers on the clay’s mineral surfaces. It is expected that adsorbed biopolymers will alter the nature of clay mineral surfaces, thereby modifying the number of properties of clay composite. There is relevance in researching such interactions and newly-formed hydrogen bonds, which can potentially lead to changes in the microstructure and properties of modified clay composites.

Research object

The object of the present research is clay composite modified with biopolymers (polysaccharides – starch, alginate and chitosan) for sustainable building applications.

Aim of the dissertation

The dissertation aims to modify the clay structure using biopolymers of different treatments (biopolymer gelation and starch retrogradation processes) to enhance the clay composite’s mechanical, hygroscopic properties and durability.

Tasks of the dissertation

To achieve the objective, the following problems had to be solved:

1. To select the biopolymers preparation technology (gelation and starch retrogradation process) and determine its processing parameters;
2. To investigate the impact biopolymers have on the physical, mechanical and hygroscopic properties of clay composites, depending on the biopolymer preparation technology;
3. To evaluate the biopolymers' impact on the structure and durability of the clay composite, depending on the biopolymer preparation technology;
4. To evaluate the interaction mechanisms between biopolymers (polysaccharides – starch, alginate, and chitosan) and clay material to determine the peculiarities of structure formation.

Research methodology

Characterisation of the raw clay was carried out using several analytical techniques, including X-ray Diffraction (XRD) and X-ray Fluorescence (XRF). The characteristics of polysaccharide water solutions, prepared with the addition of starch, alginate, and chitosan, were examined by determining pH and viscosity. The structure of the studied materials was investigated using Scanning Electron Microscopy (SEM) and X-ray Computed Tomography (XCT). All the studied properties were determined according to the different international (ASTM, EN, ISO) and national (UNE, DIN, NZS) standards. Statistical and analytical evaluation methods were used for the validation of experimental results.

The scientific novelty of the dissertation

The dissertation determines the peculiarities of mica-clay composite structure formation using different biopolymers (polysaccharides – starch, alginate, and chitosan) and their preparation technology (biopolymers gelation and starch retrogradation processes). The modification of the clay structure was achieved through the adsorption of biopolymers on the surface of the specific mica-clay aggregates, as well as the formation of additional hydrogen bonds, resulting in a change in the characteristics of the clay composite. Furthermore, the application of retrograded starch hydrogel was first implemented in the modification of clay-based building materials, enhancing its strength, moisture absorption capacity, and durability.

The obtained results on clay modification with different biopolymers may be used in masonry and finishing building materials.

The practical value of the research findings

The obtained effect of the biopolymer solutions of starch (both in gelated and retrograded forms) and alginate solutions on clay-based composites can be used in the production of eco-friendly building materials (unfired clay masonry units). This statement emerges from the significant improvement of mechanical characteristics compared to traditional unfired clay materials according to the classification by DIN 18945:2013-08 standard (Class 5). Also, all studied biopolymer admixtures (starch, alginate and chitosan) enhance the hygroscopic properties of clay-based composites, making them suitable for indoor use as finishing materials according to DIN 18947:2013 standard (Class WS-3). The effect of retrograded starch hydrogel application for modification of clay-based composites, presented in this dissertation, was used to receive the Lithuanian patent (the State Patent Bureau of the Republic of Lithuania, “A process for the production of unfired clay products with the addition of a biopolymer” (Lithuanian Patent No. LT-6964B).

Defended statements

The following statements, based on the results of the present investigation, represent the official hypotheses to be defended:

1. The biopolymers (polysaccharides – starch, alginate, and chitosan) depending on the preparation technology (biopolymers gelation and starch retrogradation processes) can interact with the surface and the interlayer space of mica-clay, thereby modifying the structure of clay composite;
2. The inclusion of biopolymers (starch and alginate), depending on the preparation technology (biopolymer gelation and starch retrogradation processes), significantly enhances the compressive strength (by 74%) and moisture adsorption capacity (by 34%) of the mica-clay composites.

Approval of the research findings

The main results of the dissertation were published in nine scientific papers: three in scientific journals included in the *Clarivate Analytics Web of Science* database with an impact factor and six papers in conference proceedings included in the

Clarivate Analytics Web of Science and *Scopus* databases. The results of the conducted research were presented at seven scientific conferences:

- International scientific conference "Actual problems of the architecture of the Belarus and adjacent regions" (2020), Polotsk, Republic of Belarus;
- The scientific conference of the young researchers "Science is the future of Lithuania" (2021), Vilnius, Lithuania;
- International Conference Binders and Materials (2021), Brno, Czech Republic;
- "XX International Symposium on Materials" (2022), Marinha Grande, Portugal;
- 5th International Conference: "Innovative Materials, Structures and Technologies (IMST 2022)" (2022), Riga, Latvia;
- 14th International Conference "Modern Building Materials, Structures and Techniques" (2023), Vilnius, Lithuania;
- International Conference "Chemicals & Environment (EcoBalt 2023)" (2023), Tallinn, Estonia.

Structure of the dissertation

The dissertation consists of an introduction, three chapters, general conclusions, an extensive list of references, a list of the author's publications on the dissertation's topic, and a summary in Lithuanian. The volume of the dissertation is 115 pages, including 39 figures, one formula, and 6 tables. The references list includes 141 literature sources.

1

Review on unfired clay, its modifications and application in clay-based building materials production

This chapter provides an overview of current trends in the development of sustainable clay-based building materials. The survey focuses on comparing the environmental impact of the most popular building materials through their life cycle assessment (LCA). Additionally, this chapter discusses the application of different natural additives, including polysaccharides, shedding light on the current state of the issue of unfired clay materials stabilisation. Furthermore, the objectives of the dissertation have been formulated based on this overview. The main research results on the topic of this chapter were published in three author's publications (Trambitski et al., 2022a; Trambitski et al., 2022b; Trambitski et al., 2023).

1.1. Sustainability as a goal

In today's world, the construction industry stands as one of the most influential sectors impacting the environment (Hammond & Jones, 2008; Zabalza Bribián et al., 2011). The production of construction materials often comes hand in hand with high energy consumption and high emissions of carbon dioxide. Furthermore, the use of low-quality and unsustainable building materials can significantly affect the comfort of individuals residing around these materials. The so-called sick building syndrome (SBS) should also be considered to ensure a comfortable environment for occupants. This phenomenon is marked by acute health or comfort issues experienced by individuals within a building, often related to the time spent inside (US Environmental Protection Agency, 1991). One of the contributing factors to this syndrome is the materials that surround individuals, which can emit volatile organic compounds (VOCs), including formaldehyde (Sarkhosh et al., 2020).

One of the commonly used methods to determine the evaluation of a product's impact on the environment is the Life Cycle Assessment (LCA). Based on the environmental management standards EN ISO 14040: 2006 and BS EN 15978: 2011, a large number of LCA databases are still being developed and updated (Ben-Alon et al., 2019; Martinez-Rocamora et al., 2016; Zabalza-Bribian et al., 2011). Focusing on the life cycle also helps to make the right decision when selecting the production technology and minimising the environmental impact of the building materials through their manufacturing, use or recycling. As was mentioned in the research of Udo de Haes & Heijungs (2007), many building materials may be rather harmless during their exploitation, but at the stage of their production or recycling, it may emit a vast amount of toxic agents. It was also concluded that LCA models can also accompany a product design. When producing an eco-friendly product, careful attention should be paid to its reuse in the future or the recycling of its components in the waste management stage. Utilising the "cradle to the grave" approach during the design of new building materials will enable seamless integration of these materials into the circular economy (Hammond & Jones, 2008). Table 1.1 presents comparative data of various building materials in terms of their embodied energy and carbon dioxide.

Table 1.1. Environmental impact of building materials – comparative data

No	Material	Density, kg/m^3	Embodied energy, MJ/kg	Embodied carbon, kgCO$_2$/kg	Reference
1	Concrete	1800–2500	0.9–1.2	~0.14	Christoforou et al., 2016; Hammond & Jones, 2008; Zabalza Bribián et al., 2011;
2	Cement	~1300	2.4–9.3	0.25–0.82	
3	Wood	500–1000	8–16	0.12–0.24	
4	Fired clay brick	1400–2200	1.2–6.5	0.06–0.24	
5	Unfired clay brick	1200–2000	~0,09	0.002–0.02	

When assessing a building material from a life cycle perspective, the most critical criteria to consider are embodied energy and embodied carbon. The embodied energy is the total energy requirements associated with the final material, encompassing its sourcing (including raw ingredients), production, and subsequent use. The embodied carbon represents the equivalent carbon emissions integrated into the energy content of the materials used. The higher both of the parameters, the greater the damage to the environment (Hammond & Jones, 2008).

A close examination of the data in Table 1.1 reveals that construction materials utilising unfired clay exhibit the highest environmental sustainability. Comparing the life cycle of ceramics and unfired clay bricks, researchers Zabalza-Bribián et al. (2011) and Christoforou et al. (2016) found that the amount of embodied energy in ceramics varies from 1.2 to 6.5 (MJ/kg), while for unfired clay, it is 0.033 to 0.170 (MJ/kg) depending on the additives used. The amount of embodied carbon ranged from 0.06 to 0.24 (kg CO_2/kg) and 0.002 to 0.02 (kg CO_2/kg) for ceramic and unfired materials, respectively.

In addition to their eco-friendliness, non-fired clay materials are also valued for their hygroscopic properties, which help maintain an optimal indoor environment. Clay, as a porous material, can absorb excess moisture in the air, thereby balancing the humidity in the room. Zhang et al. (2020) postulate that the use of earthen bricks instead of fired bricks contributes to a more favourable indoor climate. This effect is achieved due to the regulation of the temperature in the room by clay material. In the research of Binici et al. (2005), the mud bricks reinforced with different types of fibres (both natural and artificial) and stabilised by cement, basaltic pumice and gypsum showed energy savings of up to 69% for heating in the winter period and 57% for cooling in summer. The possibility of “self-regulation” of the indoor climate of a room finished with clay plaster due to the changes in ambient temperature and humidity was also described by Ashour et al. (2011), Faria et al. (2016), Jiang et al. (2020), Maddison et al. (2009), Santos et al. (2017), Romano et al. (2021a, 2021b).

Nowadays, clay-based materials have become a subject of renewed interest, because of their undeniable environmental friendliness, non-toxic, and easy-to-recycle properties. Clay is considered a “breathable” material with the ability to regulate the microclimate of interior spaces, thus creating comfort for people (Ashour et al., 2011; Jiang et al., 2020). Among other analogues, unfired clay materials have the highest environmental potential and certificates, which are reflected in low energy and carbon costs during their production, exploitation and utilisation (Table 1.1). Unfortunately, non-fired clay materials are inferior in strength and durability when compared to more “contemporary” materials such as concrete, steel, or even ceramics. When considering the durability of unfired clay materials, their water erosion resistance stands out as the most critical factor. Unfired clays are highly susceptible to water exposure, which can lead to significant material erosion and loss of strength (Heathcote, 1995; Costa et al., 2021; 2019). Therefore, non-fired clay critically requires additional stabilisation to improve its physical and mechanical properties while preserving its environmental potential. This can be achieved by introducing a stabiliser that possesses similar high environmental qualities as unfired clay itself.

1.2. Traditional stabilisation methods of clay-based materials

Building with clay or earth materials is humankind's oldest and most popular technology. The earliest mention of the use of clay as a building material dates back to 10,000 BC in the region of Mesopotamia (Heathcote, 1995). These were bricks made from a mixture of straw and clay, better known as adobe bricks, for constructing primitive temporary houses. Despite this fact, researchers can still find some examples of ancient clay architecture around the world that are included in the World Heritage List (Fratini et al., 2011; Pacheco-Torgal et al., 2012; Costa et al., 2021a; 2019b). Even today, in developing countries located in dry tropical climates, about a third of the world's population lives in houses constructed from earth-based materials (Costa et al., 2021a). The availability and cheapness of raw materials combined with the simplicity of manufacturing technology and low labour costs determine the popularity of these materials. There is a huge variety of clay-based building materials and techniques: adobe, cob, taipa, rammed earth, compressed earth blocks (CEB), etc., which have survived to this day (Fratini et al., 2011; Pacheco-Torgal et al., 2012; Costa et al., 2021a; 2019b). Most of these techniques are traditional and differ mainly in their dimensions (bricks, blocks, massive constructions), type of raw materials used (which may vary depending on a particular region), and purpose (Costa et al., 2019b).

As mentioned in sub-chapter 1.1, unfired clay materials possess inherent eco-friendly characteristics but are susceptible to environmental factors and structural instability. The concept of "stabilisation" in this context of unfired clay materials refers to the process of enhancing its mechanical strength, durability, and resistance to environmental factors, traditionally achieved by incorporating natural fibres, cement, lime, or gypsum (Zak et al., 2016).

The most common or traditional method of modifying clay or earth material modification is the use of various types of fibres to reinforce the clay-based structure. Fibers can be of natural and industrial origin. Adding fibres to the clay material helps to reduce its density, shrinkage and crack propagation (Jannat et al., 2020; Laborel-Préneron et al., 2016; Salih et al., 2020). The use of natural fibres in a clay body also improves the thermophysical, acoustic and hygroscopic properties of the material (Degrave-Lemeurs et al., 2018; Lachheb et al., 2023; Rivera-

Gómez et al., 2021; Taallah et al., 2014). However, the effect of fibre addition on the clay composite strength is controversial: in some research, (Alhaik et al., 2018; Muñoz et al., 2020) the addition of fibres contributed to an increase in the strength of the clay samples when other studies (Giroudon et al., 2019; Yetgin et al., 2008) suggested otherwise. The positive effect of such stabilisation can be attributed to the forming of additional bonds inside the clay structure (Salih et al., 2020). The negative effect of fibre addition to the clay composite is the low water or moisture resistance. Also, natural fibres are susceptible to fungal growth (Laborel-Préneron et al., 2016; 2018; Giroudon et al., 2019). The development of such clay bricks' strength properties mainly depends on forming "fibre-clay" bonds. The strength of these bonds mainly depends on the dimension, surface conditions, and quantity of additives in the soil. Increasing water content can also lead to bonds breaking in the clay material structure. A question arises about the optimal composition and protection of the adobe against the moisture ingress inside the material.

The hygroscopic properties of bio-aggregates, such as barley straw (BS), hemp shiv (HS) and corn cob (CC) were demonstrated in the research of Laborel-Preneron et al. (2018). The clay samples with bio-aggregates had different densities: 57 kg/m^3 for BS, 153 kg/m^3 for HS, and 497 kg/m^3 for CC. The investigated bio-aggregates demonstrated a high sorption rate, from 20 to 26% at 95% of RH, making them effective in increasing the sorption capacity of the clay composites.

Furthermore, cement, lime, gypsum, and specific industrial byproducts are commonly employed to enhance some properties of non-fired clay materials. Oti et al. (2009; 2012) stabilised clay soil with Portland cement, lime and ground granulated blast furnace slag. They obtained the clay materials with compressive strength values above 5 MPa. Ashour et al. (2015) present a stabilisation method of unfired earth material by adding 5–10% cement and 1–3% barley or wheat fibre. The density of unfired earth samples stabilised with the introduction of both variations of stabilisers was decreased by 34%. It was concluded, that with an increase of wheat and barley straw fibre content up to 3%, the thermal conductivity of the samples can be significantly decreased by 54%.

The technology of using different fibres, as well as cement, lime, and gypsum for stabilising unfired clay materials, is widely represented in the literature, and it can be considered traditional. These studies are interesting from the perspective of realising the ecological potential of clay materials using local raw materials and waste, but the mechanisms of interaction between clay and such admixtures are well-studied. Therefore, scientists are confronted with the need to discover new methods and techniques for stabilising clay-based materials.

1.3. Modification of clay-based materials with biopolymers

In the last decade, researchers have become increasingly interested in natural polymers (Saiter et al., 2012). Polysaccharides are complex carbohydrates made of long chains of simple sugar units bonded together (Bringham et al., 2018). They represent renewable and sustainable resources, which are sourced from many natural materials such as plant cell walls, bacterial capsules, and animal connective tissues (Walter, 1998). Polysaccharides have a wide range of applications in various industrial purposes due to their unique properties. They are usually used as thickening agents, emulsifiers, and gelling agents (Tusnim et al., 2020). In building materials such as concrete and dry-mix mortars, polysaccharides are mainly used as viscosifiers or water-retaining additives (Pacheco-Torgal et al., 2016; Plank, 2004). The use of various biopolymers for clay-based materials is a recent development.

Existing literature and reviews on using natural additives in clays frequently focus on incorporating natural fibres. The mechanisms of interaction between clay and natural fibres are well understood (Salih et al., 2020), which enables the prediction of some properties of the final unfired clay composites (Turco et al., 2021). Reviews on applying natural additives to stabilise clays have been documented in the papers by Huang et al. (2021), and Losini et al. (2021). These studies highlight the current trends and gaps in the field of eco-friendly clay stabilisation. However, little attention has been paid to the specific clay modification with polysaccharides.

1.3.1. Evaluation of the biopolymers (polysaccharides)

Polysaccharides are a class of complex carbohydrates composed of long chains of monosaccharide units (simple sugars) linked together through glycosidic bonds (Maji, 2019). Polysaccharides play a crucial role in energy storage, structural support, and as components of cell membranes in various organisms, including plants, animals, and microorganisms (Brigham, 2018). Due to their unique structural properties, the majority of natural polysaccharides can form gels when they are dissolved in water or other solvents (Rinaudo, 2006).

The affinity of natural polysaccharides to interact with water can vary depending on their structural properties and the specific polysaccharide in question. Also, when in gelling form, polysaccharides can exhibit a fruitful combination with clays enhancing the structural integrity of the resulting composite material (Liu et al., 2007; Pacheco-Torgal et al., 2016). The effectiveness of using the gelled, rather than native, polysaccharide was demonstrated in the research of

Chang et al. (2015), where the application of gelled gellan and agar gums led to an increase in the strength of the clay composite.

Many polysaccharides have long, flexible chains that can interact with each other through various chemical and physical interactions, including hydrogen bonding, van der Waals forces, and electrostatic interactions (Chang et al., 2020; Theng, 2012). This feature makes the polysaccharides easy to modify and simple for use as an application in different fields. The most important classification and parameters of the polysaccharides in question are presented in Figure 1.1.

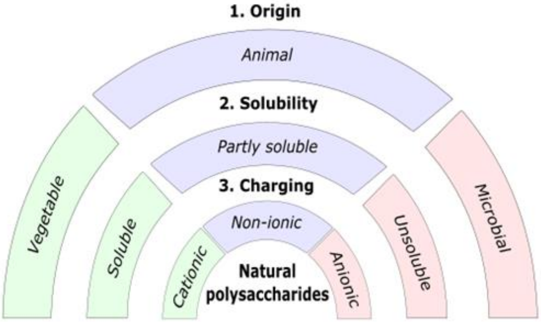


Fig. 1.1. Classification of the natural polysaccharides (based on Rinaudo, 2006)

The hydrophilicity of many natural polysaccharides is mainly attributed to the presence of hydroxyl (-OH) groups on the monosaccharide units, which can form hydrogen bonds with water molecules. These hydrogen bonds allow the polysaccharides to readily absorb and retain water (Nasrollahzadeh et al., 2021). Additionally, such properties as polymerisation degree, polymer chain length and form (linear or branched), and molecular weight of the polymer influence the ability of polysaccharides to interact with water. The principle of polysaccharide dissolution in a liquid, based on models presented in the studies of Pasqui et al. (2012) and Wang et al. (2021), is illustrated in Figure 1.2. When native polysaccharides (Fig. 1.2a) are dissolved in water, their chains can interact with each other to form a network structure that traps water molecules within the network (Fig. 1.2b). This network can then undergo further crosslinking or structural rearrangements (Fig. 1.2c) to form a more stable gel or hydrogel (Drury & Mooney, 2003). The properties of the resulting gel or hydrogel can be tuned by controlling factors, such as the concentration of the polysaccharide solution, the temperature, the pH, and the presence of other molecules or crosslinking agents (Wurm et al., 2020).

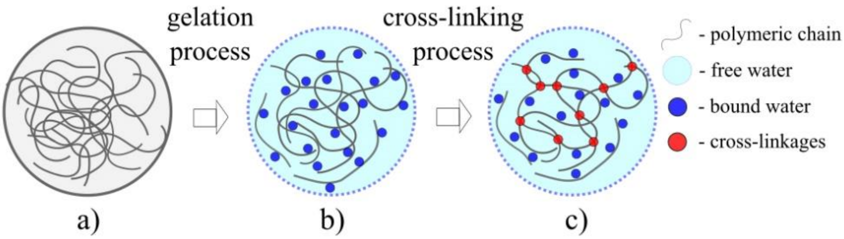


Fig. 1.2. Dissolution process of natural polysaccharides (based on Pasqui et al., 2012): a) native polysaccharide grain in solid state; b) polysaccharide molecules in liquid state; c) cross-linking of the polysaccharide molecules

During the hydration of the polysaccharide, the properties of the obtained polymer solution have a significant influence on the subsequent interaction with clay. The researchers Dove (2014) and Liu et al. (2000) postulated that higher acidity of polymeric solutions contributes to better clay-polymer interactions. The research by Theng (2012) observed that uncharged, linear polymers with higher molecular weight exhibited enhanced adsorption onto the soil surface. However, Dove (2014) noted that the higher viscosity of obtained polymeric solution can negatively affect clay–polymer interactions due to the appearance of long, tortuous chains, which can weaken polymeric structures.

Moreover, natural polysaccharides exhibit a remarkable affinity for modification due to the abundance of hydroxyl groups in their chemical structure, making them highly versatile materials for various applications (Cumpsteu, 2013). Polysaccharides can be modified through physical or chemical manipulations, facilitating alterations in the structure or properties of the biopolymer. For instance, chitosan is initially insoluble in water due to the presence of acetyl groups along the glucosamine units (Kou et al., 2021). However, to enhance its solubility and dispersion, researchers Aguilar et al. (2016) and Hataf et al. (2018) used a low hydrochloric acid solution (1%). This treatment significantly improved the solubility and dispersion of the biopolymer.

Also, some specific thermal treatments applied to certain biopolymers can provoke additional modification, thereby altering the properties of the investigated polysaccharide. For example, in the research by Soni et al. (2020), the application of retrograded starch improved the mechanical strength and water resistance of the starch-cellulose composite film. The native starch granules are well organised and have a semi-crystalline structure of linear amylose and branched amylopectin. In the centre of the starch grain, there is an amorphous core, around which there are rows of concentric layers of growth rings with a thickness of about 0.1 µm. (Cornejo-Ramírez et al., 2018).

The changes that starch undergoes during gelatinisation and retrogradation are presented in Figure 1.3 (b, c). When starch hydrogel is heated and later cooled, the disrupted amylose and amylopectin chains are reassociated into a more ordered structure. This process is well-known as starch retrogradation (Wang et al., 2015). Particles of retrograded starch have a coarser structure, noticeable "flaking" of the particles and breaking into smaller fractions (Lian et al., 2014). With the formation of additional hydrogen bonds during the retrogradation process, a large number of starch molecules bind, which leads to the formation of such flakes and an increase in the hydrogel viscosity as a result.

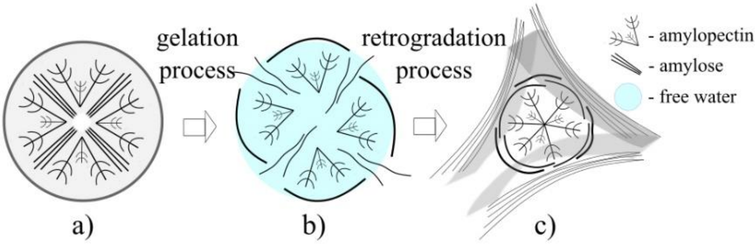


Fig. 1.3. Starch retrogradation process (based on Wang et al., 2015):
a) starch grain; b) swelling starch grain; c) retrograded starch grain

Nowadays, the starch retrogradation effect has been actively studied in the food and chemical industries (Wang et al., 2015); however, this effect has not received much attention in construction composites' modification. It can be hypothesized that the use of retrograded starch hydrogel will have a positive impact on the properties of clay composite due to the restructuration of starch, leading to the formation of more stable bonds within the clay composite.

1.3.2. Application of biopolymers in clay composites

Table 1.2 presents modern concepts for modifying clay-based composites using natural polysaccharides over the past decade, indicating the type of clay and polysaccharides, the amount of additive used, the modification technology (if specified in paper), and the main results obtained. Table 1.2 sources mainly relate to construction materials and geotechnical sciences, which face specific challenges requiring a unique approach. However, many of the studied properties are interrelated, and the systematisation of knowledge about clay–polysaccharide interactions can enable more effective solutions to be applied in both fields. Table 1.2 includes 28 original studies on the topic of modification of clay-based materials with natural polysaccharides, which include alginate, agar, carrageenan, chitosan, gellan, guar, micro-cellulose, starch, xanthan and ß-glucan.

Table 1.2. Current research in the field of clay modification with polysaccharides (PS)

Materials and Methods		**Main results**
Clay/ PS	**Special conditions**	
Aguilar et al., 2016		
Soil/ chitosan (0.5% to 3%)	1. Matrix-introduction of PS solution vs. surface-coating by PS solution;	CS increased from 2.1 to 3.9 MPa (for 3% of chitosan, matrix-introduced); BS increased from 1.3 to 2.2 MPa (for 3% of chitosan, matrix-introduced); SS increased from approx. 0.5 to 0.8 MPa (for 3% of chitosan, matrix-introduced); Water erosion resistance increased for both of the techniques: matrix-introduced and surface-coating PS incorporation technologies.
Alhaik et al., 2016		
Kaolinite/ starch and derivatives (1%)	1. Used two different PS heat treatment protocols: 20°C and 120°C;	CS increased from approx. 1.1 to 2.25 MPa (for 1% starch (coded “D”) of 20°C heat treatment, with a water/binder ratio of 1.12); Clay thixotropic index decreased by almost 50% for 1% of “D” starch; In certain conditions (heat treatment protocol – 120 °C), starch can significantly increase shrinkage behaviour, thereby provoking cracks. Physical and mechanical characteristics vary depending on the type of PS used.
Ayeldeen et al., 2016		
Collapsible soil/ xanthan, guar (0.25% to 4%)	1. Dry-mix method vs. wet-mix method;	CD reduced from 19.1 to 17.2 kN/m^3 (for 2% xanthan) and to 16.7 kN/m^3 (for 2% guar); Optimal moisture content increased from 12.4 to 15.3% (for 2% xanthan) and to 14.4% (for 2% guar); The introduction of small quantities of PS (0.25%) reduced the collapsible potential of the soil; Cohesion stress increased from 42 to 105 kPa (for 2% xanthan) and from 51 to 126 kPa (for 2% guar) after seven days.
Bagriacik et al., 2021		
Soil/ guar (1% to 3%)	1. Wet-mix method; 2. SCT (1 to 196 days);	Liquid limit increased from 42 to 74% with increasing of PS content from 0 to 3%; CD decreased from 1.73 to 1.58 g/cm^3 (for 3% guar); CS increased from approx. 0.1 to 1.5 MPa (for 1% guar) after 56 days.

Continued Table 1.2

Bozyigit et al., 2021		
Kaolinite/ xanthan, guar (0.5% to 2%)	1. SWC (25% to 40%); 2. SCT (1 to 90 days);	CS increased from 90 to 398 kPa (for 2% xanthan of 90 days treatment, with 25% of water content), and 438 kPa (for 2% guar of 90 days treatment, with 30% of water content); Guar gum shows higher viscosity and stronger bonding than xanthan gum; PS admixture (0.5–2%) changes the plasticity of clay mixtures; Less water content contributed to a better CS results.
Chang et al., 2012		
Korean residual soil/ ß-glucan (0.25% to 0.5%)	1. PS curing temperatures (20, 60, 100°C)	CS increased from 1.05 to 4.31 MPa (for 0.5% ß-glucan at 60°C curing for 28 days); Modification with PS is eco-friendly, but the cost of such modification is still high.
Chang et al., 2014		
`Natural soil; red yellow soil/ xanthan (0.5% to 1.5%)	1. Dry-mix method vs. wet-mix method; 2. SCT (28 to 750 days);	BD decreased from 1.74 to 1.63 kg/m^3 (natural soil with 1.5% of xanthan) and from 1.5 to 1.41 kg/m^3 (red-yellow soil with 1.5% of xanthan); CS increased from 3.03 to 4.17 MPa (natural soil with 1.5% of xanthan, curing for 28 days) and from 4.13 to 5.46 MPa (red-yellow soil with 1.5% of xanthan, curing for 28 days); CS of the soil composite with PS increased over time (21 to 750 days); Soil type, moisture content, PS content, and mixing method are prevalent factors to increase CS of clay composite.
Chang et al., 2015		
Clayey and sandy soil/ gellan, agar (1% to 3%)	1. Wet-mix method; 2. SCT (1 to 28 days);	CS increased from 1.05 to 4.66 MPa (for 1% gellan, curing for 28 days) and from 1.05 to 3.19 MPa (for 1% agar, curing for 28 days); EM increased from 0.05 to 0.46 MPa (for 1% gellan, curing for 28 days) and from 0.05 to 0.27 MPa (for 1% agar, curing for 28 days); Thermal treatment of the PS had a significant effect on the CS and EM of the clay composite; CS of the clay composite with PS increased over time (1 to 28 days).

Continued Table 1.2

Dehghan et al., 2019		
Collapsible soil/ xanthan, guar (0.5% to 2%)	1. Wet-mix method; 2. SCT (1 to 28 days);	CD reduced from 18.83 to 17.55 kN/m^3 (for 2% xanthan) and to 17.65 kN/m^3 (for 2% guar); Optimal moisture content increased from 13.2% to 17.2% (for 2% xanthan) and to 16.1% (for 2% guar); Soil permeability was decreased by 18.6% (for 0.5% xanthan) and by 88% (for 0.5% guar) after 28 days; Plasticity index increased from 6.1% to 71.1% (for 2% xanthan); The collapsible potential was decreased from 9 to 3.91% (for 2% xanthan); and to 5.1% (for 2% guar).
Dove, 2014		
Soil/ alginate (0.1%)	1. Wet-mix method;	BD decreased from 1.98 to 1.9 kg/m^3; SHR decreased from 9 to 5%; CS increased from 0.85 to 1.64 MPa; BS increased from 0.32 to 0.95 MPa.
Dove et al., 2015		
Three soils (U,V,W)/ alginate and derivatives (1%)	1. Wet-mix method;	BD increased from 1.85 to 2.0 kg/m^3 (U soil), from 1.94 to 2.11 kg/m^3 (V soil) and from 1.81 to 2.06 kg/m^3 (W soil); SHR decreased from 5.6 to 3.3% (U-soil), from 5.4 to 5.0% (V soil), increased from 2.7 to 5.2% (W soil); CS increased from approx. 0.5 to 1.3 MPa (U soil), from approx. 1.1 to 1.6 MPa (V soil), and from approx. 1.5 to 1.78 MPa (W soil); FS increased from approx. 0.3 to 0.7 MPa (U soil), from approx. 0.8 to 1.25 MPa (V soil), and from approx. 1.0 to 1.25 MPa (W soil); The abrasive strength coefficient increased from approx. 10 to 20 cm^2/g (U soil), from approx. 12 to 35 cm^2/g (V soil), from approx. 28 to 42 cm^2/g (W soil).
Fatehi et al., 2023		
Kaolinite/ alginate, agar (0.25% to 1.5%)	1. Dry-mix method vs. wet-mix method;	CS significantly increased from 0.316 MPa to 1.02 MPa (for 1.5% of agar) and 1.429 MPa (for 1.5% of alginate) after 14 days; EM increased from approx. 25 MPa to 75 MPa (for 1.5% of agar) and 85 MPa (for 1.5% of alginate) after 14 days; PS contributed to better durability of clay composites during wet-dry cycles: mass loss after five wet-dry cycles reduced from approx. 8 to 1% (for both 0.5% agar and alginate).

Continued Table 1.2

Guiheneuf et al., 2020		
K-soil, R-soil, S-soil/ alginate, xanthan (0.5% to 1%)	1. Wet-mix method; 2. Addition of sodium-hexametaphosphate (HMP)	The application of the PS admixtures reduces capillarity absorption by 61% (for S-soil), by 58% (for K-soil) and by 52% (for R-soil); PS reduce the density of the composites and vapour diffusion resistance.
Hamza et al., 2022		
Expansive soil/ xanthan (0.5% to 5%)	1. Dry-mix method; 2. SCT (1 to 60 days);	CD reduced from 19.2 to 17.5 kN/m^3 (for 5% xanthan); Optimal moisture content increased from 12.3 to 14.8% (for 5% xanthan); CS increased from 99 to 628 kPa (for 1.5% xanthan) after 60 days; EM increased from approx. 8 to 48 MPa (for 1.5% xanthan) after 60 days; Consolidation parameters slightly increased with increasing PS content; MS analysis showed a denser structure over time.
Hamza et al., 2023		
Expansive soil/ guar (0.5% to 5%)	1. Dry-mix method; 2. SCT (1 to 60 days);	Plasticity index of the soil increased by 29% (for 5% guar); BD reduced by 15.7% (for 5% guar); Optimal moisture content increased from 12.3 to 14.8% (for 5% guar); CS increased from 137 to 468 kPa (for 1.5% guar at 60 days period); EM increased from 7.77 to 24 MPa (for 1.5% guar at 60 days period); Durability increased over 365 days; MS analysis shows the covering effect of the hydrogel, which clogs the pores of soil composite and binds soil aggregates together.
Hataf et al., 2018		
Soil/ chitosan (0.02% to 0.16%)	1. Extracted chitosan was dissolved in 1% acetic acid; 2. SCT (1 to 28 days);	CS increased from approx. 1.85 to 2.9 MPa (for 0.16% chitosan) after seven days; Cohesion increased from 10.3 to 30.3 kPa with increasing of friction angle from 21.8 to 22.3° (for 0.16% chitosan); MS analysis showed the ability of chitosan to cover soil aggregates.

Continued Table 1.2

Kumar et al., 2021		
Soil/ xanthan, guar, ß-glucan (0.5% to 2%)	1. Dry-mix method; 2. SCT (1 to 28 days)	PS reduced the permeability of soil by the bio-clogging mechanism; The permeability of soils modified with PS increased in the first 120 days; MS analysis showed the gel-thickening at the early stage and gel shrinkage in the later stage; CS increased from 0.34 to 1.7 MPa (for 2% xanthan), to 1.26 MPa (for 2% guar), to 0.99 MPa (for 2% ß-glucan).
Kwon et al., 2023		
Kaolinite/ xanthan (0.5% to 2%)	1. Dry-mix method;	Swelling pressure increased from 5 to 37.7 kPa (for 2% xanthan); The highest final void ratio was observed for clay composite with 0.5% of xanthan; The densest structure was observed for clay composite with 1% of xanthan; PS decreased the permeability due to the pore-clogging effect.
Kwon et al., 2023		
Kaolinite/ xanthan (0.5% to 2%)		The optimal moisture content increased from 32.4 to 36% (for 2% xanthan); Maximum dry density decreased from 1.31 to 1.23 g/cm^3 (for 2% xanthan); MS analysis shows the smoothening surface of the clay. Xanthan induces direct contacts (bridges) between clay particles.
Lee et al., 2022		
Korean residual soil/ xanthan & starch mix 3:7 (2%)	1. Wet-mix method; 2. Accelerated weathering process (6 cycles of wet-drying; 6 cycles of freeze-thawing);	CS decreased significantly from 3.49 to 0.068 MPa after six wet-drying cycles and slightly decreased from 3.49 to 3.13 MPa after six freeze-thawing cycles; EM decreased significantly from 237 to 4 MPa after six wet-drying cycles and decreased from 237 to 160 MPa after six freeze-thawing cycles; The composition of xanthan and starch has less tolerance to wet drying because of the hydrophilic nature of the polysaccharides; MS analysis of soil after freeze-thaw cycles reveals that the crystallised water during freezing can cause abrasion of the polymer matrix, leading to a reduction in the composite's strength.

Continued Table 1.2

Muguda et al., 2020		
Soil/ xanthan, guar (2%)		Optimal moisture content increased by 1% (for xanthan), by 2% (for guar); Moisture adsorption increased from approx. 28 to 49 g/m^2 (for xanthan) and to 42 g/m^2 (for guar); PS significantly increased the durability of soil.
Nakamatsu et al., 2017		
Soil/ carrageenan (0.5% to 2%)	1. Matrix introduction of PS vs. surface-coating by PS;	PS coating of the soil surface significantly increased the contact angle by 101–104°; PS coating causes the appearance of a water-repellent layer on the soil surface. Matrix-introduced PS causes additional binding of the soil aggregates; CS increased from 2.1 to 3.9 MPa (for 2% PS); BS increased from 1.2 to 1.8 MPa (for 2% PS).
Nugent et al., 2009		
Kaolinite/ xanthan, guar (0.25% to 10%)	1. Wet-mix method;	PS solutions of 10% xanthan and 3% guar have almost equal viscosity – 30 000 kPa*s; Liquid limit increased from approx. 70 to 440 MPa (for 10% xanthan), and to 820 MPa (for 3% guar).
Ni et al., 2022		
Clayey soil/ carrageenan (2% to 8%)	1. Wet-mix method; 2. SCT (7 to 28 days);	Several factors such as curing period, polysaccharide content and initial moisture content influence the mechanical properties of soil composite; CS increased from 2.0 to 2.53 MPa for 2% of carrageenan after 28 days, with 24% of moisture content; Varying amounts of polymer from 2 to 8% and the initial moisture content from 24 to 36%, the mould growth rate varies from “initial growth” to “patchy growth”.
Perrot et al., 2018		
Earth/ alginate (3%)	1. Wet-mix method; 2. Obtained clay mixture was used for 3D-printing;	Yield stress increased from 3 to 20 kPa (the first hour) and from 9 to 95 kPa (after 24 hours) for earth composite, modified with 3% of alginate solution; EM increased from 30 to 200 kPa (the first hour) and from 60 to 1000 kPa (after 24 hours) for earth composite, modified with 3% of alginate solution; CS increased from 1.65 to 1.77 MPa; Alginate contributed to the fast structural build-up of the earth, increasing the mixture’s CS.

End of Table 1.2

Soldo et al., 2020		
Residual Piedmont soil/ xanthan, guar, ß-glucan, chitosan, alginate (1% to 4%)	1. Dry-mix method for xanthan, guar, ß-glucan, chitosan; 2. Wet-mix method for alginate (with $CaCl_2$);	CS increased from 1.17 to 7.09 MPa (for 4% xanthan), to 3.28 MPa (for 4% guar), to 2.47 MPa (for 4% ß-glucan), to 2.04 MPa (for 2% chitosan) after 30 days; TS increased from 0.24 to 1.06 MPa (for 4% xanthan), to 0.44 MPa (for 4% guar), to 0.42 MPa (for 4% ß-glucan); to 0.33 MPa (for 2% chitosan) after 30 days; Incorporating of PS increased the cohesion of the soil from 107 to 493 kPa (for xanthan), to 131 kPa (for guar), to 144 kPa (for ß-glucan) after 30 days; However, the friction angle was decreased from 49 to 47° (for xanthan), to 37° (for guar), to 36° (for ß-glucan).
Tourtelot et al., 2021		
Earth/ micro-cellulose, starch, alginate (1%)	1. Dry-mix method for micro-cellulose and alginate; 2. Wet-mix method for starch;	BD decreased from approx. 1.9 to 1.86 kg/m^3 (for 10% micro-cellulose), to 1.81 kg/m^3 (for 1% alginate) and to 1.82 kg/m^3 (for 1% starch); CS increased from approx. 3.4 to 5.5 MPa (for 10% m-cell.) and to 4.5 MPa (for 1% starch); EM increased from approx. 280 to 370 MPa (for 10% micro-cellulose); and to 410 MPa (for 1% starch).
Weng et al., 2021		
Red clay/ xanthan (0.5% to 2.5%)	1. Wet-mix method; 2. SCT (3 to 28 days);	CS increased from 96.34 to 161.1 kPa (for 1.5% xanthan) after 28 days; The curing period affects the CS of the PS-treated clay samples.

Note: The following abbreviation was used in the current Table:
polysaccharide – PS; bulk density – BD; compaction density – CD; shrinkage – SHR; compressive strength – CS; bending strength – BS; tensile strength – TS; special curing time – SCT; special water content – SWC; split strength – SS; elastic modulus – EM; microstructure – MS.

When observing studies presented in Table 1.2, some trends are typical for the majority of articles. The technological process is a crucial aspect of producing clay composites modified with polysaccharides. Typically, such a technological process involves three main stages. These stages include the special treatment of the polysaccharide, preparation of the clay mixture with the polysaccharide, and drying of the clay composite to a solid state (Oti & Kinuthia, 2012).

At the stage of polysaccharide treatment, the main focus is on polysaccharides and their possible modifications (Rinaudo, 2006). As presented in Table 1.2, under the column "special curing conditions", the "dry mixing method" or "wet mixing method" definitions indicate different approaches to using polysaccharides in the modification of clay-based materials. The "dry mixing" method mainly involves mixing raw clay/earth/soil with a certain amount of dry polysaccharide, with further addition of water (Hamza et al., 2022). The "wet mixing" method mostly involves dissolving the required amount of polysaccharide in the solvent (usually water) and then applying the resulting solution to dry clay (Chang et al., 2015a; Fatehi et al., 2023). This stage mainly considers such characteristics as polymer type, its structural characteristics and its affinity to interact with water. If the polysaccharide is dissolved in water, the characteristics of the resulting solutions, such as pH, viscosity, and zeta potential, should also be examined (Wurm et al., 2020).

The process of forming the clay mixture is characterised by the plastic behaviour of raw clay, earth or soil when interacting with water. Technologically, the most significant parameters at this stage are the optimal water content and the type and amount of polysaccharide used. The main criteria for the resulting clay mixture are its rheology, plasticity, compressibility, permeability, and green strength (Fatehi et al., 2021). These parameters are particularly critical in the geotechnical field, where they ensure the stability of solid structures and temporary consolidation of clay-containing soil masses, enhancing their resistance to adverse environmental conditions.

The drying stage is related to increasing the strength of the clay-based composite under certain conditions. The "special curing time" parameter is particularly common in geotechnical research but is rarely used in works devoted to building clay-based materials. After drying, the resulting clay-based material is characterised by such parameters as bulk density and shrinkage, mechanical and hygroscopic properties, durability, and microstructure (Losini et al., 2021; Pacheco-Torgal & Jalali, 2012; Turco et al., 2022). These parameters are necessary to ensure the strength and longevity of the obtained clay-based materials.

1.3.3. Effect of biopolymers on the properties and structure of clay-based materials

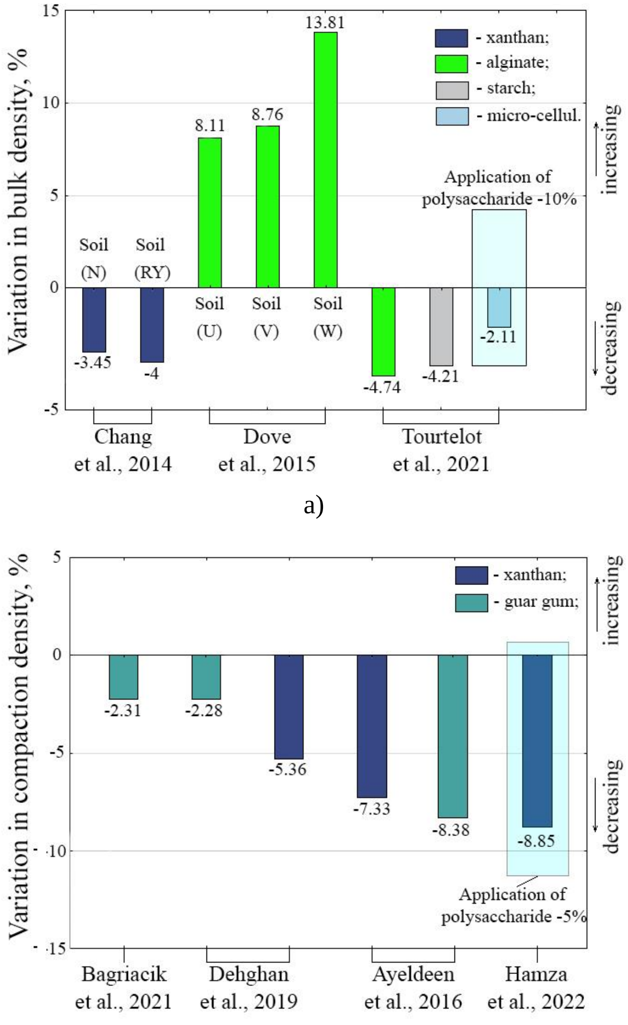
Physical properties

The presented studies in Table 1.2 pay great attention to investigating the physical properties of clay-based composites modified with polysaccharides. When systematising the influence of natural polysaccharides on the physical properties of clays, two main stages can be distinguished: forming a plastic clay mixture and forming a solid specimen after drying. The introduction of polysaccharides into clay-based composites has a significant impact on these two stages. By adding polysaccharides to the conventional “clay–water” interaction scheme, the properties of the clay-based composite, such as density, plasticity, water permeability, and shrinkage can be modified.

Clay is a plastic material which can be moulded and shaped using a certain amount of water. The optimal water content is the key parameter in regulating such properties as density, plasticity and workability of clay mixtures. Most of the studied polysaccharides, represented in Table 1.2, can dissolve in water. When dissolving, polysaccharides form gel-like solutions with a high viscosity. There are two main technologies for adding polysaccharides to clay: mixing clay and polymer in dry form with subsequent addition of water or adding a polysaccharide solution of a given concentration to dry clay. Despite the difference in technologies, researchers noted similar effects of polysaccharides on clay mixtures.

The use of polysaccharides led to an increase in the optimal water content (OWC) required to achieve the necessary plasticity of the clay mass. Ayeldeen et al. (2016), Dehghan et al. (2019), Hamza et al. (2022), and Muguda et al. (2020) showed an increase in OWC of 1–4%, depending on the type of polysaccharide used and its amount. The effect was associated with the ability of polysaccharides to interact with water: hydrophilic groups of polysaccharides attract and partially bond water molecules (Hamza et al., 2022). The higher polysaccharide concentration leads to the higher viscosity of the newly obtained gels and less free water in the clay–polysaccharide–water system (Kumar et al., 2021).

One more important physical parameter of clay modified with natural polysaccharides is its density. Depending on the research context, the density of the clay-based composite is determined differently: bulk density is measured for building materials in an undisturbed state after drying (Fig. 1.4a), while compaction density is relevant in the geotechnical field, where the clay density is achieved after applying external forces during the compaction process (Fig. 1.4b). The increase of optimal water content naturally reduced the density of clay-based composites in most of the observed studies (Fig. 1.4a, b). However, the use of polysaccharides can show an increase in the density of clay-based composites, as was mentioned in the research by Dove et al. (2016) (Fig. 1.4a). The introduction of 0.25–1.25% alginate resulted in a 15% increase in the density of clay blocks. The quantity of water used by Dove et al. (2016) remained constant as the amount of polysaccharides was increased, describing the effect of variation of the optimal water content on the density of clay-based materials.



a)

b)

Fig. 1.4. Density variation of clay-based composites, modified with polysaccharides: a) bulk density; b) compaction density

The introduction of natural polysaccharides into clay mixtures also significantly impacted the clay's plasticity. In the research by Bagriacik et al. (2021) and Dehghan et al. (2019), an increase in the amount of polysaccharide resulted in a substantial increase in the liquid limit of the clay-based composite. However, the plastic limits of the mixtures remained almost unchanged. Therefore, the clay materials' plasticity index increased with the addition of the polysaccharide. These findings suggest the ability of natural polysaccharides to enhance the plasticity of clay mixtures, making them more suitable for various applications. The obtained effect was explained by Bozyigit et al. (2021) as a result of the polysaccharide's ability to flocculate soil aggregates as well as trapping water inside the sample.

Polysaccharides are capable of increasing the cohesion of soil aggregates and reducing the permeability and collapsible potential of soils, which is particularly important in geotechnical engineering. Soil permeability was reduced after some time because of the polysaccharides and bio-clogging mechanism inside the studied material (Dehghan et al., 2019; Kumar et al., 2021). A significant increase in cohesion stress was observed in the research by Ayeldeen et al. (2016) and Soldo et al. (2020). Polysaccharides contribute to increasing the cohesion of soil aggregates, which can reduce the likelihood of soil collapse and improve the load-bearing capacity of the soil (Hataf et al., 2018). As a result, the use of natural polysaccharides in soil modification can be an effective way to address collapsible potential in geotechnical applications.

Shrinkage is a natural process that occurs in clay-based materials during drying as a result of water evaporation and moisture distribution in clay. This process can cause cracks or deformations in the material and can affect its structural integrity. The introduction of polysaccharides into the structure of clay-based materials positively affects their shrinkage behaviour. Chang et al. (2015), Dove et al. (2015), and Lagouin et al. (2021) reported that the addition of polysaccharides to clay-based materials can result in a slight reduction in shrinkage. This was attributed to the polysaccharides covering the clay aggregates and reducing the internal propagation of shrinkage defects. However, the introduction of polysaccharides can also have a reverse effect. The use of certain types of starch in the research by Alhaik et al. (2017) led to the formation of significant cracks in kaolinite samples. The formation of excessive cracks could be a result of aggressive drying conditions, which is also very important to achieve the optimal shrinkage value.

Mechanical properties

Mechanical properties are key parameters in assessing the effectiveness of modifying unfired clay-based composites. One of the most critical parameters of soil/clay composites is their compressive strength. Figure 1.5 presents a comparison of the effect various biopolymers have on the strength of clay materials. For a more equitable comparison of clay-based composites, the results were selected based on the studies, presented in Table 1.2 with the following parameters: the amount of polysaccharide – 1%, wet mixing method as material production technology, and curing time in the range from 21 to 30 days (if specified in the research).

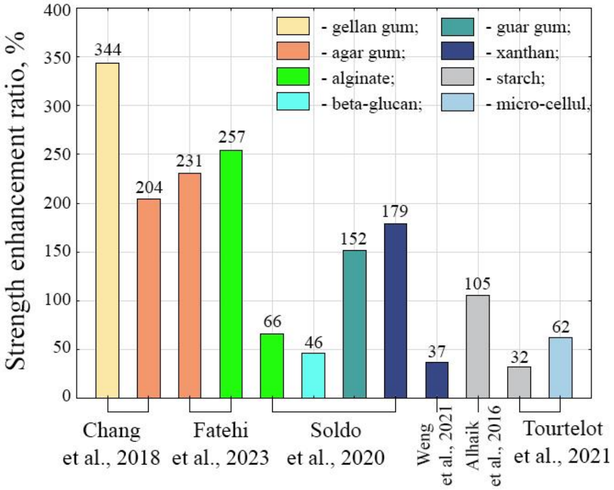


Fig. 1.5. Strength enhancement ratio of the clay-based composites, modified with different polysaccharides (1%)

When modifying with polysaccharides, the compressive strength of the clay is influenced by several parameters such as the type of clay and polysaccharides used, the amount of admixture, the curing time and the water content. The special treatment of the polysaccharide can also play a significant role in strengthening the clay composite (Alhaik et al., 2017; Chang et al., 2015; Soldo et al., 2020). According to modern concepts, the addition of polysaccharides to the clay mixture can increase its compressive strength by inducing additional hydrogen bonding between the clay and polysaccharide particles (Theng, 2012). Application of the polysaccharides increased the elastic modulus of the clay-based samples, which can also be an indicator of a more bonded and cohesive structure (Chang et al., 2020; Fatehi et al., 2021; Hamza et al., 2022; Perrot et al., 2018). Some polysaccharides can cover the clay aggregates, thereby filling the empty space inside the composite and reducing its porosity (Zhou et al., 2020).

Dove (2014) proposed the modification of unfired clay-based materials with alginate and its derivatives, the main structural polysaccharide of brown algae (seaweeds). The results showed that some types of alginate products significantly improved the compressive strength (47–92%) of the clay bricks. Moreover, Cabalar et al. (2017) postulated that a small amount (up to 3%) of xanthan gum tends to coat the soil grain surface, thereby increasing the contact area among the soil particles. As a result, such modification methods significantly increased the compressive strength of soil. Chang et al. (2012) showed that β-1,3/ 1,6-glucan biopolymer treatment enhanced the strength of natural soil with an increment ratio of up to 300–400%. The application of thermal-gelated polysaccharides (i.e., gellan gum and agar gum) for soil modification was discussed in the research by Chang et al. (2015a). The compressive strength values of 1–3% biopolymer-treated clayey soil and sandy soil were significantly higher (3–12 MPa) than those of non-treated natural soils (1–2.5 MPa).

The curing time is also an important factor considered by many researchers. Many research efforts postulate that longer curing times allow for better strength of the clay-based composite due to the formation of stronger bonds between the clay particles (Kumar et al., 2021). Furthermore, certain studies have highlighted the influence of moisture content on the compressive strength of clay. For instance, Bozyigit et al. (2021) found that an increase in water content led to a more ductile behaviour of kaolinite, increasing axial deformation of the sample.

Hygroscopic properties

Hygroscopicity is the ability of a material to interact with surrounding moisture by its ad- and desorption. Hygroscopicity is characterised by parameters such as moisture adsorption degree, water vapour permeability, equilibrium moisture content, etc. Currently, the determination of the hygroscopicity of clay materials is regulated by ISO 24353:2008, DIN 18947:2013, and JIS A1470:2002 standards, as well as the Nordtest protocol (Rode et al., 2008). In the research of McGregor et al. (2014), clay-based plasters showed average moisture adsorption of 55 to 60 g/m^2 over 8 hours, while the adsorption degree of lime and cement-based plasters was about 20 g/m^2, which is approximately 65% lower.

Also, McGregor et al. (2016) noted that incorporating organic additives into clays can increase the moisture adsorption of a composite. However, different polysaccharides can interact with water differently, which can result in either an increase or a decrease in water adsorption of the clay composite. Clay is already possessed as a highly hygroscopic material, so the incorporation of natural additives should be regulated. Unfortunately, only a few studies describe the effect of different polysaccharides on the hygroscopic properties of clays.

Muguda et al. (2020) reported that incorporating xanthan and guar gum (2%) led to a significant increase in soil moisture adsorption by 75% and 50%, respectively. Such an effect was explained by the moisture-absorbing properties of obtained polysaccharide hydrogels, which can facilitate the adsorption and diffusion of ambient moisture.

However, the increase in the hygroscopicity of this non-fired clay composite was associated not only with the hydrophilic or hydrophobic properties of polysaccharides but with the modification of the structure of the clay composite (Muguda et al., 2020). Greater water adsorption is explained by the presence of smaller pores distributed in the structure of the clay composite. Parameters, such as the type of clay, its mineralogical composition and structure, also play an important role in the ability of the clay composite to interact with water molecules (Cagnon et al., 2014; McGregor et al., 2016). Modification of the clay structure with natural polysaccharides is also presented in Figure 1.6.

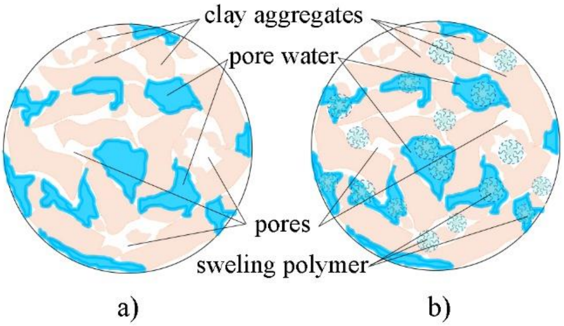


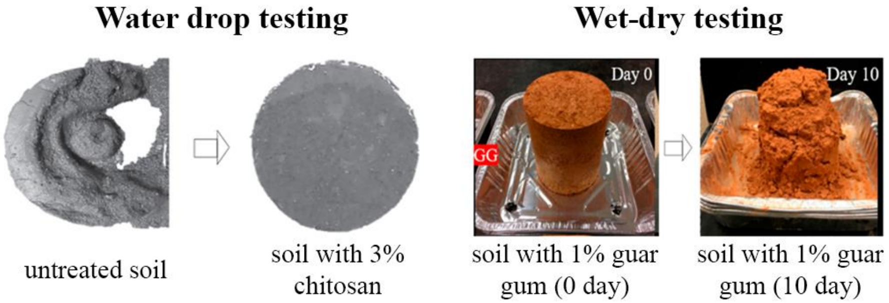
Fig. 1.6. Distribution of polysaccharides within the clay material (based on the model of Zhou et al., 2020):
a) clay internal structure before polymer treatment;
b) clay internal structure after polymer treatment

Zhou et al. (2020) postulated, that the incorporation of the biopolymers changes the pore volume in the matrix of the soil composites. Figures 1.6a and 1.6b present the model of the soil structure that describes the influence of the biopolymer on the clay material. Zhou et al. (2020) proposed that the incorporated biopolymer partially occupies the porous space of the composite, altering the overall pore volume (Fig. 1.6b). Additionally, the authors suggested that the introduced polymer can retain water within the pores and swell in response. On the other hand, soil aggregates are capable of restraining the swelling of the polymer.

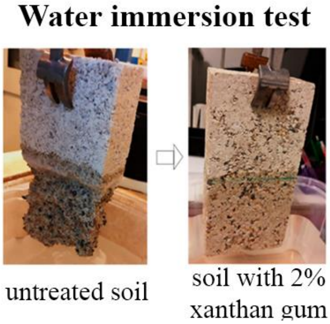
Durability

Durability refers to the capacity of a building material to resist adverse environmental exposure over a specific period. Various factors contribute to the durability of a material, but for unfired clay materials, the most significant factor is water erosion resistance. Unfired clays are highly vulnerable to water exposure; therefore, several methods can be used to determine the durability of clay composites in the context of water erosion resistance (Fig. 1.7).

The rain drip test (Fig. 1.7a), which is based on the Geelong method (Walker, 2002), has several modifications specified in such standards as UNE R41410:2008 and NZS 4298:1998. The test involves simulating rainfall and subsequently measuring the eroded area of the tested specimens.



a) Nakamatsu et al., 2017 b) Soldo & Miletic, 2022



c) Muguda et al., 2022

Fig. 1.7. Durability evaluation of clay-based composites, modified with biopolymers

The wet-drying test (Fig. 1.7b) evaluates the response of clay materials to cyclic wetting and drying conditions, which are typical in natural environments. The test is based on ASTM D559 and ASTM D560, which was originally designed for cemented soil; however, for polymer-modified clay materials, the test is used in a modified way (Lee et al., 2022; Soldo & Miletic 2020). The changes in the clay's weight, volume, and mechanical properties after each cycle help assess its stability and resistance to deterioration due to repeated wetting and drying. The immersion and suction tests (Fig. 1.7c) assess the durability of clay materials when submerged in water over an extended period. The immersion test evaluates the ability of the clay to retain its integrity, strength, and other physical properties under constant exposure to water. The suction test demonstrates the ability of capillary water to spread within the clay material.

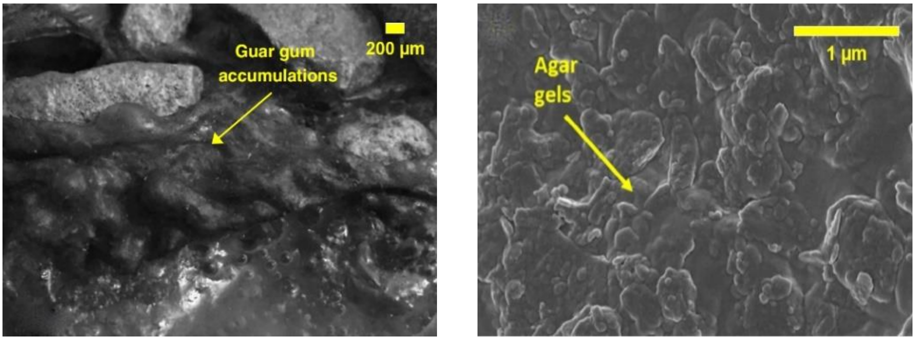
In the research by Aguilar et al. (2016), the addition of 1 and 3% chitosan solution to modify unfired clay samples increased their surface water erosion resistance. Another alternative method for clay modification with a polysaccharide was also found effective: coating the clay sample with a chitosan solution formed a hydrophobic film on its surface, which prevented liquid from penetrating inside the sample. The use of 0.5 to 2% carrageenan (Nakamatsu et al., 2017) also contributed to an increase in the durability of the clay sample. The observed effect was explained by the ability of polysaccharides to bind clay aggregates, which prevented the active destruction of the clay sample during water exposure.

The type of clay or soil, and its mineralogical and chemical composition are among the most important parameters that affect the hygroscopic properties and erosion resistance of the material (Cagnon et al., 2014; Ouedraogo et al., 2021). It is also important to understand that natural polysaccharides are subject to biodegradation. Therefore, prolonged exposure to water on a clay-based material with the addition of a biopolymer can lead to a decrease and loss of previously obtained properties (Ayeldeen et al., 2016; Chang et al., 2020). Durability is a complex parameter that can include other factors such as resistance to weathering, chemical exposure, microorganisms, and longevity. For example, the research by Laborel-Preneron et al. (2019) specified such durability parameters of unfired clay-based materials as dry abrasion, impact resistance, and fungal growth. Ni et al. (2022) proposed an evaluation of mould growth in clay-based materials modified with natural polysaccharides. The obtained results showed that increasing the polysaccharide (carrageenan) from 2 to 8% can significantly increase the mould growth on the clay sample. However, the number of such tests with other combinations of "clay–polysaccharide" and by other authors does not allow for assessing and discussing the obtained results. Thus, the effect of natural polysaccharides on the durability of clay materials should be additionally investigated in a more complex way.

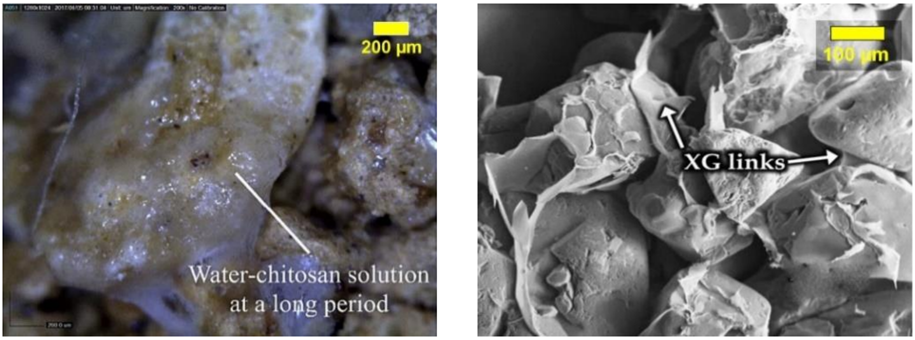
Microstructure of the clay-polymer composites

A review of the aforementioned studies identified some common points applicable to clay-based composites modified with natural polysaccharides. When the polysaccharides are introduced into the clay matrix, they can alter composite properties by creating additional hydrogen bonds and making the whole structure more cohesive (Liu, 2007).

Figure 1.8 illustrates typical clay/soil microstructures, modified with various polysaccharides that are characteristic of the majority of the studies used in this review. The microstructure analysis shows the different modification mechanisms depending on the type of polysaccharides used. Applied guar and agar polysaccharides (Fig. 1.8a, b) coat the surface of soil particles, partially filling some structural irregularities such as pores and cracks. The described effect is seen in Figure 1.8b, where agar gel coagulates the entire structure of clayey soil. The chitosan polysaccharide is evenly distributed among the soil particles, covering some of the aggregates (Fig. 1.8c). Polysaccharides change the porous network of the soil by forming three-dimensional bridges between the sol-gel nature of the solution and the detached clay particles (Hataf et al., 2017). Meanwhile, the beta-glucan forms fibre bundles inside the soil structure, which may bind the soil aggregates, increasing the strength of the composite and deterring the water flow. A similar effect is observed in soil modified with xanthan gum, resulting in the formation of polymeric bridges that interacted directly between soil particles, forming additional hydrogen bonds between them (Fig. 1.8d).



a) Ayeldeen et al., 2016 b) Chang et al., 2015



c) Hataf et al., 2017 d) Soldo et al., 2020

Fig. 1.8. Microstructure of the clays, modified with polysaccharides:
a) guar gum; b) agar gum; c) chitosan; d) xanthan gum

The microstructure images show the ability of polysaccharide molecules to form a stiff clay matrix. Depending on the type of biopolymer, two different contact types – direct and indirect – exist between clay and polysaccharides. Direct contact involves the connection of clay aggregates with polymer chains (Fig. 1.8d). Chang et al. (2015) described this type of interaction between the polymer and clay aggregates as “web-like linkages”, which form a polymer matrix inside the clay composite. Indirect contact entails the coating of the clay aggregates by biopolymers. Polysaccharide molecules effectively “wrap” the surface of clay particles, leading to the coagulation of the entire structure (Fig. 1.8 a–c). These polysaccharide molecules form inter-connected cation bridges between clay particles, cover their surfaces with a thick gel, and increase the contact area between soil particles. All the contacts between polysaccharide and clay aggregates can be explained by electrostatic and hydrogen bonding (Barani & Barfar 2021), which occurs in the structure of clay composites. Different contacts may depend on the type of the polysaccharide: direct contacts are typical for polysaccharides of microbial origin, while indirect contacts are common for polysaccharides of vegetable and animal origin (Fatehi et al., 2022). In addition, it may be influenced by variations in molecular weight and the length of the formed molecular chains of the polysaccharide used.

Micrographs provide a logical explanation of the results, discussed above. The biopolymers are evenly distributed throughout the clay composite structure, filling in the empty pores and voids. This statement is in good agreement with the structural model by Zhou et al. (2020), presented in Figure 1.6. More uniform microstructure with additional polymeric bonds, as well as the hardening of hydrogel over time, are the attributes that significantly improve the strength of the clay-based composite.

1.4. Conclusions of the First Chapter and formulation of the objectives

This literature overview shows the great potential of green clay or earth raw materials with different additions in the building industry. Modified clay may support the production of more durable and sustainable materials and may be an alternative to other building materials. There are some trends and problems that can be highlighted when observing current research on the modification of clay-based composites with biopolymers:

1. Insufficient attention has been directed towards the specific clay modification with biopolymers and the technological aspect of biopolymer preparation. When utilizing biopolymers in building materials, there lacks of clarity regarding the appropriate amount, type, or form of additives. There are examples of using both minimal (0.1–0.2%) and excessively high (up to 20%) quantities of biopolymers, in dry or liquid form and in a pure or rough state. Utilizing biopolymers without considering their distinct properties during interaction with water would prove impractical;
2. There are few studies examining the effect of modified biopolymers on clay materials. For instance, the impact of starch retrogradation as a modifier for clay-based construction materials has not received much attention. Most of the papers are devoted to the research of the physical or mechanical properties of clay-based materials. Certainly, these properties

are among the most important factors when designing construction materials, but characteristics such as durability or hygroscopicity are almost not considered at all;

3. There is a lack of research with an explanation of the clay-biopolymer interactions. Such interactions, as well as the structural characterisation of clay-based composites modified with biopolymers, required more careful research.

Therefore, based on the literature survey and the problems identified during the review, the following basic issues should be considered:

1. To select the biopolymer preparation technology (gelation and starch retrogradation process) and determine its processing parameters;
2. To investigate the impact of biopolymers on the physical, mechanical and hygroscopic properties of clay composites, depending on the biopolymer's preparation technology;
3. To evaluate the biopolymer's impact on the structure and durability of the clay composite, depending on the biopolymer's preparation technology;
4. To evaluate the interaction mechanisms between biopolymers (polysaccharides – starch, alginate, and chitosan) and clay material to determine the peculiarities of structure formation.

2

Experimental and research methodologies

This chapter is dedicated to exploring the materials used (clay and biopolymers), their processing techniques, and testing methodologies used to evaluate the impact of biopolymers on unfired clay composites. The author discussed the technology employed to produce gelated biopolymers (water-polymer solutions) from starch, alginate, and chitosan. Additionally, the chapter covers the method for starch modification, specifically the retrogradation process. It details the research methodologies and equipment used. The main research results on the topic of this chapter were published in three of the author's publications (Trambitski et al., 2022a; Trambitski et al., 2022b; Trambitski et al., 2023).

2.1. Specification of the raw materials

This sub-chapter provides information about the raw materials used in the research, including clay and biopolymers, detailing their specifications and properties.

2.1.1. Characterisation of clay

The raw clay was obtained from the factory “Palemono keramika” (Lithuania). Before using as a base material for the clay composites, it was dried (105 ± 5 °C), milled and sieved (0.5 mm). The Atterberg limits of raw clay are as follows: liquid limit – 34 ± 0.2%, and plastic limit – 16 ± 0.1%. The clay plasticity index is 18.0 ± 0.1, which corresponds to medium plasticity. The chemical and granulometric characteristics of the raw clay are given in Table 2.1.

Table 2.1. Characteristics of the raw clay

Characteristics of the clay	**Value**
Chemical composition, %	
SiO_2	48.76
Al_2O_3+TiO_2	17.43
Fe_2O_3	5.53
CaO	9.87
MgO	4.57
K_2O	2.24
Na_2O	0.42
Loss on ignition	11.18
Granulometric composition, %	
> 50 µm	3.48
50–10 µm	13.62
10–5 µm	16.51
5–1 µm	24.78
< 1 µm	41.61

The XRD analysis of the raw clay material is presented in Fig. 2.1.

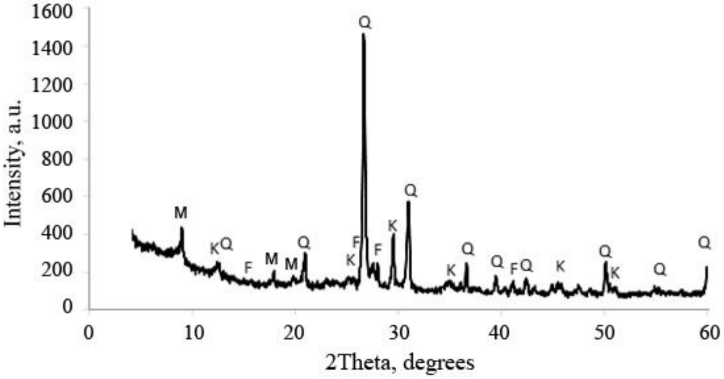


Fig. 2.1. XRD pattern of raw clay (M – mica, Q – quartz, K – kaolinite, F – feldspar)

The mineralogic composition of the clay shows that it consisted of quartz (17%), mica clay (62%), feldspar (12%) and kaolinite (9%). Figure 2.2 presents the distribution of clay particles by their size. According to the classification presented in the research of Guzlenaa et al. (2019), the studied material is sorted into the following components: clay, silt and sand particles, depending on their size. The content of clay particles up to 0.002 mm is about 66.39%. The amount of the silty component varying from 0.002 mm to 0.02 mm is approx. 30.13% and the percentage of the sandy-sized fraction over 0.02 mm is 3.48%.

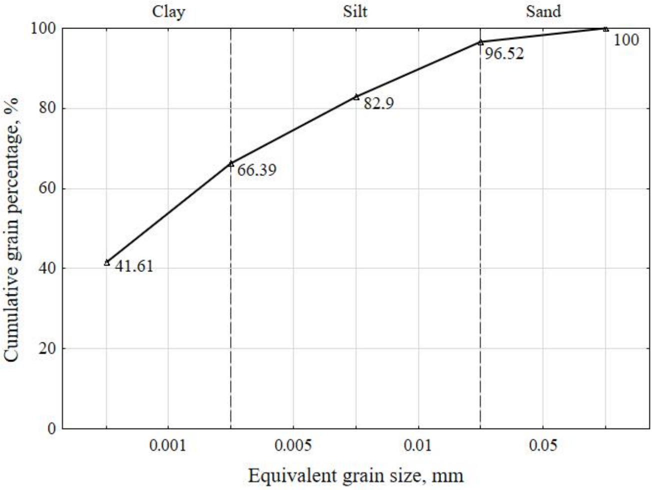
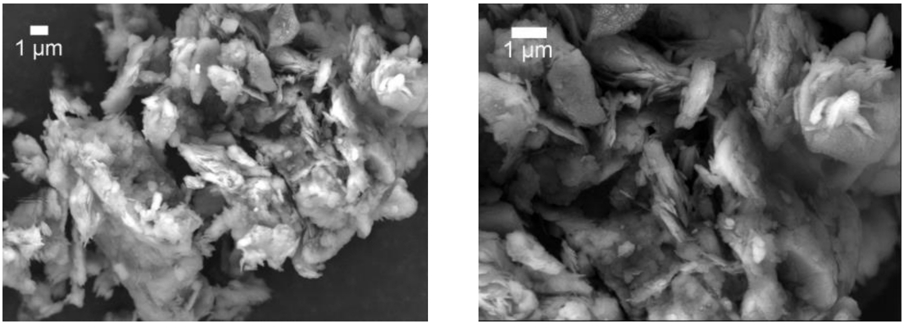


Fig. 2.2. Clay particle size distribution

Figure 2.3 presents the morphology of the raw clay observed under SEM. The observed clay particles have a porous structure with abundant groups of mica plates, resulting in a cluster of slim flakes that are roughly 0.5–2 µm in size.



a) b)

Fig. 2.3. Surface morphology of clay particles: a) ×5000; b) ×10 000

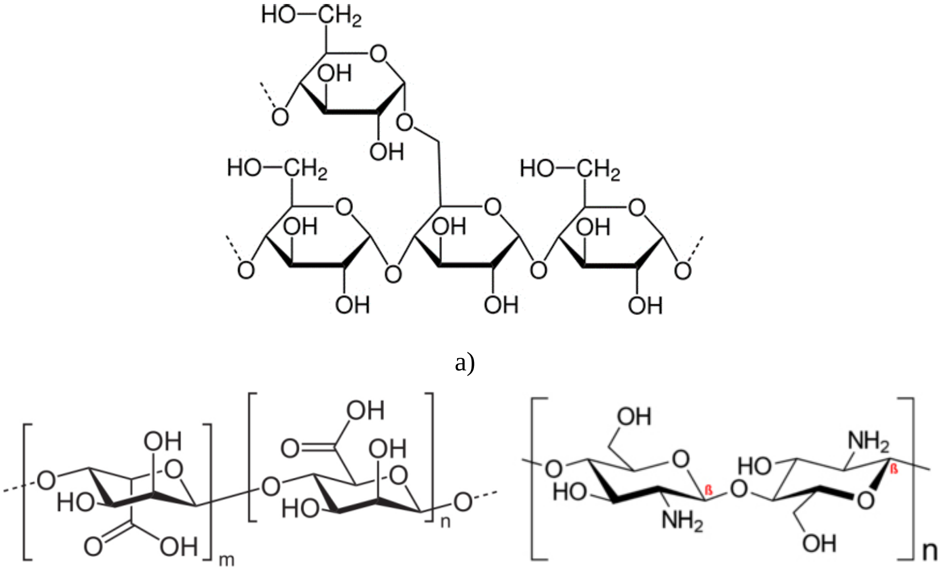
2.1.2. Characterisation of biopolymers

Three different polysaccharides were used as modifiers: starch, alginate, and chitosan. These biopolymers differ by origin, structure, and ways of interacting with water.

Starch of plant origin (corn) was obtained from a Roquette manufacturer in France. Natural starch (Fig. 2.4a) is a polysaccharide containing α-(1→4)-linked and α-(1→6)-glucans bonds (Buleon et al., 1998); it occurs in granule form in such plants as wheat, corn, potato, etc. The starch granules in question are constructed from linear amylose (26%) and highly-branched amylopectin (62.5%) molecules.

Alginate was procured from Sigma-Aldrich Company, USA. Alginate (Fig. 2.4b) is a polysaccharide of plant origin, found in brown algae, consisting of two monomeric units: β-(1→4)-linked D-mannuronic acid (M) residues and α-(1→4)-linked L-guluronic acid (G) residues (Ching et al., 2017).

Chitosan was purchased from the Roig Farma factory in Spain. Chitosan is a polysaccharide of animal origin, a deacetylation product of chitin contained in crustacean shells. This polysaccharide (Fig. 2.4c) is made up of β-(1→4)-linked 2-amino-2-deoxy-D-glucopyranose derived by N-de-acetylation of chitin (Kou et al., 2021).

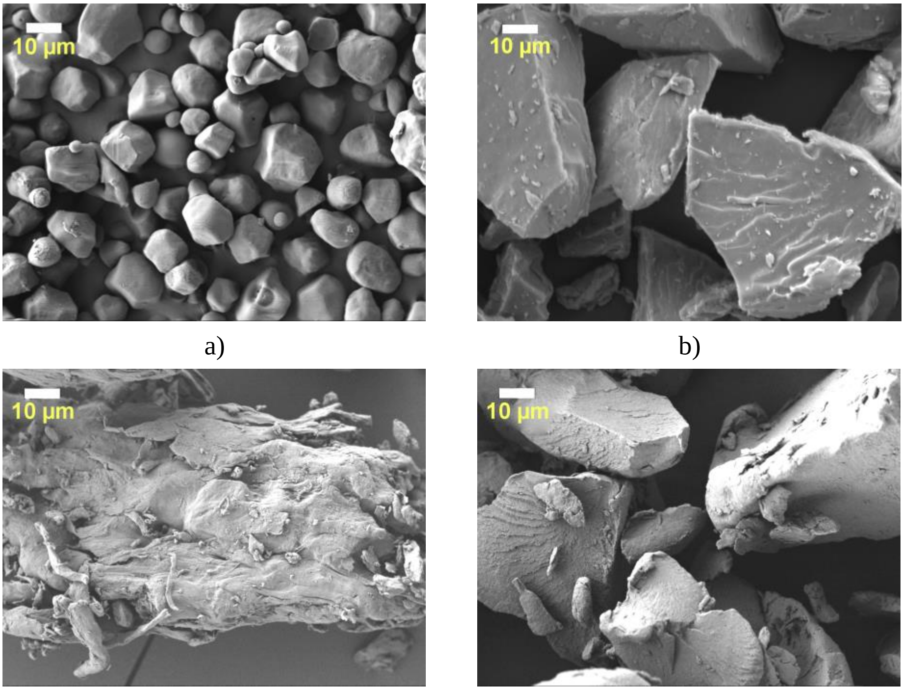


a)

b) c)

Fig. 2.4. Chemical structure of the studied biopolymers (Nasrollahzadeh et al., 2021; Rinaudo, 2006): a) starch; b) alginate; c) chitosan

The considered polysaccharid are widely distributed in nature, presenting non-toxic and biodegradable polymers. Recently, they have been widely used in the chemical, environmental, and industrial fields due to their unique properties. The choice of these biopolymers is due to their ability to dissolve in water, thus forming gel-like solutions (Nasrollahzadeh et al., 2021; Rinaudo, 2006). SEM images of the studied biopolymers are presented in Figure 2.5.



a) b)

c) d)

Fig. 2.5. Surface morphology of biopolymers (x1000): a) starch in primary form; b) starch in retrograded form; c) alginate; d) chitosan

Starch is presented in primary (Fig. 2.5a) and retrograded (Fig. 2.5b) forms. The primary form of starch is globular with a smooth surface, and its particles are finely dispersed with a size ranging from 5 to 15 µm. The retrograded starch granules are coarser, with flakes on the surface, the dimensions of the grains varying from 30 to 60 µm. The alginate (Fig. 2.5c) biopolymer has a fibrous structure, with fibre lengths varying from 20 to 40 µm, occasionally capable of forming larger agglomerates up to 100 µm in size. The microstructure of chitosan (Fig. 2.5d) is more similar to starch, with a relatively smooth surface and regular shape, with dimensions of 20 to 60 µm.

2.2. Preparation of biopolymer solutions and technological parameters of clay mixtures

This sub-chapter provides information about the preparation technologies for biopolymer solutions of starch, alginate, and chitosan and the preparation of retrograded starch hydrogel. Additionally, it details the technological parameters of clay mixtures and the principles of clay composite modification with biopolymers implemented in this research.

2.2.1. Preparation of biopolymer solutions

It was decided to use the biopolymer admixtures of starch, alginate and chitosan in the form of water solution to modify the unfired clay composite. These biopolymers were selected based on their capacity to dissolve in water, resulting in the formation of solutions with a gel-like consistency. To form a gel-like solution, specific manipulations were employed for each type of biopolymer: hot water treatment for starch, cold water treatment for alginate, and acid solution treatment for chitosan, as shown in Table 2.2. Different manipulations are justified by the different ability of each of the biopolymers to dissolve in water.

Table 2.2. Preparation of biopolymer solutions and clay composites

Step	**Hot water treatment**	**Cold water treatment**	**Acid solution treatment**
	Starch	**Alginate**	**Chitosan**
1	Sifting the raw biopolymer through a sieve (d = 0.315 mm) to avoid clumping the granules		
2	Starch + hot water (water temperature 90 °C) → mixing (no less than 2 min) → gelated starch solution (GSS)	Alginate + cold water (water temperature 20 °C) → mixing (no less than 2 min) → gelated alginate solution (GAS)	Chitosan + 1M HCl water solution (solution temperature 20 °C) → mixing (no less than 2 min) → gelated chitosan solution (GCS)
	Note: When mixing biopolymer with solvent (water or 1M HCl solution), the maximum homogeneity of the resulting solution should be achieved		
3	GSS, GAS, GCS + clay → mixing (no less than 3 min) → → keeping under room conditions at 20–22 °C for 24 h		
	Note: GSS, GAS and GCS are added to the clay instead of water		
4	Preparation of the prismatic/cylindrical clay samples		
5	Drying of clay samples at 20–22 °C for 7–10 days, humidity 50–55%		

The main principle of such modification is the complete replacement of water with a water-polymer solution of the required concentration during the manufacturing process of clay composites. To achieve the required concentrations of 2.5%, 5%, 7.5%, and 10%, a certain biopolymer was dissolved in water using a weight/volume (w/v) ratio.

2.2.2. Preparation of retrograded starch hydrogel (RSH)

The retrograded starch hydrogel (RSH) was prepared using the following technology: starch was mixed with hot water (90 °C) to obtain the required concentration (2.5%, 5%, 7.5% and 10%). Later, the obtained gelated starch solution (GSS) was placed in an oven at 150 °C for 3 or 5 hours for further modification. When keeping the starch-water solution in an oven at 150 °C, the process of moisture evaporation is inevitable. To reduce moisture loss, cups with hydrogel were covered with aluminium foil (Fig. 2.6).

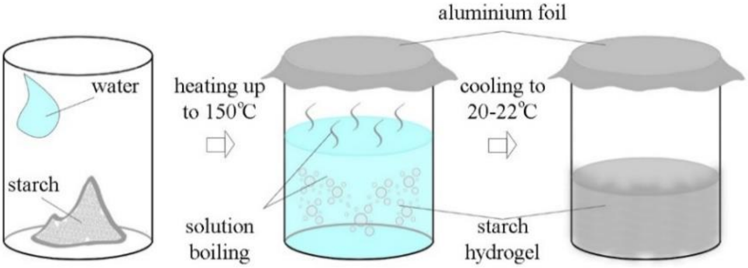


Fig. 2.6. Preparation of the retrograded starch hydrogel

Increasing heating for more than five hours is irrational due to excessive evaporation of water. After the heat treatment, the resulting starch hydrogel was re-weighed. The mass difference was compensated by the addition of hot water (90 °C) to the initial value. While hot, the solution was mixed again to avoid delamination of the water and the resulting starch hydrogel. After this step, the starch hydrogel was kept in a laboratory at 20–22 °C for 24 h to achieve the retrogradation effect. Then, the obtained RSH of the required concentration was added to the clay and mixed according to the principle, specified in Table 2.2.

2.2.3. Preparation of clay mixture with biopolymer solutions

After the specific treatment of the biopolymers, the obtained water-polymer solutions of the required concentrations were added to the clay to achieve the optimal plasticity of the resulting mass. Plasticity is an important parameter while preparing a clay mixture. Excessively high or low plasticity can result in structural defects in the clay composite, such as cracks and irregularities. To ensure the same processing conditions in the case of plasticity, the amount of biopolymer solution should be strictly regulated. Therefore, the amount of biopolymer solution was chosen to obtain the same plasticity as all clay mixtures. The technological parameters of the resulting clay mixtures are presented in Table 2.3.

Table 2.3. Technological parameters of the studied clay mixtures

Mixture code	**Solution characteristics**			**Clay mixture characteristics**	
	Biopolymer	**Treatment**	**Concentration, %**	**Liquid amount, %**	**Mixture plasticity**
Control (C)	–	–	–	20.0	17.0–18.0
SC-2.5	Starch	Hot water treatment	2.5		
SC-5			5	22.5	
SC-7.5			7.5		
SC-10			10		
AC-2.5	Alginate	Cold water treatment	2.5	20.0	
AC-5			5	22.5	
AC-7.5			7.5		
AC-10			10	25.0	
CC-2.5	Chitosan	Acid solution treatment	2.5	20.0	
CC-5			5	22.5	
CC-7.5			7.5		
CC-10			10		
RSH-2.5 (3)	Starch	Retrogradation process (3 or 5 h)	2.5	20.0	
RSH-5 (3)			5	22.5	
RSH-7.5 (3)			7.5		
RSH-10 (3)			10		
RSH-2.5 (5)			2.5	20.0	
RSH-5 (5)			5	22.5	
RSH-7.5 (5)			7.5		
RSH-10 (5)			10		

It was also observed that a higher concentration of the biopolymer solution requires a more liquid amount to maintain the same plasticity of clay mixtures. As specified in sub-chapter 2.2.1., the main feature of such modification is the complete replacement of water with a water-polymer solution of a given concentration (2.5; 5; 7.5; 10%). The obtained clay mass was placed in a desiccator in humid conditions (relative humidity (RH) – of 70–75%) for 24 hours. After the clay was held in wet conditions, samples were formed for further testing. To determine physical and mechanical characteristics, five prism samples were formed with dimensions of 60×30×20 mm. For the hygroscopicity and durability tests of the obtained composites, five-cylinder samples 50 mm in diameter and 10 mm in height were formed. The samples of the given shapes were dried at a temperature of 20–22 °C for 7–10 days until their weight stabilization. After drying, the surface was evaluated for defects and cracks.

The clay composite with the highest concentration of alginate solution, 10%, faced some difficulties during manufacturing. After the drying, it was observed that approximately half of the AC-10 samples exhibited cracks on the surface. Therefore, the specimens with defects on the surface were not examined for mechanical and hygroscopic properties.

2.3. Research methodology

This sub-chapter explains the methodologies employed to investigate raw materials and clay composites.

2.3.1. Research of the raw materials

The chemical clay composition was determined using a wavelength dispersive X-ray fluorescence (WD-XRF) spectrometer Rigaku ZSX Primus IV. Cylindrical samples of 37 mm in diameter and 3 mm in height were prepared using a 200 kN capacity hydraulic press Herzog TP20. Measurements were taken at 36.6 °C under a vacuum. The scan was set to identify the elements greater than 0.01% by mass.

The mineralogical content of the clay in question was carried out using an X-ray diffractometer DRON-7 with the following set parameters: 30 kV voltage, 12 mA current, and 2θ diffraction angle ranging from 4° to 60° with increments of 0.02° measured every 2 s.

The granulometric composition of the clay was determined by the sieving method according to the ISO 3310-1:2016 standard. The sieving method involves systematically passing the raw clay through a series of mesh sieves with varying pore sizes, followed by weighing the clay residue obtained on each sieve.

The plasticity and the Attenberg limits of clay were established in accordance with the ISO 17892-12:2018 standard.

The biopolymer solutions were prepared using a magnetic stirrer under specific conditions, which were described in more detail in paragraph 2.3. The characteristics of the resulting biopolymer solutions were measured at an ambient temperature of 22 °C. Solution viscosity was measured using an SV-10 vibrating viscometer with two sensor plates at a constant frequency of 30 Hz. The pH of the obtained biopolymer solutions was determined by Oakton-1100 pH meter with ±0.01 accuracy.

Microstructure images of the studied materials were obtained with a scanning electron microscope (SEM) JEOL SM–7600F. Before structural analysis, the materials were coated with a gold layer under vacuum using a sputter coating machine QUORUM Q150R ES.

2.3.2. Research of the clay composites

The physical and mechanical properties were evaluated on prismatic clay samples (60×30×20 mm) after a drying period of 7–10 days at room conditions (20–22 °C with relative humidity of 45–50%).

Bulk density was determined following the LST EN 772-13:2003 standard, evaluating the mass-to-volume ratio of the sample in its equilibrium state (after achieving a constant weight, with mass changing not more than 0.01 g).

The linear shrinkage was measured in accordance with ASTM C326-09:2014 standard. The measurements involved comparing the length variations between the freshly formed and dried clay samples, after achieving a constant mass.

Mechanical properties, such as compressive strength, were measured on an H10KS Hounsfield testing machine, following the LST EN 826:2013 standard. Also, the DIN 18945:2013-08 standard, designed especially for earth bricks, was used to classify the obtained clay-based composites according to their compressive strength. The following classification was used in this research:

- Class 2 (low-load height construction (huts, sheds, etc.), or secondary structures), with compressive strength from 2.5 to 3.8 MPa;
- Class 3 (non-load bearing structure or high-rise walling structure), with compressive strength from 3.8 to 5 MPa;
- Class 4 (inner walls, low-rise walls, middle-rise buildings), with compressive strength from 5.0 to 6.3 MPa;
- Class 5 (load-bearing walls, inner walls), with compressive strength of more than 6.3 MPa.

The ultrasonic measurements were evaluated with a PUNDIT-7 device (electric transducers 54 kHz). Before testing, the opposite surfaces of the clay sample were treated with petroleum jelly. During the tests, the emitter and receiver were pressed as tightly as possible to the opposite surfaces of the clay sample. Each sample was tested at least three times to ensure stable and consistent results. Five cylindrical clay samples with a diameter of 50 mm and a height of 10 mm were tested. Ultrasound pulse velocity (UPV) was calculated according to the formula:

$$U = h/\tau, \tag{1}$$

where: h – sample thickness, m; τ – signal propagation time, s.

The hygroscopic properties of clay composites were measured in the climate chamber MEMMERT HPP110eco. The hygroscopicity testing of clay composites was carried out in accordance with ISO 24353:2008 and ISO 12571:2013 standards. The change in mass characterizing moisture uptake was recorded over a period of one hour using a laboratory balance (± 0.01 g). The testing program is presented in Table 2.4, specifying the steps performed.

Table 2.4. Moisture buffering capacity assessment methodology

Characteristics	**1st step**	**2nd step**	**3rd step**
Relative humidity, %	50	75	50
Temperature, °C	22		
Time, h	24	12	12
Surface area, mm^2	100		
Sample thickness, mm	10		
Process	Mass stabilisation	Adsorption	Desorption

The following classification was used to assess the moisture adsorption capacity of obtained clay composites, based on the DIN 18947:2013 standard, designed for earth plasters:

– WS 1 for earth plasters with adsorption degree ≥ 35 g/m^2 per 12h;
– WS 2 for earth plasters with adsorption degree ≥ 47.5 g/m^2 per 12h;
– WS 3 for earth plasters with adsorption degree ≥ 60 g/m^2 per 12h.

When observing the hygroscopic properties of a material, one of the fundamental characteristics is its sorption hysteresis (Fig. 2.7).

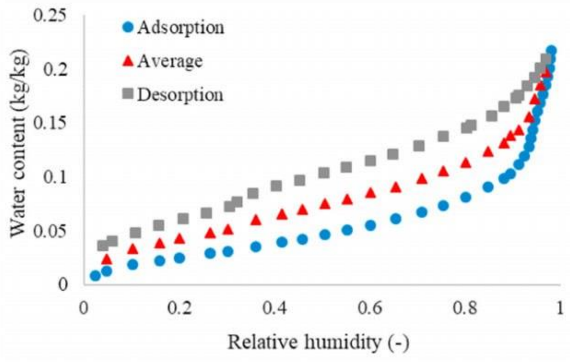
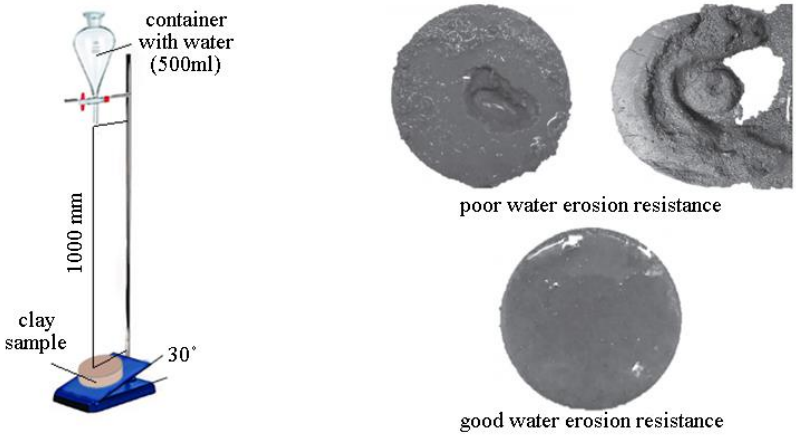


Fig. 2.7. Representation of sorption hysteresis effect, based on Latapie et al., 2023

The magnitude of the hysteresis effect is usually expressed as the difference between the degree of moisture adsorption and desorption, at a given relative humidity (Fig. 2.7). Sorption hysteresis can provide some insights into the internal structure of the materials with complex porous networks (Latapie et al., 2023). In the current research, the maximum sorption hysteresis rate was taken at relative humidity (RH) equal to 80% due to the complexity of adequately determining the desorption degree at 90%.

The durability of clay composite was defined as its resistance to water erosion, based on the Geelong method, specified in the UNE R41410:2008 and NZS 4298:1998 standards and the Australian Earth Building Handbook by Walker (2002). This method simulates the fall of raindrops (with a total water volume of 500 ml) from a height of 1 m onto a sample placed at an angle of 27–30° to the horizontal for 10 min (Fig. 2.8a). The newly formed defects on the surface of the clay sample, captured by the digital camera allow for the estimation of the erodibility of the material (Fig. 2.8b).



a) b)

Fig. 2.8. Water erosion tests based on the Geelong method: a) testing installation; b) examples of the clay's surface after water erosion tests by Aguilar et al., 2016

The water permeability of clay composites was determined by measuring the static contact angle of sessile water drop according to the ISO 9211-4:2022 standard. Static contact angle measurement was performed on a Theta Lite optical tensiometer with One Attention 1.0 software.

SEM characterisation of clay composites was performed with a microscope JEOL SM–7600F. 3D characterisation of the clay composite's structure and its particles and pore distribution was obtained using an Xradia 620 Versa X-ray microscope (from ZEISS). Samples were scanned using 60 kV voltage and 4.5 W power of X-ray source and LE5 filter. A flat panel detector was used, to convert transmitted X-rays into grey-value images for clay composite. Datasets with 3201 angular projections with 0.08 seconds timing per projection were used for a scan.

Distance from the source-detector was set to -17, and the sample-detector distance was 230 with an efficient 1:20 h scanning time, obtaining a resolution of 5.1 μm effective pixel size. The image analysis of the reconstructed data was carried out using the software Avizo (Thermo Fisher Scientific).

2.4. Conclusions of the Second Chapter

This chapter introduces the raw materials used in this research: mica clay and biopolymers (starch, alginate, and chitosan). Additionally, it describes the preparation technology of biopolymer solutions to modify the mica-clay composites, which are suitable for sustainable building material applications. The testing methodology for the comprehensive evaluation of the effect of biopolymers on unfired clay composites is also detailed in this chapter. The following conclusions can be drawn:

1. To address the research objectives, the experimental part was divided into stages: Stage 1 – Selection of biopolymer preparation technology (biopolymers gelation and starch retrogradation processes) based on its type and origin to modify the clay structure; Stage 2 – Assessment of the impact of biopolymers, considering the preparation technology, on the properties, structure and durability of clay-based composites for potential use as sustainable building materials;
2. The selected research methods enable the determination of the physical, mechanical, and hygroscopic properties of clay-based materials, examination of the microstructure of the resulting materials, and assessment of durability, particularly in the context of its water erosion.

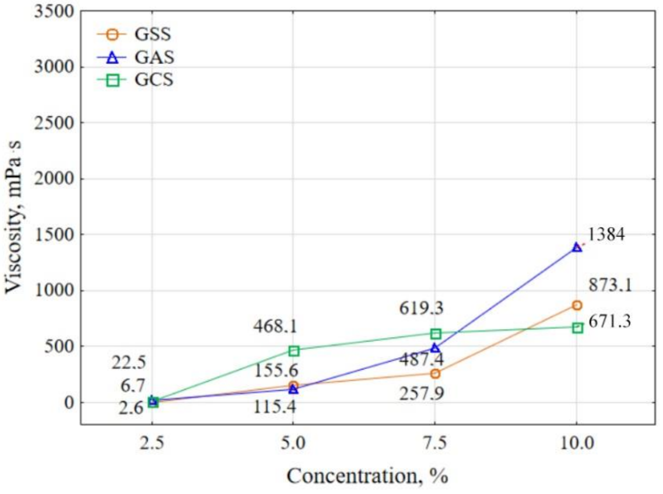
3

Research on the effect of biopolymers on clay composites

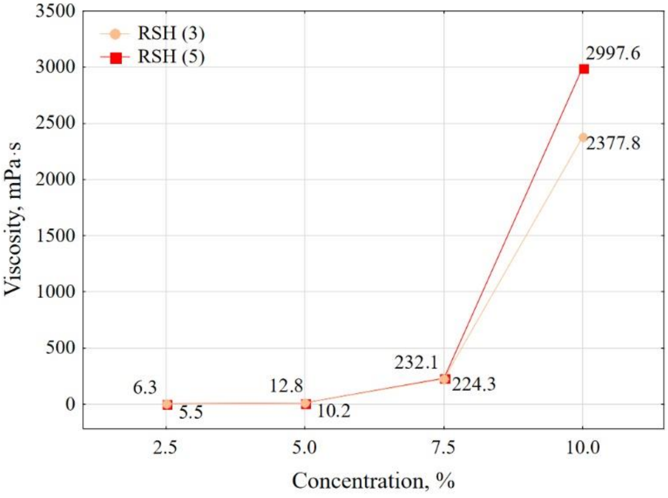
This chapter determines the effect of biopolymers (starch, alginate, and chitosan) on clay-based composites. The influence of biopolymer concentration on the physical, mechanical, and hygroscopic properties of clay composites has been investigated. The effect of the biopolymers on the structure and durability of clay composite has also been revealed. The main research results on the topic of this chapter were published in the three author's publications (Trambitski et al., 2022a; Trambitski et al., 2022b; Trambitski et al., 2023).

3.1. Research of the biopolymer solutions properties

The viscosity results of the different water-polymer solutions are presented in Figures 3.1 and 3.1a showcases the viscosity of starch, alginate, and chitosan solutions, and Figure 3.1b details the viscosity specifications of the retrograded starch hydrogel (3 or 5 hours). The viscosity of the starch and alginate solutions significantly increases after reaching 5% concentration of polysaccharide in water (Fig. 3.1a, b). The viscosity of the chitosan solution significantly increased after the application of 2.5% concentration. However, the viscosity of the water–chitosan solution at the maximum concentration was 671.3 mPa·s, which is lower than that of comparable starch solutions (873.1 mPa·s) and alginate solutions (1384.0 mPa·s). It is well-known that during the gelation process, the polysaccharide granules dissolve, increasing in volume and thereby significantly increasing the viscosity of the water solution (Rinaudo, 2006). The starch retrogradation process significantly increased the viscosity of polymer solutions RSH(3) and RSH(5) to 2377.8 mPa·s and 2997.6 mPa·s, respectively (Fig. 3.1b).



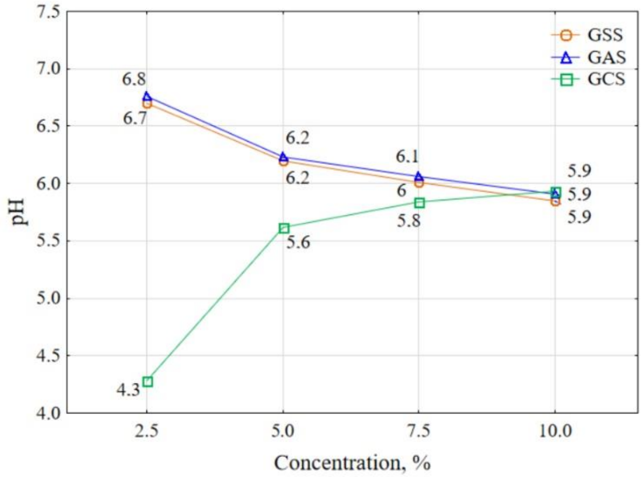
a)



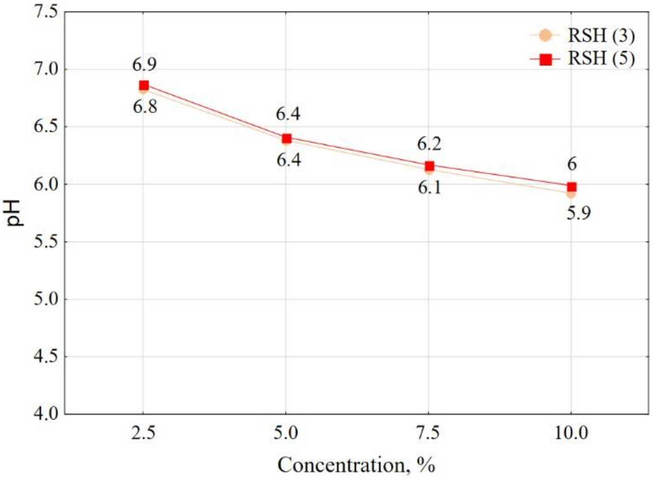
b)

Fig. 3.1. Viscosity of different biopolymer solutions:
a) GSS, GAS, GCS; b) RSH

The pH results of different water-polymer solutions are presented in Figure 3.2. The initial pH of the water used to dissolve starch and alginate polysaccharides was 7.0. Different concentrations of polymer solutions also affect the change in their pH. With an increase in the concentration of starch or alginate in the polymer solution, the pH decreases uniformly from 6.8 to 5.9 (Fig. 3.2a). Despite the additional modification, the pH of the retrograded starch hydrogel (Fig. 3.2b) remained identical to that of gelatinised starch.



a)



b)

Fig. 3.2. pH of the different biopolymer solutions:
a) GSS, GAS, GCS; b) RSH

With a higher concentration of chitosan in the solution, its pH increased from 4.2 to 5.9. This phenomenon is explained by the 1M HCL solution (with a pH of 3.1) required to dissolve chitosan. However, when the maximum concentration of the chitosan solution (CC-10) was achieved, its pH levelled off with other polymers (SC-10, AC-10) and became around 5.9.

3.2. Research of physical and mechanical properties of clay composite

This sub-chapter provides information about the effects of biopolymers on the physical and mechanical properties (including density, shrinkage, compressive strength, and ultrasonic characterization) of clay composite materials.

3.2.1. Effect of biopolymers on bulk density

The effect of the introduction of gelled solutions of biopolymers (polysaccharides) on the bulk density of the clay composite is shown in Figure 3.3.

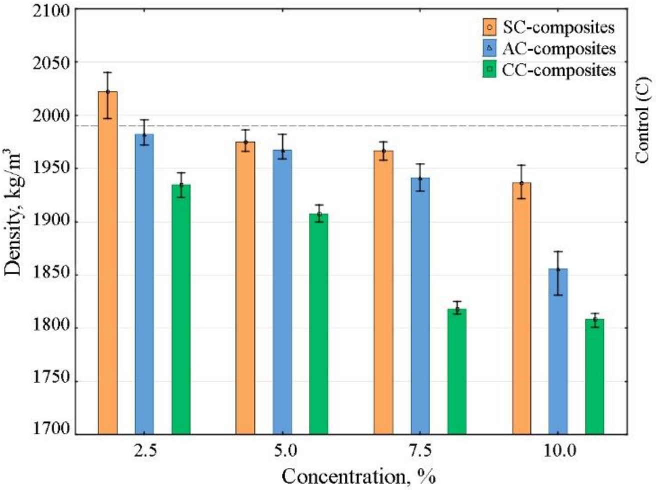


Fig. 3.3. Bulk density of the clay composites, modified with GSS, GAS, and GCS biopolymers

The bulk density of the control clay composite without biopolymer modification is 1990 kg/m^3. It can be noted that with an increase in the concentration of the active matter in the gel (starch, alginate, and chitosan), there is a trend toward a decrease in the bulk density of the final clay composite.

The introduction of a 2.5% starch solution into the clay mixture increases the density of the clay composite to 2030 kg/m^3. However, as the concentration of the starch solution increases from 5% to 10%, the bulk density of the remaining clay composites (SC-5, SC-7.5, and SC-10) decreases from 1970 kg/m^3 to 1940 kg/m^3, respectively. The addition of an alginate solution to the clay composite in the 2.5–10% concentration range shows a drop in its density from 1970 kg/m^3 to 1855 kg/m^3. Therefore, the bulk density of the clay composites: AC-2.5, AC-5, AC-7.5 and AC-10 are 1–6.7% lower than the control clay composite. The most characteristic drop in bulk density is demonstrated by a clay composite modified with a different concentration of chitosan solution. Varying the concentrations of the chitosan solution from 2.5 to 10%, the bulk density of the clay composites decreases from 1940 kg/m^3 to 1810 kg/m^3, which is 2.5–9.0 % lower than the control clay composite.

However, during the modification of the clay composite with retrograded starch hydrogel, there is a trend towards an increase in the sample's density. As shown in Figure 3.4, the bulk density increases with increasing amount of RSH. By enhancing the amount of RSH (heating time of 3 h), the resultant clay materials become denser. This clay material's bulk density ranges from 2010 kg/m^3 to 2040 kg/m^3. Also, when the RSH heating time is 5 h, the clay materials bulk density varies from 1990 kg/m^3 to 2015 kg/m^3. Clay materials with 2.5%, 5.0%, 7.5% and 10 % RSH (heating time 3h) exhibited about 1.0%, 1.4%, 2.0%, and 2.5% higher bulk density than control clay. On the other hand, clay materials with 2.5, 5.0, 7.5 and 10 % RSH (heating time 5 h) exhibited about 0%, 0.5%, 1.25%, and 1.4% higher bulk density, than the control sample.

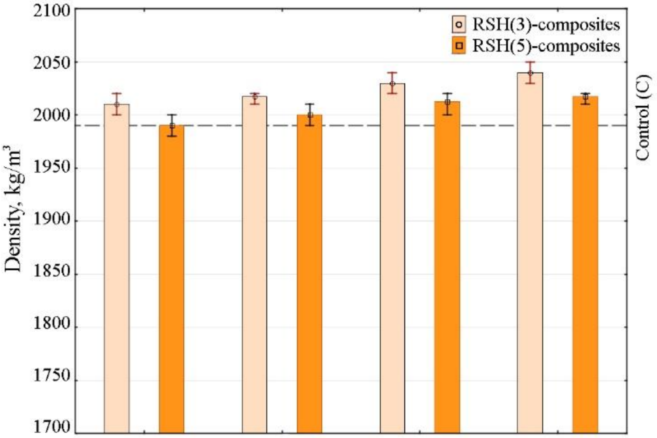


Fig. 3.4. Bulk density of the clay composites, modified with RSH biopolymers

Summarising the above, the introduction of gelling biopolymers into the clay structure contributes to reducing the density of the clay composite according to the following principle: the higher the concentration of natural modification in solution, the lower the bulk density of the clay composite. This statement is true for most natural additives: natural fibres (Giroudon et al., 2019; Binici et al., 2005; Salih et al., 2020) or even biopolymers (Losini et al., 2021). In similar research, Galán-Marín et al. (2010) reported that adding 19.25% alginate in clay materials decreases the density but not significantly (about 1.1%), always between 1820 kg/m^3 and 1840 kg/m^3. Thus, with the replacement of some quantity of soil by less dense additives, the density of a clay composite is predictably decreased. However, there are some exceptions, e.g., with the introduction of 2.5–10% retrograded starch hydrogel, the density of the clay composite increased (from 1990 kg/m^3 to 2040 kg/m^3). This phenomenon is explained as a result of the "coarseness" of the starch structure after the retrogradation process and the ratio of free water in the hydrogel–clay system. The retrogradation process is associated with increasing starch grain hardness, cohesiveness and adhesiveness due to the changing of its molecular structure (Anbarani et al., 2021; Kumar et al., 2018). The adhesion between clay particles and RSH also improves. RSH tends to fill some clay pores that are formed during the drying process. As a result, the density of the RSH 2.5 – RSH 10 clay materials increases. A similar effect is demonstrated in the work by Dove et al. (2016) when with the introduction of an alginate biopolymer, the density of clay composite is also increased up to 18% (from 1810 kg/m^3 to 2140 kg/m^3). The increase in the density of clay composite can also be a consequence of the compaction process, which is highly dependent on the Optimum Water Content (Ayeldeen et al., 2016; Dehghan et al., 2019; Turco et al., 2020). Also, by increasing the concentration of the polymer, the amount of free water in the solution is reduced. Less free water reduces the plasticity of the clay composite during the sample formation step. Thus, to achieve optimal plasticity, the amount of liquid (polymer solution) in the clay mixtures should be varied, which is confirmed by the clay mixture technological parameters presented in Table 2.3.

3.2.2. Effect of biopolymers on shrinkage

The shrinkage behaviour of clay composites modified with gelled biopolymer solutions is shown in Figure 3.5. The shrinkage of the control clay composite is 6.2%. The introduction of gelatinised starch solution of different concentrations ranging from 2.5 to 10%, contributes to a decrease in the shrinkage of the clay composite from 5.4% to 4.6% (SC-2.5 and SC-10). Using alginate contributes to the highest shrinkage of the composite of 6.1% at the minimum polymer concentration in solution (AC-2.5 composite) and the lowest shrinkage of 4.2% at the highest concentration (AC-10 composite). On the contrary, the introduction of chitosan exhibits an inverse correlation. Unlike the others, with an increase in the concentration of chitosan in the gelling solution from 2.5% to 7.5%, the shrinkage of the clay composite gradually increases from 5.1 to 5.6%, respectively.

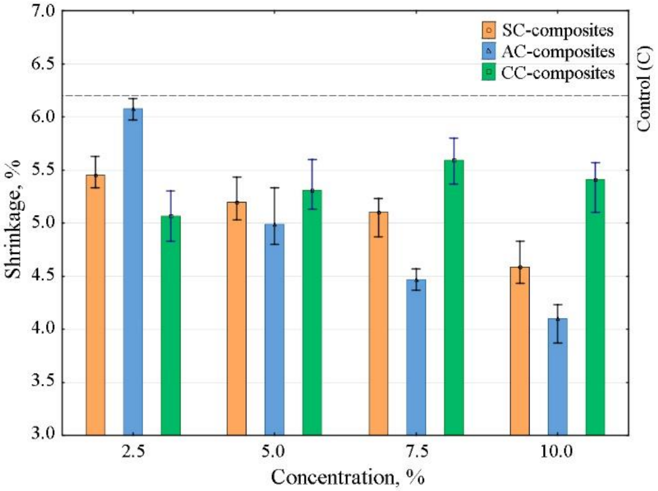


Fig. 3.5. Shrinkage of the clay composites, modified with GSS, GAS, and GCS biopolymers

Figure 3.6 presents the shrinkage results of clay composites modified with RSH. The shrinkage of the composites decreases with increasing RSH amounts.

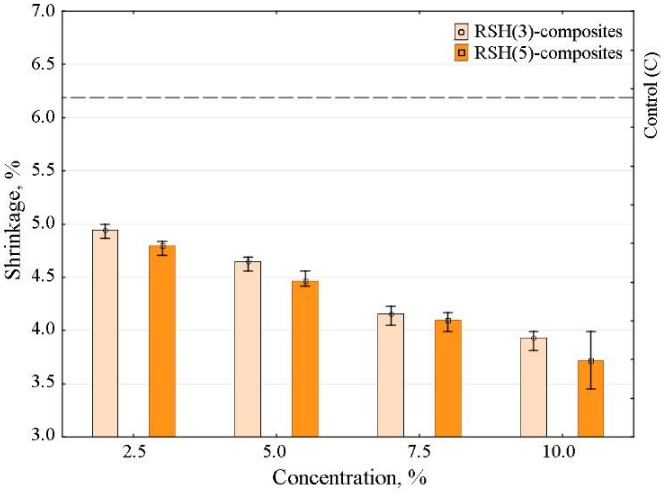


Fig. 3.6. Shrinkage of the clay composites, modified with RSH biopolymers

Based on Figure 3.6, the heating time of RSH has a positive influence on the shrinkage reduction of the clay specimens. Among others, the specimen with a 10% concentration of RSH (heating treatment for 3 h to 5 h) has the smallest shrinkage value of 3.7%.

The phenomenon of linear shrinkage is inevitable in any clay-based materials. Shrinkage occurs during the drying of the clay as a result of evaporation and redistribution of moisture in its internal space. During redistribution processes, free water within the clay composite can provoke additional internal stresses in the structure, which can lead to some defects, such as cracks (Chertkov, 2003; Tang et al., 2011).

To prevent excess shrinkage and cracks appearing in the non-fired clay composites, researchers often use various natural fibres (Salih et al., 2020). The introduction of fibres into the structure of the clay composite creates additional friction between the components, forming a “clay-fibre” system, which prevents abundant shrinkage. The use of natural polymers may also reduce the shrinkage of the clay-based composite due to the formation of additional cohesion between clay aggregates and hydrogen bonds inside the structure (Ayeldeen et al., 2016a; Soldo et al., 2020). The incorporation of 0.1% dried alginate into the clay structure reduced the shrinkage of the composite from 9% to 5% (Dove, 2014). Gelled polymers can “cover” clay particles, preventing the propagation of excessive shrinkage and affecting the bulk density of clay materials (Chang et al., 2015).

The use of biopolymers can also influence the amount of free water distributed within the clay composite. An increase in the concentration of the biopolymer in the aqueous solution significantly increases its viscosity, as was demonstrated in Figures 3.1a and 3.1b. The higher the concentration of the polymer in a water solution, the less free water in it (Rinaudo, 2006). The lack of free water in the “clay–polymer solution” system contributes to a lower plasticity of the clay mixture, which can also reduce the shrinkage of the dried clay composite. The biopolymer admixtures of gluten and ovalbumin in the research of Alhaik et al. (2017) increased the need for water in earth material. By adding excess water to the earth modified with biopolymers, researchers increased the shrinkage of the clay composite.

3.2.3. Effect of biopolymers on compressive strength

The results for the compressive strength of clay composites modified with biopolymer solutions of starch, alginate and chitosan are shown in Figure 3.7. The compressive strength of the control clay composite is 6.6 MPa. Clay composites modified with starch (SC-marked) and alginate (AC-marked) solutions show a trend toward increasing compressive strength. However, the addition of chitosan to the clay composites (CC-marked) shows a reverse trend to a decrease in the compressive strength of clay composites.

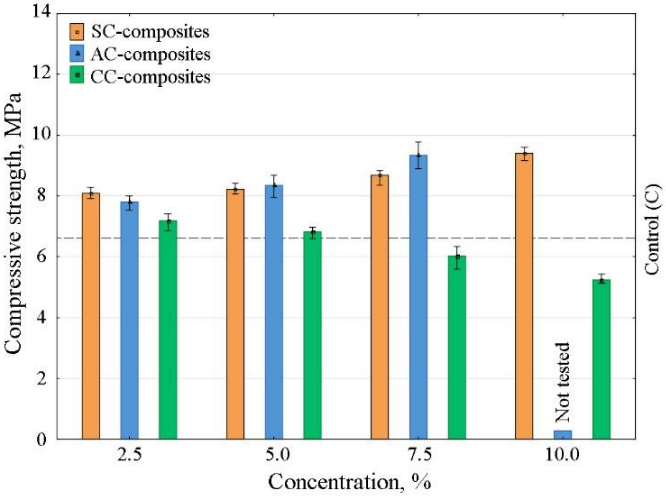


Fig. 3.7. Compressive strength of the clay composites, modified with GSS, GAS, and GCS biopolymers

With an increase in starch concentration from 2.5 to 10%, the compressive strength of clay composites increases from 8.1 MPa to 9.4 MPa. Thus, the compressive strength of starch-modified clay composites is 21–42% higher compared to the control clay composite. The application of starch in the research of Alhaik et al. (2017), also shows the strength improvement of clay composite. Adding different starches increases the clay composite's strength from 1.0 MPa to 2.0 MPa.

An increase in compressive strength from 7.8 MPa to 9.3 MPa is also demonstrated by clay composites modified with alginate solution of 2.5%, 5%, and 7.5% concentrations. The compressive strength of the AC-2.5, AC-5, and AC-7.5 composites is 18–40% higher than the control one. The mechanical strength of the AC-10 samples cannot be properly determined due to the possible defects (cracks) inside, which can be formed during the drying process. Some difficulties at the moulding stage and the appearance of cracks in AC-10 composites after drying have been mentioned in sub-chapter 2.1.3. Similar studies of the effect of alginate admixture on the soil by Dove (2014) show an increase in the strength of the sample from 0.85 to 1.64 MPa (about 50%) even with the small percentage of biopolymer ~ 0.1%. However, an increase in the amount of alginate from 0.1 to 0.5% does not lead to a significant increase in the strength of the composite (Dove et al., 2016).

The use of a chitosan solution reduces the compressive strength from 7.2 MPa to 5.3 MPa (CC-2.5 and CC-10 composites). These results may indicate that the chitosan solution does not interact well with the clay particles. Chitosan additive for clay-based materials is also mentioned in the works by Aguilar et al.

(2016) and Hataf et al. (2018). In the research of Aguilar et al. (2016), the application of a 3% chitosan solution led to an increase in the compressive strength of the clay composite by 85% an average meaning. The application of small percentages (0.02–0.16%) of chitosan in the research by Hataf et al. (2018) also led to an improvement in the compressive strength of the soil at the early stages (first seven days). However, the current research showed that the chitosan solution does not have a positive effect on the compressive strength of the clay composite. This fact may be attributed to the weak interaction between the biopolymer and clay and the different types and characteristics of the clay and polymer used.

The strength improvement of the clay composite, modified with starch and alginate water solutions can be associated with a more stable and bound structure inside the composite. Researchers (Chang et al., 2018; Fatehi et al., 2021; Hataf et al., 2017; Theng et al., 2012) explain a similar effect by the appearance of additional van der Waals forces and the formational of new hydrogen bonds inside the clay matrix.

Figure 3.8 shows the compressive strength of clay composites, modified with retrograded starch hydrogel (RSH). With the increase of RSH concentration, the compressive strength of the clay materials also increases. The compressive strength of all clay materials varies from 6.8 MPa to 11.8 MPa. The compressive strength of the clay materials is strongly depending on RSH concentration and RSH heating time. The influence of retrograded starch polymer on the compressive strength is very significant since the compressive strength of clay materials increased by 40–74%.

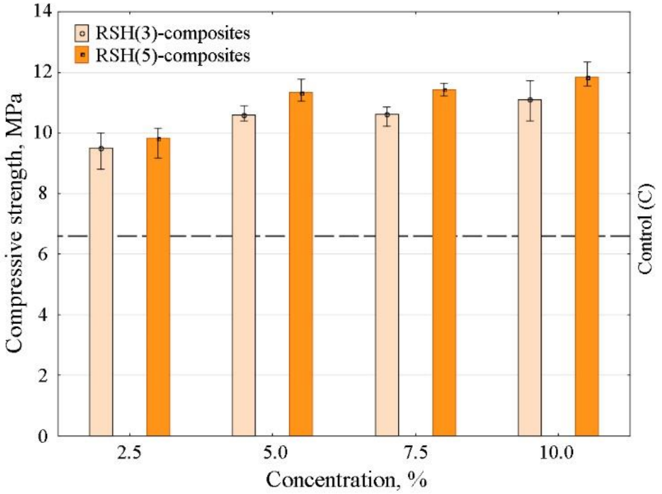


Fig. 3.8. Compressive strength of the clay composites, modified with RSH biopolymers

Longer heating of RSH contributes to better strength characteristics of the clay composite. Clay composites (RSH-2.5 to RSH-10) after five hours of treatment exhibited a compressive strength increase of approx. 1 MPa to 1.5 MPa, compared with the clay composites with a retrograded starch hydrogel of three hours of treatment. Longer heating contributes to a more intensive dissolution of starch granules in the hydrogel and, thereby, a more effective retrogradation process. The obtained effect may be caused by the formation of new hydrogen bonds in the clay/RSH structure, the formation of the semi-crystalline structure of starch during retrogradation (Soni et al., 2020; Lian et al., 2014; Zhang et al., 2007; Buleon et al., 1998; Cornejo-Ramirez et al., 2018; Wang et al., 2015).

3.2.4. Effect of biopolymers on ultrasonic velocity results

The results of ultrasonic testing of clay composites modified with aqueous solutions of starch, alginate, and chitosan are presented in Figure 3.9. The control clay sample demonstrated a result of 1265 m/s.

The use of gelatinised starch contributed to an increase in the ultrasonic velocity values for SC-composites, from 1384 to 1471 m/s. Significant enhancement of the ultrasonic velocity was demonstrated for clay composites modified with alginate. Increasing the biopolymer concentration from 2.5% to 7.5% led to an increase in the ultrasonic velocity from 1603 to 1782 m/s. However, with the increase in chitosan concentration, the ultrasonic velocity decreased from 1474 to 1359 m/s for SC-composites.

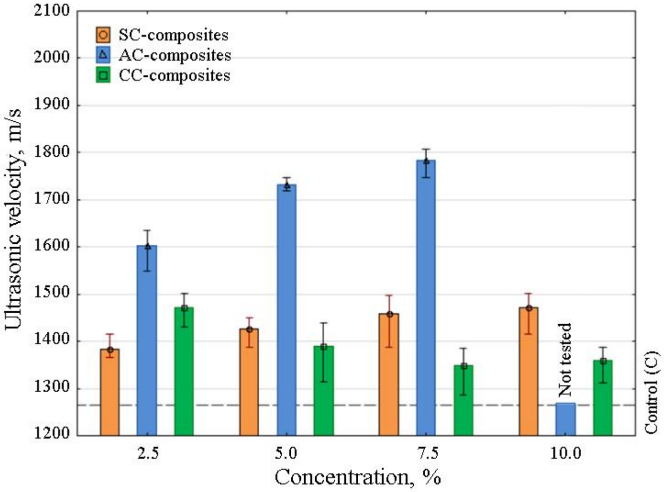


Fig. 3.9. Ultrasonic velocity of the clay composites, modified with GSS, GAS, and GCS biopolymers

Ultrasonic velocity results of clay materials are given in Figure 3.10. The results of clay composites modified with RSH vary in the range of between 1370 m/s and 1460 m/s. The obtained results for clay, modified with RSH are somewhat similar to the values of SC composites.

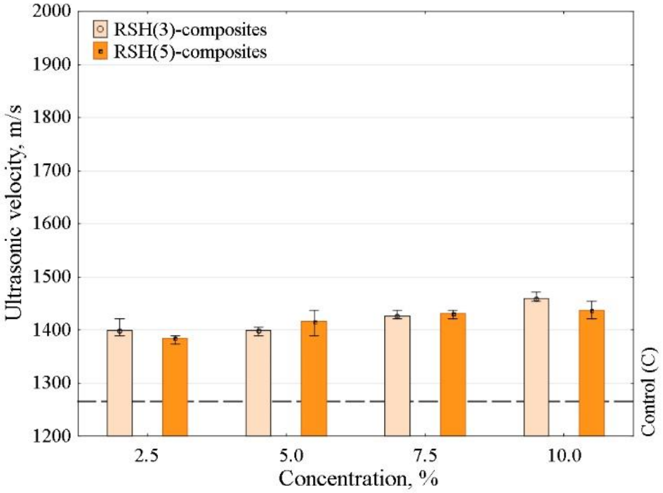


Fig. 3.10 Ultrasonic velocity of the clay composites, modified with RSH biopolymers

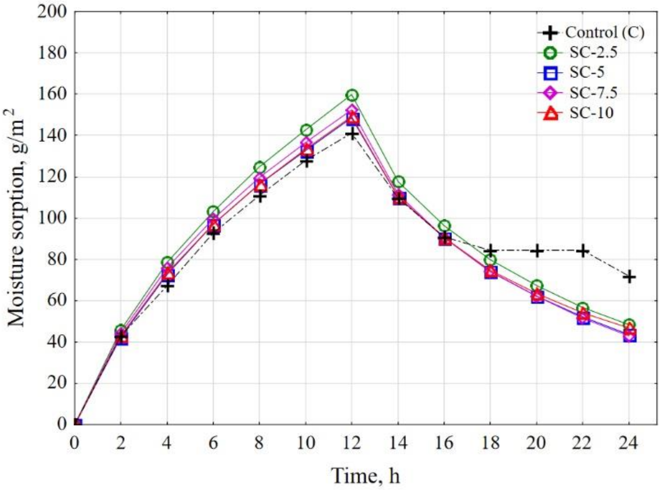
The reason behind the increasing ultrasonic velocity values of the clay samples can be associated with the porosity and structure integrity of clay composites modified with different biopolymers. The biopolymer solutions, while distributed within the structure of the clay composite, can partially fill its internal defects and pores, thereby making the structure more homogeneous. The increase of the ultrasonic velocity was also demonstrated by the research of Galan-Marin et al. (2010), where the addition of alginate to clay materials increased its ultrasonic velocity results by 38%.

3.3. Research of hygroscopic properties of clay composite

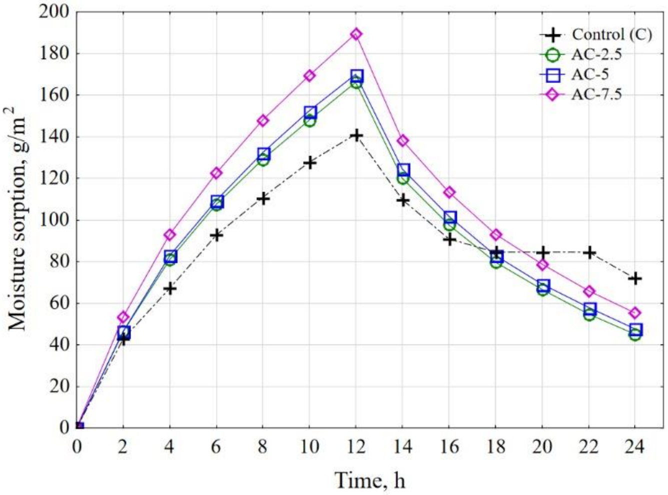
This sub-chapter provides information about the effect of biopolymers on the hygroscopic properties (including moisture buffering capacity and sorption hysteresis) of clay composite materials.

3.3.1. Moisture buffering capacity

The moisture buffering capacity was expressed in sorption isotherms, presented in Figures 3.11 and 3.12. The moisture capacity indicates the difference in equilibrium moisture content (EMC) between two chosen RH levels (50–75%) in the hygroscopic domain.

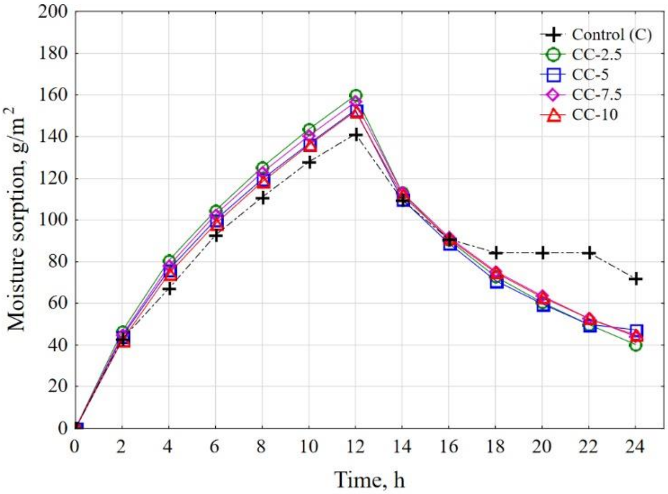


a)



b)

Fig. 3.11. To be continued

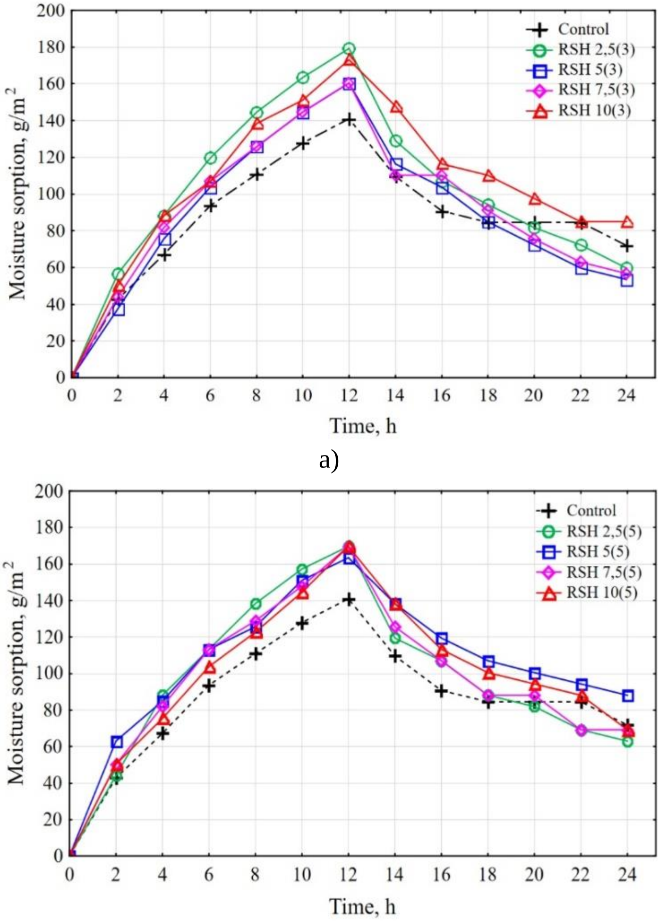


c)

Fig. 3.11. Moisture buffering capacity of the clay composites:
a) SC composites; b) AC composites; c) CC composites

Figures 3.11a and 3.11c show the sorption curves of clay composites modified with starch and chitosan solutions of a given concentration (2.5%, 5%, 7.5%, and 10%), respectively. The adsorption behaviour of these composites is almost identical. Maximum adsorption – 159.8 g/m^2, is characteristic of the SC-2.5 and CC-2.5 composites modified with the minimum concentration of the polymer solution. The maximum concentration of 10% corresponds to some lower sorption but still exceeds the value of the control sample (the control sample adsorption is 141.1 g/m^2). Furthermore, the clay composites modified with starch and chitosan polymer solutions exhibit a slight reduction in moisture adsorption as the solution concentration increases from 2.5% to 10%. The decrease in moisture adsorption, from 159.8 g/m^2 to 148.6 g/m^2 for SC-2.5 and SC-10 composites respectively, can be attributed to the restructuring of starch caused by the syneresis effect (Wang et al., 2015). This phenomenon occurs during the cooling of the starch solution, resulting in the hydrophobic properties of the biopolymer that can impact the moisture adsorption of the clay composite modified with such a gel (Cornejo-Ramírez et al., 2018). The moisture adsorption for chitosan-modified composites SC-2.5 to SC-10 ranges from 159.8 g/m^2 to 152.2 g/m^2, indicating a minimal influence of chitosan concentration (2.5%, 5%, 7.5%, 10%) in the polymer solution on the hygroscopicity of the clay composite. Modification with alginate exhibits an inverse relationship (Fig. 3.11b). The maximum adsorption equal to 189.4 g/m^2 corresponds to the maximum concentration of the polymer additive used, i.e., – 7.5%. The AC-2.5 and AC-5 samples show a sorption value of 166.1 g/m^2 and 169.9 g/m^2, respectively, which is superior to samples with the addition of starch and chitosan. This observation suggests increased hydrophilicity of the surface in alginate-modified clay composites. The results of AC-10 are not presented in this figure because it is impossible to correctly determine its surface sorption due to internal and external cracks formed during the drying process.

The moisture sorption of clay composites, modified with retrograded starch hydrogel (RSH), varied between 141.1 and 180 g/m^2 (Fig. 3.12a, b). The highest sorption increase of the RSH 2.5(3) sample was up to 180 g/m^2, compared with the control sample – 141.1 g/m^2. The value of the increase was 27%. The moisture sorption of the RSH 10(3) sample was 173 g/m^2 (increased by 23%), and for RSH 5(3) and RSH 7.5(3), it was 160.4 g/m^2 (increased by 14%) (Fig. 3.12a).



a)

b)

Fig. 3.12. Moisture buffering capacity of the clay composites:
a) RSH(3) composites; b) RSH(5) composites

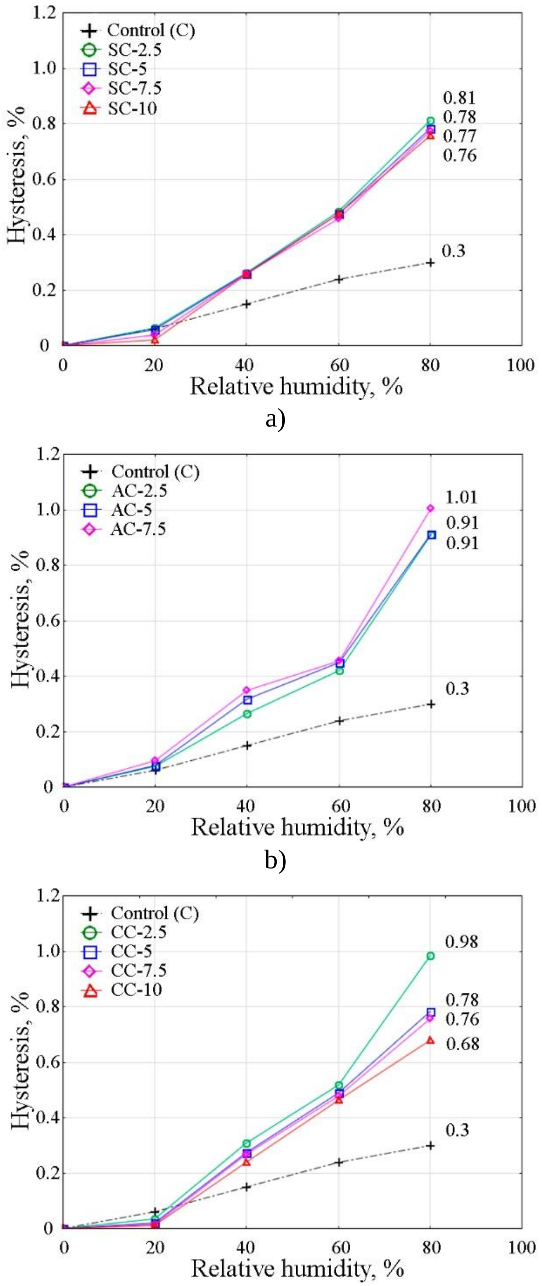
Figure 3.12b shows that after 5-hour heat treatment of clay composites with RSH, the increase in moisture adsorption of the RSH 5(5) sample was up to 163.6 g/m^2 (increased by 16%) and for RSH 2.5(5), RSH 7.5(5), and RSH 10(5), it was up to about 170 g/m^2 (increased by 20%). Based on Figure 3.12a, the clay composites with RSH after 3-hour heat treatment are characterised by a wider scatter of clay samples sorption isotherms (values of maximum moisture uptake after 12 h varied between 141.1 and 180 g/m^2). However, clay composites with RSH of 5-hour thermal treatment demonstrate an equalising moisture uptake value regardless of the RSH concentration used (maximal moisture uptake varied from 163.6 to 170 g/m^2). Finally, all clay composites with RSH showed better hygroscopic properties than the control sample. It can be explained by RSH admixture that tends to partially fill the pores and capillaries of clay composites, therefore making them smaller in size. The smaller pores, in contrast to large ones, promote greater sorption and hygroscopicity due to the ink-bottle effect (Arrigoni et al., 2017; Pinson et al., 2018; McGregor et al., 2016).

The moisture adsorption test is often used to characterise different types of plasters (Ashour et al., 2011; Jiang et al., 2020; Faria et al., 2016). According to the DIN 18947:2013 standard, designed especially for earth plasters, all studied clay composites comply with the WC-3 adsorption class, with an adsorption capacity of more than 60 g/m^2 per 12 h. The standardisation presented in the Nordtest project (Rode & Grau, 2008) characterises the adsorption capacity of presented clay composites as “excellent” with an adsorption rate of more than 50 g/m^2 per 8 h. Consequently, all the studied clays have a great potential for indoor use.

Researchers (McGregor et al., 2014; 2016; Cagnon et al., 2014) postulate that adding organic matter to the various plaster types tends to increase its adsorption capacity. However, the incorporation of natural polymers sometimes leads to opposite results. Ouedraogo et al. (2021) reported that the addition of 2% and 4% ovalbumin to the soil material decreased the adsorption capacity of the composite at 1.2 g/m^2. This effect is explained by the surface-active properties of the ovalbumin biopolymer, i.e., the formation of a hydrophobic film on the surface of soil aggregates, which prevents the penetration of moisture into the material.

3.3.2. Sorption hysteresis

When assessing the hygroscopicity of a material, special attention can be paid to the difference between its adsorption and desorption isotherms, also called hysteresis. Figures 3.13a–c show the hysteresis rate for clay composites modified with gelled biopolymer solutions of starch, alginate, and chitosan. The maximum hysteresis rate for the control sample is 0.30%.



a)

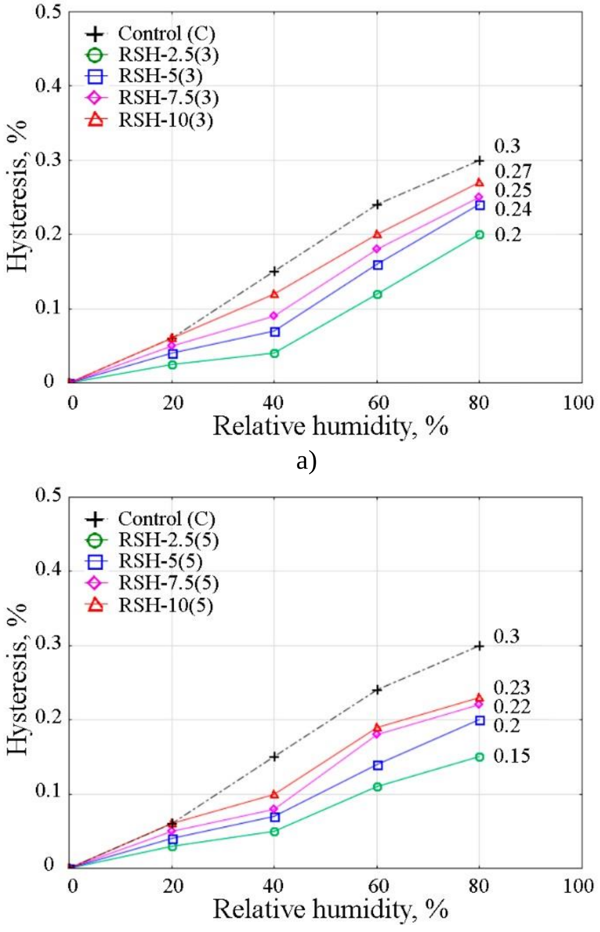
b)

c)

Fig. 3.13. Hysteresis of the clay composites:
a) SC composites; b) AC composites; c) CC composites

The hysteresis rate of SC composites varied from 0.76% to 0.81% at relative humidity (RH) equal to 80%. The highest hysteresis value was demonstrated by AC composites in the range of 0.91% to 1.01%, which is also correlated with the highest moisture absorption degree, presented above in Figure 3.11b. Hysteresis of CC composites varied from 0.68% to 0.98%.

Figure 3.14 represents the hysteresis value for clay composites modified with retrograded starch hydrogel. Clay composites modified with RSH tend to increase in hysteresis with increasing RSH concentration. The maximum hysteresis value for all modified samples varies from 0.15% to 0.27%, which does not exceed the value for the control clay sample.



a)

b)

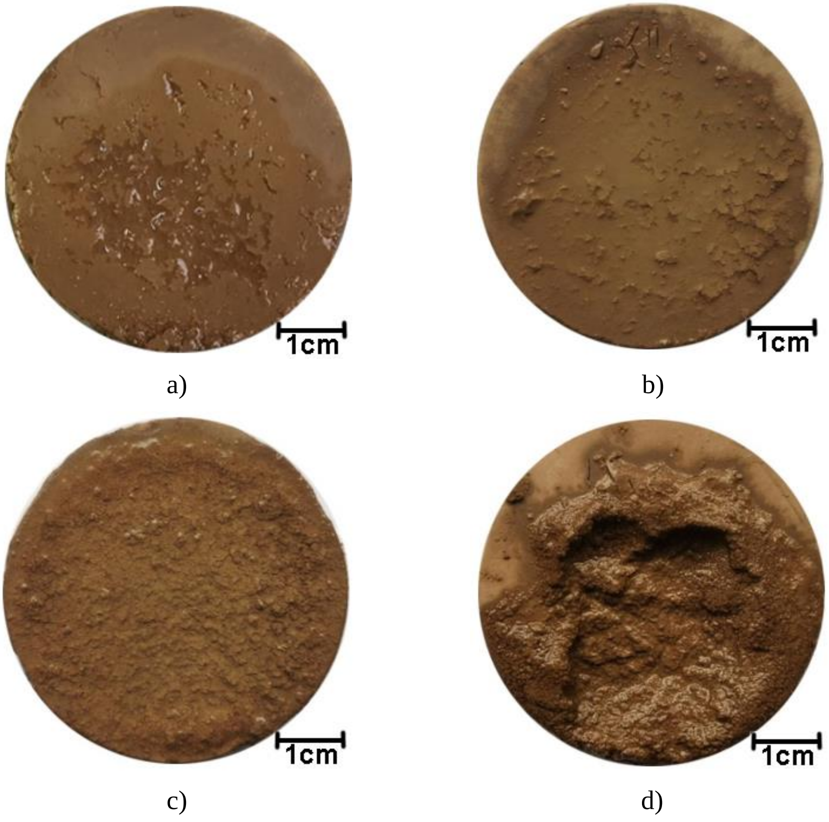
Fig. 3.14. Hysteresis of the clay composites:
a) RSH(3) composites; b) RSH(5) composites

A strong relation between density (Figs. 3.3 and 3.4) and hysteresis results of clay composite can also be noted. With increasing the concentration of biopolymer solutions of starch, alginate, and chitosan from 2.5% to 10%, the densities of such composites decreased from 1990 kg/m^3 to 1940 kg/m^3 for SC composites; to 1855 kg/m^3 for AC composites; to 1810 kg/m^3 for CC composites, comparing to the control clay composite. However, the maximum hysteresis rate was increased: from 0.3% to 0.78% for SC composites, to 1.01% for AC composites, and 0.98% for CC composites. On the contrary, the application of retrograded starch hydrogel led to the opposite effect: by increasing the clay composite's density from 1990 kg/m^3 to 2040 kg/m^3, the hysteresis rate drops from 0.3% to 0.15%, compared to the control clay composite. Thus, it can be assumed, that the higher the density of the clay composite, the lower the hysteresis value. McGregor et al. (2014; 2016) suggest that the phenomenon of hysteresis is also associated with the structure of the materials under research. The higher this parameter, the greater the multi-scale porosity of the sample and its hygroscopic properties. Cagnon et al. (2014) proposed the evaluation of the hygroscopic properties of various soil types without some additives or treatment. The maximum hysteresis value was 0.7% at 80% of RH. This value corresponded to a soil of a sandier composition with a bulk density of 2060 kg/m^3. The minimum hysteresis value at the same relative humidity was 0.45% for silty earth with a lower density of 2030 kg/m^3.

3.4. Research of durability (water erosion resistance) of clay composite

Figs. 3.15a–d demonstrate the erosion results after the raindrop test for clay composites with polymer solutions of starch, alginate, and chitosan. The water erosion degree is determined by visual assessment of the sample surfaces. Substantial defects are found on the surface of the control sample after conducting the test. However, despite the flaking of clay particles on the surface, the structure of the control sample remains relatively strong (Fig. 3.15a). The progressive development of erosive defects is visible in the area of water drop impact.

Moreover, Figures 3.15a–d demonstrate the different nature of the composite surface erosion, depending on the biopolymer. For example, in the control sample, the depth of the defects does not exceed 0.5 mm. However, the extensively affected surface area can be noted (about 35%). For SC-2.5 composite, erosion defects occur initially through the delamination of clay flakes. Those defects are not deep (less than 0.1 mm) and are evenly distributed on the entire surface. Sample AC-2.5 is characterised by severe surface erosion with extensive flaking of the sample surface (Fig. 3.15c). This effect may be associated with an increase in the hydrophilicity of the alginate-containing composite surface, which is discussed in sub-chapter 3.3.1. During testing, water droplets are more actively absorbed and moisture spreads faster over the surface than in the samples with the addition of starch, chitosan, or even in the control clay sample. The lowest erosive resistance is demonstrated by the CC-2.5 composite (Fig. 3.15d). On a strongly erosive surface, a pit is formed with a depth of 0.5–2.5 mm (the pit occupies 40% of the sample area), which is most consistent with the description in the NZS 4298:1998 standard characterising the formation of a “deep pit”.



a) b)

c) d)

Fig. 3.15. The surface of the clay composite after the water erosion test:
a) control clay composite; b) SC-2.5 composite;
c) AC-2.5 composite; d) CC-2.5 composite

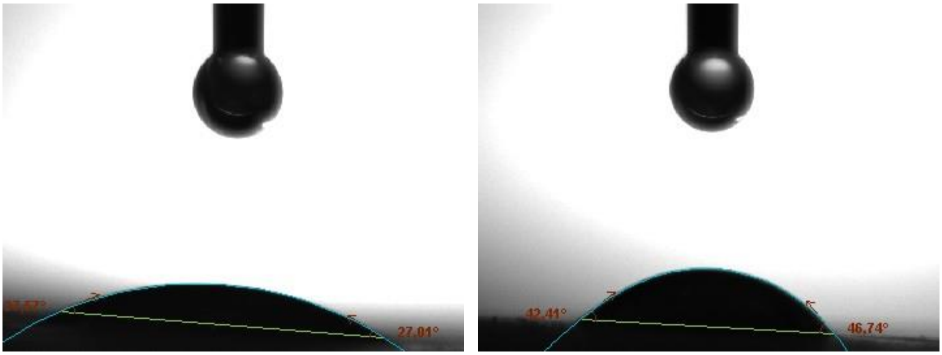
Figure 3.16 demonstrates the results of water erosion for RSH-2.5(3) and RSH-2.5(5) composites. Inspection of the clay composite (Fig. 3.16a) also indicates that the clay composites with even the lowest RSH concentration showed better water erosion results compared to the control clay sample (Fig. 3.16a). Both modified samples showed almost no damage after 10 min of testing. The other clay composites modified with various RSH concentrations (5%, 7.5% and 10%) and different heat treatment times (3 or 5 hours) also showed the enhancement of water erosion resistance compared to the control clay sample. The defects that appeared on their surface were the same or even absent compared to the surface of the RSH 2.5 (3 or 5 hours) samples (Fig. 3.16a, b).


a) b)

Fig. 3.16. The surface of the clay composite after the water erosion test:
a) RSH-2.5(3) composite; b) RSH-2.5(5) composite

The effect of RSH on the erosive resistance of clay composite can be associated with the syneresis effect. In the process of retrogradation, the starch hydrogel restructures, i.e., becomes “coarser”, contributing to the hydrophobicity of the newly obtained structure (Wang et al., 2015; Cornejo-Ramirez et al., 2018). The hydrophobic RSH, covering the surface of clay particles and filling the pores, prevents the penetration of water into its structure. The high durability of the clay specimens modified with starch (in gelled and retrograded forms) can also be attributed to the formation of an effective bonding medium within the clay composite structure, promoting the cohesion of clay particles and preventing active destruction caused by water erosion.

The water permeability of the control and RSH-2.5(3) was determined by measuring the static contact angle of the sessile water drop (Fig. 3.17). The shape of the water droplet on the surface of the clay composite can indicate the composite’s ability to absorb water (Nakamatsu et al., 2017). The control clay composite showed a contact angle of approx. 27° (Fig. 3.17a). The addition of 2.5% retrograded starch hydrogel increased the contact angle to 42–46° (Fig. 3.17b), indicating a higher hydrophobicity of the clay composite compared to the control sample. This fact correlates well with the results of water erosion tests presented earlier in Figures 3.15a and 3.16a.



a) b)

Fig. 3.17. Water permeability of the clay surface:
a) control clay composite; b) RSH-2.5(3) composite

The type of biopolymer, and its ability to interact with water play a crucial role in ensuring the durability of clay composite. Furthermore, other researchers have recently conducted similar durability (water erosion) experiments. The introduction of a small amount (0.5%, 1%, and 2%) of carrageenan biopolymer into the clay structure contributed to a significant improvement in its water erosion resistance (Nakamatsu et al., 2017). It was noted that even with a high degree of water adsorption, there was no visible damage on the surface of the clay with biopolymer admixture. The use of chitosan biopolymer also improved the water resistance of clay composites (Aguilar et al., 2016). With a minimal chitosan admixture concentration of 0.5%, the clay sample showed poor water resistance, with a pit obtained on its surface. However, with increasing chitosan content up to 1% or 3%, clay composites were able to withstand the water exposure for 10 minutes without any defects on the surface. In contrast to the control sample, the structure of both composites modified with different biopolymers was not disturbed. Ouedraogo et al., (2021) explained the enhancement of water erosion resistance by the formation of a hydrophobic biopolymer film on the surface of clay aggregates. This film facilitates the repulsion of liquid water and acts as a barrier, preventing its penetration into the composite structure.

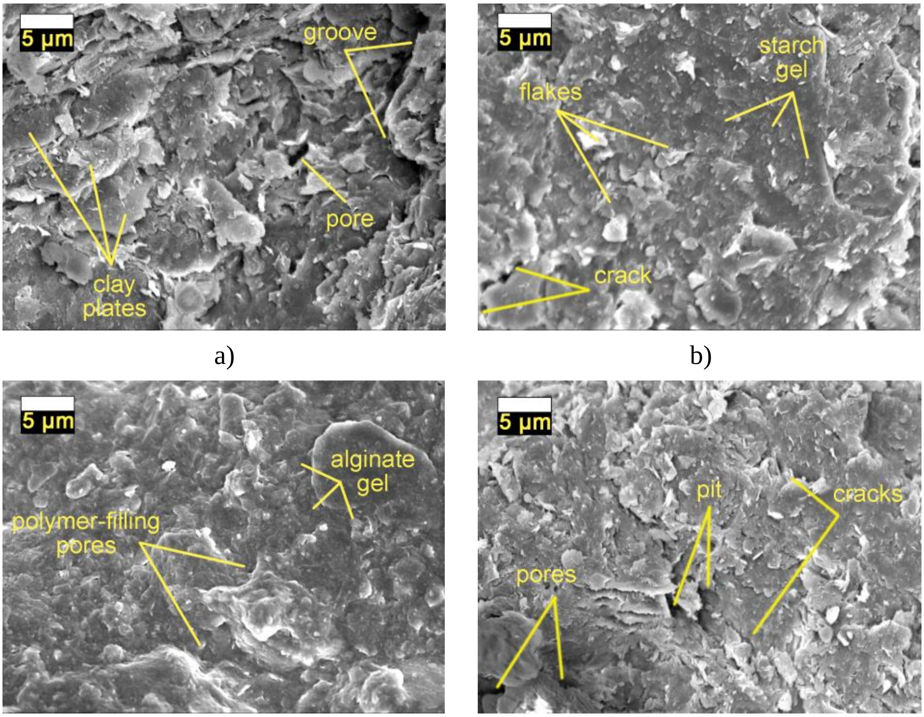
As mentioned above, during its modification, starch becomes hydrophobic, and a polymer in clay can act as a protective barrier against excessive water erosion. The use of alginate and chitosan, on the contrary, reduces the water erosion resistance of the clay composites. The hydrophilicity of the surfaces of alginate-containing clay composites is demonstrated earlier in sub-chapter 3.3.1, showing the highest moisture adsorption compared to the composites modified with starch and chitosan solutions.

3.5. Research of the clay composite structure

This sub-chapter provides information about the effect of biopolymers on the peculiarities of clay composite structure formation using scanning electron microscopy (SEM) and micro-computed tomography (XCT).

3.5.1. Microstructural characterisation

Figures 3.18a–d show the microstructure of clay composites modified with biopolymer solutions of a maximum concentration (SC-10; AC-10, CC-10 clay composite) and the control sample. The choice of such composites is due to the largest deviation of results in mechanical and physical characteristics compared to the control sample.



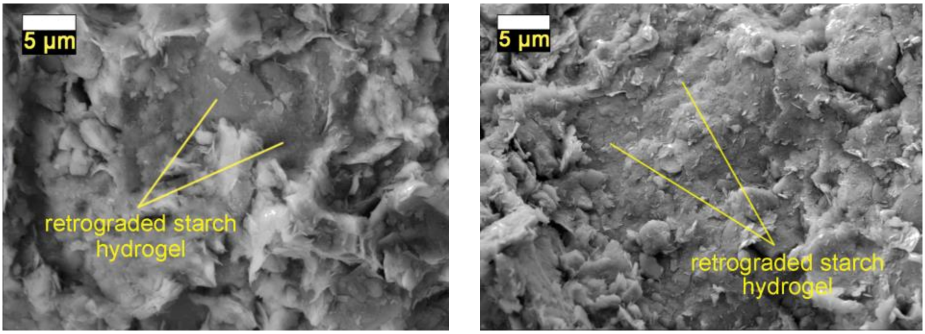
a) b)

c) d)

Fig. 3.18. Microstructure of the clay composites (x3000): a) control clay composite; b) SC-10 composite; c) AC-10 composite; d) CC-10 composite

Figure 3.18a shows the microstructure of the control clay composite. Microaggregates, including typical mica plates, are not oriented; their contacts vary from “face to face” and “edge to edge” to “face to edge”. These features are indicative of the matrix structure that is characteristic of mica clay (Ural, 2021; Sergeyev et al., 1980). The micropores are heterogeneous and vary in size from 1 μm to 5 μm. The microstructure of the composite modified with 10% starch solution (Fig. 3.18b) is more oriented, and “face-to-face” contacts predominate. Compared to the control sample, the surface is smoother and does not have deep, large pores, grooves, or pits. There is some “peeling” on the surface of larger clay plates. The smaller flakes with a clearly defined contour and 1–3 μm in size are evenly distributed on the entire surface of the sample. Figure 3.18c shows the microstructure of a clay composite modified with a 10% alginate solution. The presented microstructure is the most different from the previous two samples (Fig. 3.18a, b). The alginate gel coats the clay plates, filling all structural irregularities such as pores and gaps, thereby coagulating the structure. The smaller flakes (1–3 μm) on the surface have a vague shape. A similar effect is observed in the work of Chang et al. (2015a) when the clayey soil was modified with an agar gum solution. The effect of modifying the clay composite with a 10% chitosan solution is shown in Figure 3.18d. There are more structural defects, than in starch or alginate modifications, such as cracks and pits, and the structure is rougher in general.

Figure 3.19 presents the microstructure of the clay composites, modified with 2.5% and 10% of the retrograded starch hydrogel of 3-hour treatment. On the clay surface of RSH 10(3) (Fig. 3.19b), there is a thin layer of a finely dispersed substance, which smooths out the sharp relief without visible large or deep pores. RSH interacts strongly with the clay particles, forming a kind of surface upon them. Thanks to the colloidal properties of the clay and RSH, the hydrogel can ensure the cohesion of clay particles (Shaikh et al., 2017).



a) b)

Fig. 3.19. Microstructure of the clay composites (×3000):
a) RSH-2.5(3); b) RSH-10(3)

Generally, polysaccharides have good sorption properties and strong microstructural interaction with clay (Chenu, 1993; Shaikh et al., 2017). Chang et al.

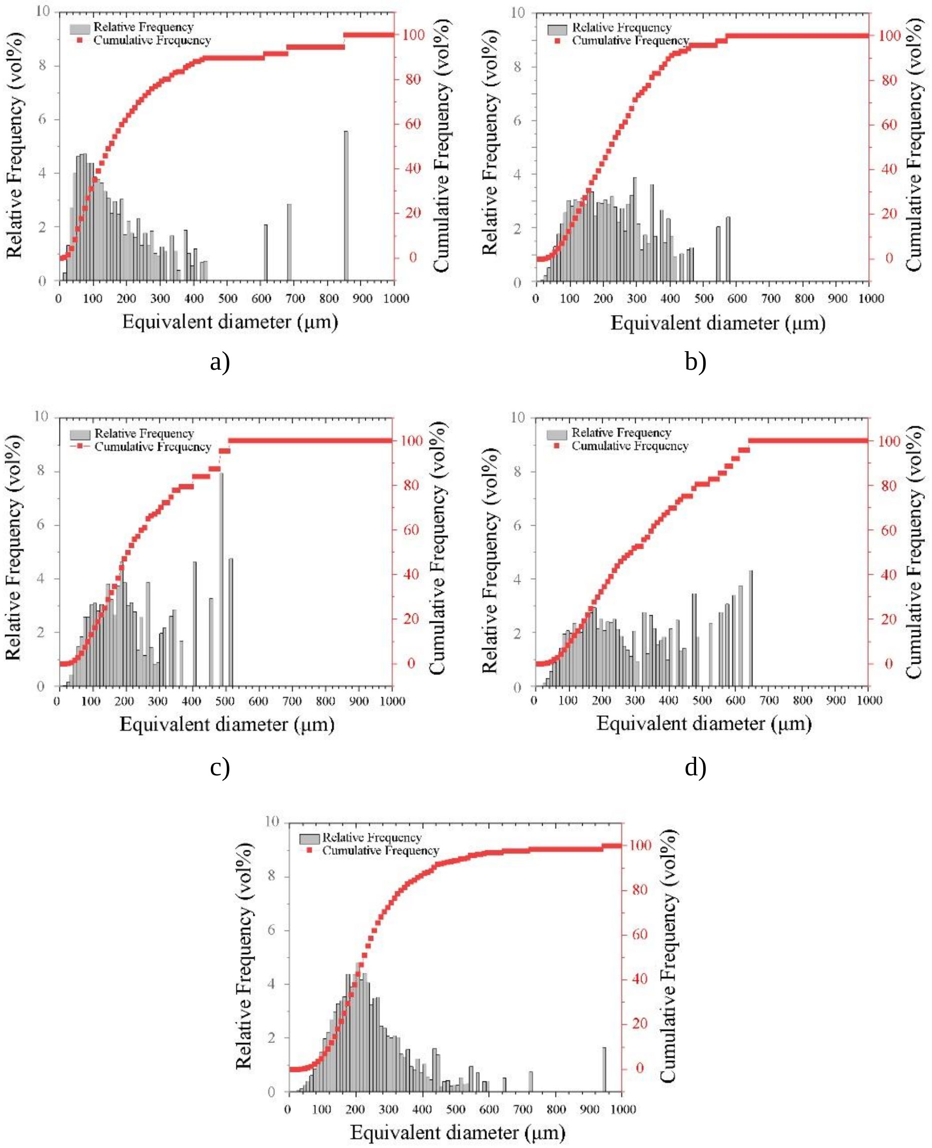
(2015) investigated the effect of using agar and gellan gum biopolymers on the modification of clayey and sandy soils. When examining the microstructure of clayey soil with agar gum addition, it is noted that the gelled polymer seemed to “cover” the soil aggregates, making its surface smoother. Authors also characterise this effect as the “formation of massive soil–biopolymer aggregates via gelation”. The longer molecular chains of agar gum (vegetable origin) are capable of wrapping around soil particles, thereby coagulating the entire structure (Chang et al., 2015). This assumption is in good agreement with the obtained microstructure images in Figures 3.18 and 3.19. The polymeric solutions of starch and alginate more clearly modify the surface of the investigated clay, smoothing its surface and partially filling its structural defects. The more homogeneous structure of the clay composite modified with starch and alginate solutions has a positive effect on the compressive strength, resulting in an increase of 42% and 40% for SC-10 and AC-7.5 composites, respectively. Moreover, the obtained SEM results align with the statement put forward in sub-chapter 3.2.4, indicating that the addition of the biopolymer solution contributes to enhancing the homogeneity of the clay composite structure.

3.5.2. Microtomography characterisation

The XCT method was used to observe the internal structure of the clay composites, modified with biopolymers. Figures 3.20a–e present data on the equivalent diameter of the granules within the obtained composites. Both relative and cumulative grain frequencies are expressed in the (vol%) format, providing a more accurate representation of the grain size distribution. Such a format represents the distribution of grains based on their volume fraction within the material, providing a more accurate representation of the grain size distribution.

The structure of the control clay composite appears homogeneous (Fig. 3.20a). The majority of particles are concentrated in the range of up to 400 μm (80% of the sample volume). However, there are spikes at 620, 680, and 860 μm, which may be related to technological defects in the clay composite structure, such as cracks, voids or inter-connected pores.

In contrast to the control clay composite, the cumulative frequency of clay particles in the SC-10 composite (Fig. 3.20b) is more uniformly distributed within the range of 50 to 480 μm (approx. 90% of the sample volume). Application of retrograded starch hydrogel (RSH-10(3)) contributes to the distribution of clay particles in the range of 50 to 600 μm, with a predominant distribution in the region of 150 to 250 μm (Fig. 3.20e). This fact may correspond to partial coagulation of the clay particles using starch in gelled and retrograded forms.



a)

b)

c)

d)

e)

Fig. 3.20. Particle size distribution within clay composite:
a) control clay composite; b) SC-10 composite; c) AC-10 composite;
d) CC-10 composite; e) RSH-10(3) composite

The particle size distribution of the clay composite with the addition of 10% alginate solution (AC-10) is shown in Figure 3.20c. Approx. 70% of the particles are distributed in the range of 50 to 350 μm. However, there are strong peaks at 400, 450, 480 and 520 μm, which can be associated with some defects within the clay composite structure.

The addition of 10% chitosan biopolymer solution (Fig. 3.20d) causes a shift in the cumulative frequency curve towards particles ranging from 300 to 650 μm, which represents 45% of the clay sample volume. As previously noted, when chitosan interacts with a 1M HCl solution, it does not dissolve completely but forms a spherical structure with a size range of 200 to 600 μm. The size of such chitosan granules or their conglomerates ranges from 200 to 600 μm. When chitosan is added to the clay composite, the undissolved polymer granules can be distributed throughout the entire composite structure, which may cause the observed reorganisation of particles.

The micro-CT scans are presented as a maximum-intensity projection image, which is displayed using a range of grey shades that reflect the level of X-ray absorption in different areas. The shades of black, white, and grey correspond to differences in density, where black represents areas with low X-ray absorption and low density, while white represents areas with high X-ray absorption and high density. The 3D images were obtained for all the clay composites, modified with 10% biopolymer solutions of starch, alginate and chitosan (Figs. 3.21a–e).

For all the investigated composites, certain features can be noted. Bright white spots, randomly distributed in the structure of each composite, characterise high-density granules, which can be associated with sand particles, with the content in the raw clay about 3.48% (Fig. 2.2). According to obtained 3D images, the introduction of biopolymers into the clay structure significantly increases the volume of less dense particles in the composite, which explains the decrease in their density (sub-chapter 3.2.1).

Figure 3.21a shows the structure of the control composite with the distributed pores and defects inside. The small pores are randomly distributed throughout the volume of the sample. Also, there are some elongated voids, which are characteristic of technological defects and cracks inside the clay sample. The presence of such defects is also confirmed by the particle distribution graph (Fig. 3.21a).

The structure of the clay composite modified with gelatinised starch and retrograded starch hydrogel is shown in Figures 3.21b and 3.21e, respectively. The obtained 3D images are similar and show a uniform structure with relatively few internal defects, pores, and starch agglomerations. This assumption is in good agreement with the obtained surfaces, which are also presented in Figures 3.21b and 3.21e in the right part. The amount of black and dark grey areas, which characterize voids and polymeric matter, is lower than in the control clay composite (Fig. 3.21a).

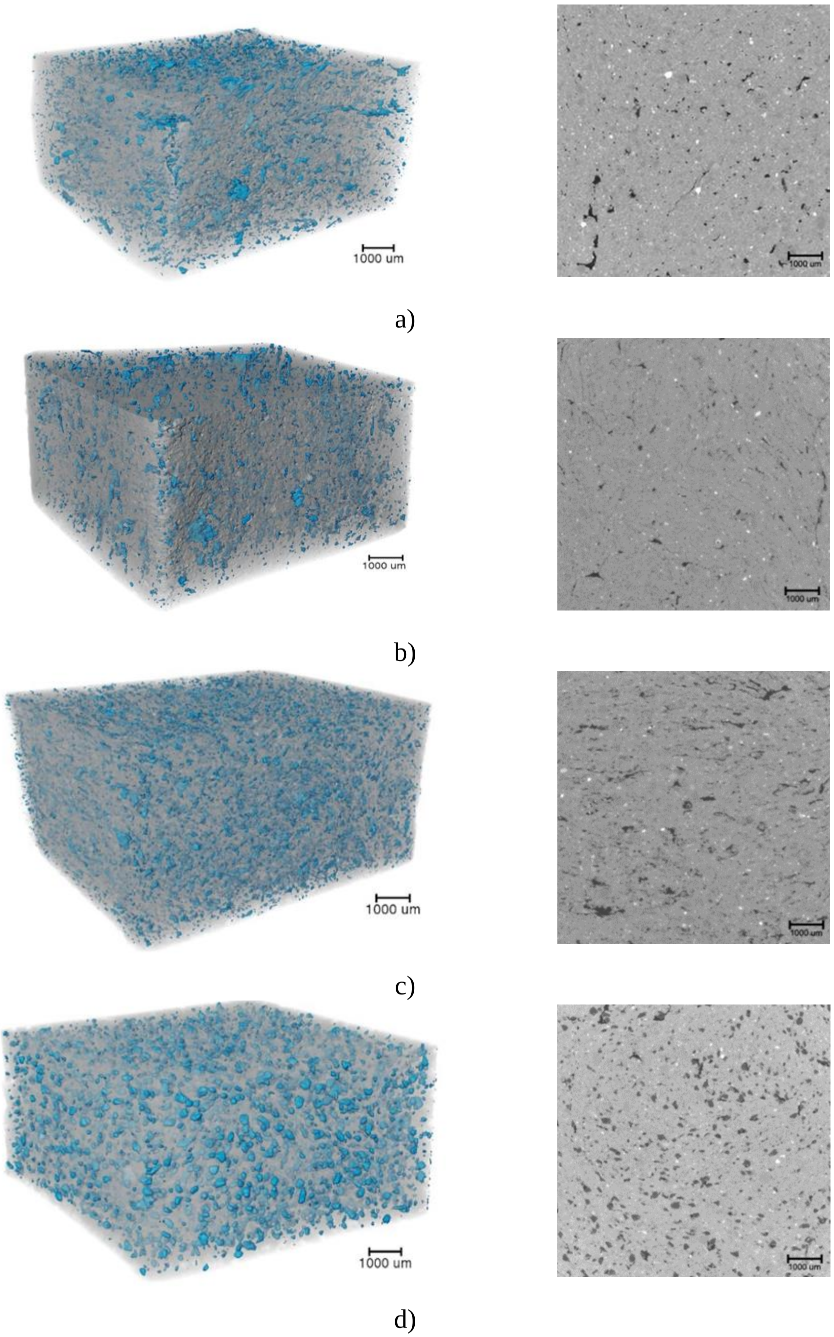
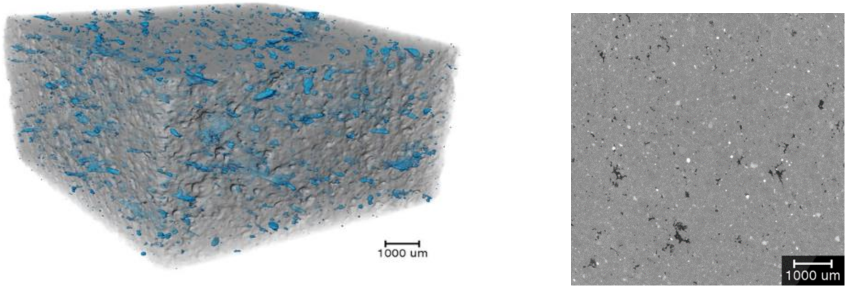


Fig. 3.21. To be continued



e)

Fig. 3.21. Micro-CT images of the clay composite:
a) control clay composite; b) SC-10 composite; c) AC-10 composite;
d) CC-10 composite; e) RSH-10(3) composite

The 3D image, as well as the internal surface of the clay composite modified with alginate solution (AC-10), is presented in Figure 3.21c. In the 3D image, a significant number of blue areas can be observed, which indicate voids or polymer material within the structure of the AC-10 composite. Some prolonged, wavy polymeric matter uniformly distributed within the whole matrix of the clay composite can also be noted on the internal surface.

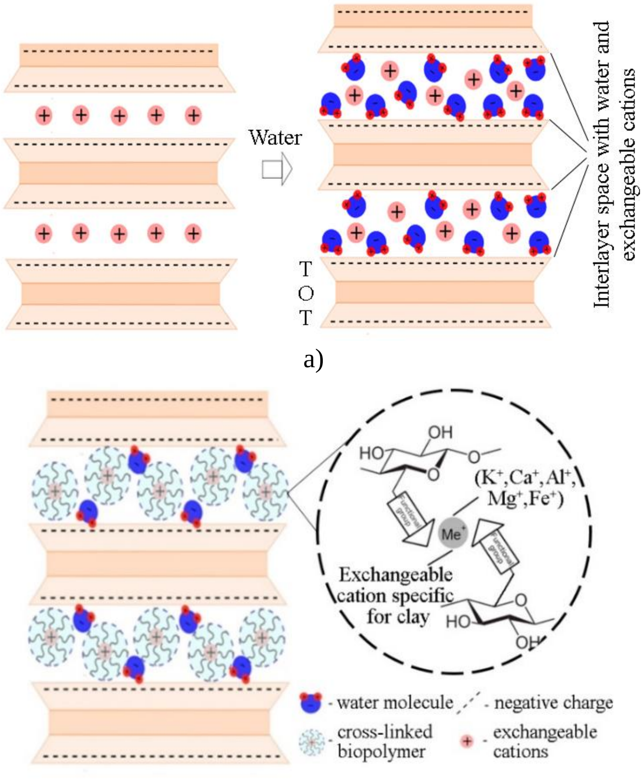
The structure of the CC-10 composite is shown in Figure 3.21d. The obtained image significantly differs from those of the other clay composites: control, SC-10, AC-10, and RSH-10(3) composites (Figs. 3.21a–c, e). The dark grey chitosan spots are evenly distributed throughout the clay matrix. The extensive inclusions of large chitosan particles with a diameter of 200 to 600 μm are also observed in the obtained 3D images. After incorporating a 10% chitosan solution, the density of the clay composite decreased significantly, dropping from 1990 to 1810 kg/m^3. As a result, the compressive strength of the material was also reduced.

3.6. Discussion on the interaction mechanisms between clay and biopolymers

Modification of clay with biopolymers affects several clay composite properties. Other researchers often correlate the improvement in properties with the formation of new hydrogen bonds in the structure of clay-based materials, as well as the formation of van der Waals forces, which provide stable “clay-biopolymer” interactions (Table 1.2). Biopolymers can exhibit strong interactions with clays through different mechanisms, specified below:

(a) Hydrogen bonding. Polysaccharides contain numerous hydroxyl (-OH) groups, which can form hydrogen bonds with water molecules and other hydrogen bond donors or acceptors (Maji, 2019; Rinaudo, 2006). In the presence of clay minerals, the hydroxyl groups of the polysaccharides can also participate in hydrogen bonding with the surface hydroxyl groups or water molecules associated with the clay surfaces (Alcântara et al., 2014; Theng, 2012). These hydrogen bonding interactions contribute to the adsorption of polysaccharides on the clay surfaces.

(b) Electrostatic interactions. Clay minerals normally possess a net negative charge on their surface (Fig. 3.22a). Polysaccharides, on the other hand, can carry positive, negative or neutral charges depending on their type, composition and pH conditions (Liu et al., 2000). Electrostatic interactions can take place between the charged groups of the polysaccharides and the oppositely charged clay surfaces, resulting in the formation of polymer-clay complexes (Liu, 2007).



a)

b)

Fig. 3.22. Modification of the mica-clay structure with biopolymer solutions:
a) classical representation of mica-clay structure (Brigatti et al., 2013);
b) clay–polysaccharide interaction principle (based on the current research)

(c) Physical entanglement. Polysaccharide chains can become physically entangled with the clay particles, especially in the case of long-chain polysaccharides. The entanglement occurs when the polymer chains thread through the porous structure of the clay, leading to the formation of a network or gel-like structure (Nascimento, 2021). This physical entanglement can enhance the stability and viscosity of the polysaccharide-clay system.

Figure 3.22 demonstrates the modification principle used in this research. On the left is a typical 2:1 mica clay structure, where one octahedral sheet (O) intercalates between two tetrahedral sheets (T) (Brigatti et al., 2013; Orta et al., 2020). Exchangeable cations and water molecules are located in the interlayer space (Fig. 3.22a). As mentioned in sub-chapter 2.2.3, the principle of clay modification implies the complete replacement of water with polymeric solutions of gelated starch, alginate, and chitosan. Thus, it can be assumed that the interactions between clay and polymers in the form of water solution may appear in the interlayer space containing exchangeable cations, typical for the clay used (Fig. 3.22b). The exchangeable cations in the double layer (Fig. 3.22a) of the clay mineral create a negatively charged surface. The negatively charged and neutral biopolymer molecules may be attracted to the clay surface through electrostatic interactions (Orta et al., 2020). The charged functional groups of the biopolymers can form electrostatic bonds with the positively charged exchangeable cations on the clay surface (Fig. 3.22b).

This electrostatic attraction allows the biopolymers to adsorb onto the clay mineral (Fatehi et al., 2021). Additionally, physical adsorption may play a role in the interaction between biopolymers and clay minerals. The biopolymer molecules can undergo non-covalent interactions, such as hydrogen bonding, van der Waals forces, or hydrophobic interactions, with the surface of the clay mineral (Fatehi et al., 2023). These interactions contribute to the binding of the biopolymers to the clay mineral and can explain most of the obtained effects in this research. Researchers (Chang et al., 2018; Fatehi et al., 2021; Hataf et al., 2017; and Theng et al., 2012) attributed the increasing compressive strength to the formation of new hydrogen bonds. The same effect was observed in the current research by the clay composites modified with starch and alginate biopolymers. The strength of the SC composites increased from 21% to 42%, and that of AC composites increased from 18% to 40%, compared to the control clay composite. The addition of retrograded starch hydrogel (RSH (3;5)) increased the compressive strength of clay composites significantly from 40% to 74%. Increasing the moisture sorption can also be associated with newly obtained hydrogen bonds.

Based on the theoretical and practical studies, the obtained effect of biopolymers on the clay structure is represented in Figure 3.23. Figures 3.23a and 3.23b were already specified in sub-chapter 1.3.3, which described the current understanding of the effect of biopolymers on the structure of clay composite. Figure 3.23b shows the occupation of the clay composite’s porous space by swelling biopolymer, based on the model by Zhou et al. (2020). Biopolymers inside the structure alter the overall pore volume, also retaining water from the clay structure.

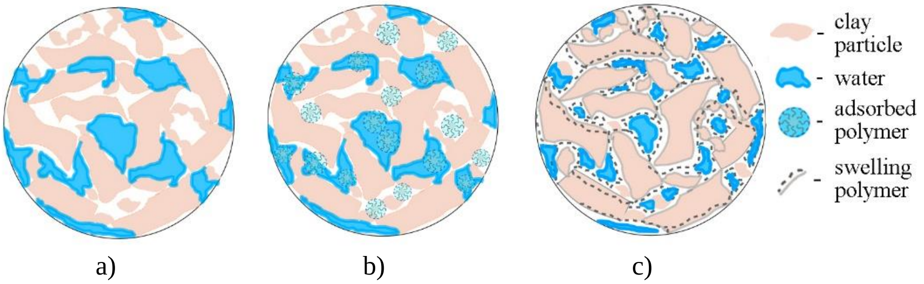


Fig. 3.23. Microstructure model of clay, modified with biopolymer: a) example of clay structure without biopolymer; b) clay with biopolymer model based on Zhou et al., 2020; c) clay with biopolymer model based on the results of current studies

Figure 3.23c illustrates the modification principle of the clay structure by a biopolymer based on the current research. The strong interaction between clay and biopolymer may signify the adsorption of the biopolymer on the clay's surface, thereby altering the microstructure of the clay composite. A similar effect was observed in microstructural images presented in sub-chapter 3.5.1. Biopolymer admixtures of starch and alginate significantly impact the structure of the unfired clay composite (Fig. 3.18b, c). The specified biopolymers modify the surface of the investigated clay, smoothing its surface and partially filling its structural defects (cracks, pores, and grooves), which were observed on the surface of the control clay (Fig. 3.18a). Apart from modifying the pores with biopolymers and the ink-bottle effect (Arrigoni et al., 2017; Pinson et al., 2018), additional hydrogen bonds can attract water molecules, thus enhancing the hygroscopicity of the observed clay composites (Rosa Latapie et al., 2023). Application of all the biopolymers (starch, alginate, and chitosan) of different preparation technologies (biopolymer gelation and starch retrogradation processes) increased the moisture adsorption of the clay composites by 13.3% to 34.2%. Nonetheless, the high hydrophilicity of certain biopolymers can also lead to some negative effects. The application of alginate and chitosan led to a decrease in the water erosion resistance of the clay composite, primarily attributed to the hydrophilic characteristics of these biopolymers. Conversely, the introduction of retrograded starch hydrogel substantially enhanced the durability of the clay composite as a consequence of the biopolymer's hydrophobic nature after the retrogradation process. The impact of the biopolymer's hydrophobic characteristics on the water erosion resistance of the clay composite was also demonstrated in the research of

Ouedraogo et al. (2021). In this research, the hydrophobic biopolymer functioned as a protective barrier, preventing water from infiltrating the clay structure.

However, this research demonstrates that not all types of clay and biopolymers exhibit strong interactions with each other. The deterioration of some properties of the clay composite with the chitosan admixture was quite unexpected. The application of chitosan showed a negative effect on the compressive strength, resulting in a decrease of 19.7%, and adversely affected the clay composite's durability. Aguilar et al. (2016) and Hataf et al. (2018) showed an improvement in both the mechanical properties and durability of a clay composite modified with chitosan. Contradictory results can be attributed to the different types of clay used and their chemical and mineralogical compositions. Furthermore, despite using the same biopolymer (chitosan) in the current and reference studies, the polymer characteristics may vary. For example, Hataf et al. (2018) extracted chitosan from shrimp shells themselves, which could potentially influence the final properties of the biopolymer.

When gels are formed, biopolymers can interact with different cations (Wurm et al., 2020). Depending on the polysaccharide type, these cations may differ. Ma et al. (2010) postulated that Ca^{2+} and Mg^{2+} cations could significantly enhance the aggregation effect of the starch, thus increasing its adsorption on the kaolinite surfaces. In the case of alginate, during the interaction with divalent ions, the structure of the alginate gel is formed according to the "egg-box" principle when the connecting zones of the curved sheet structure of the polysaccharide are cross-linked by those ions. To form strong alginate gels, the following cations are used: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ (Ching et al., 2017; Drury et al., 2003; Walter, 1998). To ensure strong cross-linkages of the chitosan gel, the most preferred cations are $Cu^{2+} > Fe^{2+} > Hg^{2+} > Pb^{2+}$ (Drury et al., 2003; Walter, 1998). Thus, it can be assumed that the effect of biopolymers on clay modification may strongly depend on the chemical and mineralogical composition of the raw clay materials. According to the chemical composition (Table 2.1), the clay under research contains up to 15% Ca- and Mg-containing oxides (CaO – 9.87%, MgO – 4.57%), which can positively affect the interaction of clay and starch and alginate solutions. At the same time, the total amount of Fe-containing oxides (Fe_2O_3) is 5.53%, which may be insufficient for the proper interaction of the clay and chitosan solution. It is worth noting that the accessibility of these cations to the biopolymers will depend on the specific composition of the clay and the characteristics of the biopolymers used. The extent of interaction will vary based on factors such as the concentration and charge density of the biopolymer solution and the surface chemistry of the clay minerals.

Moreover, the pH of the components and viscosity of the biopolymer solution has a great influence on the "clay-biopolymer" interactions. For example, Dove (2016) indicated that a more acidic environment contributes to a better interaction of clay and biopolymers. Also, this fact was confirmed by Liu et al. (2000), where a lower pH (approx. 6–6.5) promotes greater adsorption of starch polysaccharides on the surface of some minerals, such as hematite (Fe_2O_3), which is typical for the clay in question. According to Figure 3.2, it is observed that the pH of starch and alginate solutions decreases as the concentration increases, reaching a value of 5.9. This decrease in pH can potentially enhance the adsorption of these polysaccharides onto the surface of minerals, that are typical for the clay used. However, an acidic solution of chitosan with a pH of 4.3 to 5.9 does not show a noticeable effect on the properties of the clay composite. Regarding the viscosity parameter, Dove (2016) associated the high viscosity of the polymer solution with the presence of larger polymer chains within it. Large polymer chains have a tortuous structure and can negatively affect the interaction of the biopolymer and clay. In this research, the polysaccharides are applied in a gel-like form, so as the concentration of the biopolymer increases, the viscosity of the solution also increases significantly (Fig. 3.1). In the case of starch and alginate, the increase in viscosity does not worsen the properties of the clay composite. A more appropriate explanation is that larger polymer chains contribute to the "coating" of clay aggregates, thus modifying its structure (Chang et al., 2015).

In designing the clay composite modified with biopolymers, particular attention should be paid to the research of the raw materials used: clays and polysaccharides. There are many types of clay whose chemical, mineralogical, and granulometric properties play a significant role in shaping the properties of the final composite and in the interaction with certain polysaccharides. However, not every "clay-polysaccharide" combination has the potential to improve specific properties of the composite. Parameters such as the chemical and mineralogical composition of clay, the type of biopolymer, and its technological treatment (biopolymer gelation and starch retrogradation processes), and the method of its introduction are important for creating an effective unfired clay building material.

3.7. Conclusions of the Third Chapter

This chapter described the research on the effect of different biopolymer solutions of starch, alginate and chitosan on the physical, mechanical, and hygroscopic properties and the durability and structure of unfired clay composites. The following conclusions can be drawn:

1. The better interactions with clay were demonstrated by the biopolymers of starch and alginate, which can interact with Ca^{2+} and Mg^{2+} cations that are specific for the mica clay in question. Chitosan showed the worst clay–biopolymer interaction ability due to the insufficient amount of Fe^{2+} cations in the clay composition.

2. With increasing the concentration of biopolymer solutions of starch, alginate, and chitosan from 2.5% to 10%, the densities of such composites decreased by 1–9%: from 2030 kg/m^3 to 1940 kg/m^3 for SC composites, from 1970 kg/m^3 to 1855 kg/m^3 for AC composites, and from 1940 kg/m^3 to 1810 kg/m^3 for CC composites. However, the application of RSH led to the opposite effect: the density of the clay composite, modified with RSH (3;5), increased by 2.5% from 1990 kg/m^3 to 2040 kg/m^3.
3. The incorporation of biopolymers (2.5% to 10%) of different preparation technologies (biopolymer gelation and starch retrogradation processes) contributed to a decrease in the shrinkage of clay composites. Compared to the control clay, the maximum decrease in shrinkage was from 6.2% to 3.7% for the RSH(5)-10 composite.
4. Increasing the concentration of biopolymer solutions from 2.5% to 10% increased the compressive strength of clay composites. Compared to the control clay composite, the strength of the SC composites increased from 21% to 42%, and that of AC composites increased from 18% to 40%. The addition of retrograded starch hydrogel (RSH (3;5)) increased the compressive strength of clay composites significantly from 40% to 74%. Therefore, such clay materials can be assigned to the highest 5th class (load-bearing walls and inner walls) according to the earth brick standard DIN 18945:2013-08 due to compressive strength greater than 6.3 MPa. However, the application of maximum chitosan concentration showed the opposite effect; the strength of the CC-10 composite decreased by 19.7% compared to the control sample.
5. Moisture adsorption rate increased for all the clay composites, modified with biopolymer solutions, compared with the control sample: up to 13.3% for SC and CC composites; and up to 34.2% for AC composites. The application of retrograded starch hydrogel (RSH (3;5)) also contributed to an increase in moisture adsorption rate of up to 27%. According to the DIN 18947:2013 standard, all studied clay composites comply with the WC-3 class, which corresponds to an “excellent” moisture adsorption capacity, with an adsorption rate of more than 60 g/m^2 per 12 h.
6. The maximum hysteresis rate increased for the clay composites, modified with starch, alginate and chitosan admixtures: up to 0.78% for SC composites, up to 1.01% for AC composites, and up to 0.98% for CC composites. However, the application of retrograded starch hydrogel (RSH (3;5)) showed the opposite effect: the maximum hysteresis rate decreased from 0.27% to 0.15%. The hysteresis results showed a strong correlation with the results of the clay composite’s densities.

7. The highest water erosion resistance was demonstrated by clay composites, modified with retrograded starch hydrogel (RSH (3;5)) biopolymers. Due to the re-structuration of the starch during the retrogradation process, the biopolymer became hydrophobic, which increased the water erosion resistance of the clay composite. The worst water erosion resistance was demonstrated by CC composites, which can be a result of weak clay-biopolymer interactions, as well as the hydrophilic nature of the biopolymer after the gelation process.

General Conclusions

1. When interacting with mica-clay, biopolymers (polysaccharides – starch, alginate, and chitosan), depending on the preparation technology (biopolymer gelation and starch retrogradation processes), can form new hydrogen and electrostatic bonds with the surfaces of specific clay. Biopolymers, such as starch and alginate, exhibited better interactions with mica clay because of their capacity to interact well with Ca^{2+} and Mg^{2+} cations, which are specific for the clay used. Structural characterisation of clay composites showed the adsorption of the starch and alginate biopolymers on the clay surface, which modified the structure of the composite, making it more homogeneous. In contrast, chitosan interacted with clay less effectively, primarily due to the limited presence of Fe-contained oxides in the clay's composition.
2. Biopolymers, such as starch and alginate (concentration in solution 10% and 7.5%, respectively), after undergoing the gelation process, exhibited up to 40% increase in compressive strength, compared to the control clay-based composite. Starch application (from 2.5% to 10%) after the retrogradation process results in an increase of clay composite's compressive strength by 40% to 74%. Thus, the mentioned composites can be assigned to the 5th class, following the DIN 18945:2013-08 standard, as their com-

pressive strength exceeds 6.3 MPa. This makes the obtained clay composites suitable for use as constructional building materials, particularly for load-bearing and inner walls.

3. The introduction of biopolymers (polysaccharides – starch, alginate, and chitosan) of different preparation technologies (biopolymer gelation and starch retrogradation processes) increased the moisture adsorption of the surface of clay composites by 13% to 34%. The effect was achieved due to newly obtained hydrogen bonds inside the structure of clay material. According to the DIN 18947:2013 standard, all studied clay composites comply with the WC-3 adsorption class, which corresponds to an “excellent” moisture adsorption capacity, with an adsorption rate of more than 60 g/m^2 per 12 h. Therefore, the obtained clay composites can be used for producing finishing materials, such as clay plasters.
4. The application of alginate and chitosan resulted in the reduction of water erosion resistance of clay composites due to the hydrophilic nature of such biopolymers. On the contrary, the incorporation of the retrograded starch hydrogel significantly increased the durability of the clay composite, due to the hydrophobic nature of the biopolymer after the retrogradation process.

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Summary in Lithuanian

Įvadas

Problemos formulavimas

Nedegto molio medžiagos gali būti tvari alternatyva tradiciniams statybos produktams, tačiau vis dar reikia tobulinti jų mechanines ir eksploatacines savybes. Šių savybių gerinimas efektyviausiai pasiekiamas pridedant natūralių, ekologiškų priedų, kad būtų išsaugotas nedegto molio gaminių (pvz., nedegto molio mūro gaminiai, tinkai) tvarumas. Plačiai paplitęs molio stabilizavimas įterpiant skirtingus pluoštus, tačiau modifikavimas naudojant biopolimerus vis dar plačiai nenagrinėjamas. Būtina ištirti „molio ir biopolimero“ sąveiką, taip pat biopolimerų įtaką molio kompozitų savybėms, ilgaamžiškumui bei struktūrai. Šiuo metu atliktų tyrimų nepakanka, kad būtų galima efektyviai panaudoti biopolimerus atsižvelgiant į jų unikalias savybes (prigimtį, formą ir pan.) gaminant statybos produktus molio pagrindu. Taip pat retai kalbama apie biopolimerų įtaką molio medžiagų struktūrai ir ilgaamžiškumui. Yra daug molio rūšių, kurių cheminė, mineraloginė ir granuliometrinė sudėtis atlieka svarbų vaidmenį sąveikaujant su skirtingais polisacharidais, o tai daro įtaką galutinio molio kompozito savybėms. Atsižvelgiant į šių dienų realijas, akivaizdus aplinkai nekenksmingų statybinių medžiagų poreikis, o įvairių biopolimerų panaudojimas leistų sukurti aukštų eksploatacinių savybių molio kompozitus (pvz. nedegto molio mūro gaminiai, tinkai), kuriuos pasibaigus gyvavimo ciklui būtų galima lengvai perdirbti.

Darbo aktualumas

Ekologiškos statybos, tvarių statybinių medžiagų gamybos klausimas šiuo metu yra labai aktualus. Todėl pastaraisiais metais išaugo susidomėjimas draugiškomis aplinkai, netoksiškomis ir lengvai perdirbamomis molio medžiagomis. Žinoma, kad nedegto molio medžiagos turi didžiulį aplinkosauginį potencialą, pasižymi mažomis energijos sąnaudomis ir anglies pėdsaku jas gaminant, eksploatuojant ir naudojant, tačiau taip pat šios medžiagos kartais turi nepakankamas stiprumines savybes ir ilgaamžiškumą, palyginti su „šiuolaikinėmis“ medžiagomis. Todėl nedegto molio medžiagas labai svarbu papildomai modifikuoti, kad būtų pagerintos jų fizikinės ir mechaninės savybės bei ilgaamžiškumas, išsaugant jų aukštą ekologinį potencialą. Tai galima pasiekti įterpiant biopolimerus, kurie pasižymi panašiomis aukštomis aplinkosauginėmis savybėmis kaip ir pats molis. Molio kompozitų savybės gali pasikeisti dėl biopolimerų adsorbcijos ant molio mineralų paviršių, nes adsorbuoti biopolimerai gali pakeisti molio mineralų paviršių prigimtį, todėl labai svarbu tirti šias sąveikas, naujai susidariusias vandenilines jungtis, dėl kurių gali pasikeisti modifikuotų molio kompozitų mikrostruktūra.

Tyrimo objektas

Šio tyrimo objektas yra biopolimerais (polisacharidais – krakmolu, alginatu ir chitozanu) modifikuotas molio kompozitas, skirtas tvariai statybai.

Darbo tikslas

Disertacijos tikslas yra modifikuoti molio struktūrą, panaudojant įvairias biopolimerų paruošimo technologijas (biopolimerų geliavimo ir krakmolo retrogradacijos procesus), siekiant pagerinti molio kompozito mechanines, higroskopines savybes ir ilgaamžiškumą.

Darbo uždaviniai

Norint pasiekti tikslą, reikėjo išspręsti šiuos uždavinius:

1. Parinkti biopolimerų paruošimo technologiją (geliacijos ir krakmolo retrogradacijos procesą) ir nustatyti apdorojimo parametrus.
2. Ištirti biopolimerų, priklausomai nuo jų paruošimo technologijos, įtaką molio kompozitų fizinėms, mechaninėms ir higroskopinėms savybėms.
3. Įvertinti, priklausomai nuo biopolimero paruošimo technologijos, biopolimerų įtaką molio kompozito struktūrai ir ilgaamžiškumui.
4. Įvertinti biopolimerų (krakmolo, alginato, chitozano) ir molio medžiagos sąveikos mechanizmus, siekiant nustatyti struktūros formavimosi ypatumus.

Tyrimų metodika

Molio žaliavos apibūdinimas buvo atliktas taikant keletą analitinių metodų, įskaitant rentgeno spindulių difrakciją (XRD) ir rentgeno fluorescenciją (XRF). Polisacharidų vandeninių tirpalų, paruoštų pridedant krakmolo, alginato ir chitozano, charakteristikos buvo tiriamos nustatant pH ir klampumą. Tirtų medžiagų struktūra ištirta naudojant skenuojančią elektronų mikroskopiją (SEM) ir rentgeno kompiuterinę tomografiją (XCT). Visos tirtos savybės buvo nustatytos pagal atitinkamus tarptautinius (ASTM, EN, ISO) ir nacionalinius (UNE, DIN, NZS) standartus. Eksperimento rezultatams patvirtinti buvo taikomi statistiniai ir analitiniai vertinimo metodai.

Darbo mokslinis naujumas

Rengiant mokslinį darbą nustatyti hidrožėrutinio molio kompozitinės struktūros formavimosi, naudojant skirtingus biopolimerus (polisacharidai – krakmolas, alginatas, chitozanas) ir jų paruošimo technologijas (biopolimerų geliavimo ir krakmolo retrogradacijos procesus), ypatumai. Molio struktūros modifikavimą bei savybių ir ilgaamžiškumo pokyčius lemia adsorbuoti hidrožėrutinio molio dalelių paviršiuje biopolimerai, taip pat papildomų vandenilinių ryšių susidarymas. Retrograduotas krakmolo hidrogelis buvo pasiūlytas modifikuoti statybinius molio kompozitus. Toks priedas padidina molio kompozitų stiprumą, drėgmės adsorbciją ir ilgaamžiškumą. Gauti rezultatai gali būti panaudoti mūro ir apdailos statybinių medžiagų srityje.

Darbo rezultatų praktinė reikšmė

Gauti biopolimerų, krakmolo (gelio pavidalo ir retrograduotos formos) ir alginato tirpalų, modifikuojant molio kompozitus, tyrimo rezultatai gali būti naudojami ekologiškų statybinių medžiagų (nedegto molio mūro gaminių) gamyboje. Tokį teiginį lėmė itin pagerintos gauto molio kompozito, palyginus su tradiciniais nedegto molio gaminiais, mechaninės charakteristikos, kurios pagal DIN 18945:2013-08 standartą atitinka aukščiausią 5 klasę. Taip pat, visų ištirtų biopolimerų (krakmolo, alginato ir chitozano) naudojimas padidina molio kompozitų higroskopines savybes, todėl, pagal DIN 18947:2013 standartą (WS-3 klasė) tokie molio kompozitai tinkami naudoti patalpose kaip apdailos medžiagos. Šiame darbe nustatytas molio kompozitų, panaudojant retrograduotą krakmolo hidrogelį, modifikavimo efektas buvo aprašytas Lietuvos patente Nr. LT-6964B (Lietuvos Respublikos valstybinis patentų biuras „Nedegtų molio produktų su biopolimero priedu gavimo būdas“).

Ginamieji teiginiai

1. Biopolimerai (polisacharidai – krakmolas, alginatas, chitozanas), priklausomai nuo paruošimo technologijos (biopolimerų geliavimo ir krakmolo retrogradacijos procesai), gali sąveikauti su hidrožėrutinio molio paviršiumi ir tarpsluoksniu taip modifikuodami molio kompozito struktūrą.
2. Biopolimerų (krakmolo ir alginato), priklausomai nuo paruošimo technologijos (biopolimerų geliavimo ir krakmolo retrogradacijos procesai), įterpimas leidžia iki 74 % padidinti molio kompozitų gniuždymo stiprį bei iki 34% drėgmės adsorbciją.

Darbo rezultatų aprobavimas

Pagrindiniai darbo rezultatai buvo paskelbti devyniuose moksliniuose straipsniuose: trys moksliniuose žurnaluose, įtrauktuose į *Clarivate Analytics Web of Science* leidinių sąrašą ir turinčiuose citavimo indeksą, keturi straipsniai *Clarivate Analytics Web of Science* duomenų bazės *Conference Proceedings*, du straipsniai kitų tarptautinių duomenų bazių leidiniuose. Remiantis disertacijos rezultatais, išduotas Lietuvos patentas. Septyni pranešimai buvo pristatyti nacionalinėse ir tarptautinėse mokslinėse konferencijose:

- Tarptautinėje mokslinėje konferencijoje „Aktualios Baltarusijos ir gretimų regionų architektūros problemos“ (2020), Polockas, Baltarusijos Respublika.
- Jaunųjų mokslininkų konferencijoje „Mokslas – Lietuvos ateitis“ (2021), Vilnius, Lietuva.
- Tarptautinėje mokslinėje konferencijoje *Binders and Materials* (2021), Brno, Čekija.
- XX tarptautiniame medžiagų simpoziume (2022), Marinha Grandė, Portugalija.
- 5-ojoje tarptautinėje konferencijoje „Inovatyvios medžiagos, struktūros ir technologijos (IMST 2022)“ (2022), Ryga, Latvija.
- 14-ojoje tarptautinėje konferencijoje „Šiuolaikinės statybinės medžiagos, konstrukcijos ir technologijos“ (2023), Vilnius, Lietuva.
- Tarptautinėje konferencijoje *Chemicals & Environment* (EcoBalt 2023) (2023), Talinas, Estija.

Disertacijos struktūra

Disertaciją sudaro įvadas, trys skyriai, bendrosios išvados, literatūros sąrašas, autoriaus publikacijų disertacijos tema sąrašas, santrauka lietuvių kalba ir trys priedai. Disertacijos apimtis – 115 puslapių, neįskaitant priedų, tekste panaudota 1 formulė, 39 paveikslai ir 6 lentelės. Rašant disertaciją buvo panaudotas 141 literatūros šaltinis.

1. Nedegto molio, jo modifikacijų ir pritaikymo molio pagrindu pagamintų statybinių medžiagų gamyboje apžvalga

Labiausiai paplitęs molio medžiagų modifikavimo būdas yra įvairių pluoštų naudojimas molio struktūrai sustiprinti. Pluoštų panaudojimas leidžia sumažinti molio gaminių tankį, susitraukimą, gali pagerinti akustines, higroskopines ar stiprumines savybes (Giroudon et al., 2019; Yetgin et al., 2008; Salih et al., 2020), tačiau taip pat gali turėti neigiamą poveikį vandens atsparumui (Laborel-Préneron et al., 2016a; 2018b; Giroudon et al., 2019). Pastarąjį dešimtmetį mokslininkai vis labiau domėjosi natūralių polimerų panaudojimu statybinių medžiagų gamyboje, nes tai yra atsinaujinantys ištekliai, gaunami iš daugelio natūralių medžiagų (Tusnim et al., 2020; Pacheco-Torgal et al., 2016). Tačiau įvairių biopolimerų naudojimas molio medžiagoms modifikuoti kol kas mokslinėje literatūroje nėra plačiai nagrinėjamas. Įvairių polisacharidų, t. y. polimerų, sudarytų iš daug monosacharidų molekulių, įterpimas į molio mišinius teigiamai veikia jų susitraukimą (Dove et al., 2015 ir Lagouin et al., 2021), stiprumines savybes (Alhaik et al., 2017; Chang et al., 2015; Soldo et al., 2020), nes tarp molio dalelių ir polisacharidų susidaro papildomi vandeniliniai ryšiai (Theng et al., 2012), taip pat pagerina struktūrą, kuri tampa labiau homogeniška (Chang et al., 2020; Fatehi et al., 2021; Hamza et al., 2022; Zhou et al., 2020). Literatūroje teigiama, kad nedegto molio medžiagų higroskopiškumo padidėjimas gali būti susijęs ne tik su hidrofilinėmis ar hidrofobinėmis įvairių polisacharidų savybėmis, bet ir su molio medžiagos struktūros modifikavimu (Muguda et al., 2020), nes didesnis vandens sugėrimas paaiškinamas mažesnių porų, pasiskirsčiusių molio kompozito struktūroje, buvimu. Taip pat literatūroje randama prieštaringų duomenų apie biopolimerų poveikį molio gaminių ilgaamžiškumui, vertinant vandens erozijos aspektu (Aguilar et al., 2016 m; Nakamatsu et al., 2017). Verta pabrėžti, kad molio tipas, mineraloginė ir cheminė sudėtis yra vieni iš svarbiausių parametrų, turinčių įtakos gautų medžiagų higroskopinėms savybėms ir atsparumui vandens erozijai (Cagnon et al., 2014).

Atlikta literatūros apžvalgos analizė parodė, kad panaudojant biopolimerus nedegto molio medžiagų gamyboje kartais gaunami prieštaringi gautų eksploatacinių savybių tyrimų rezultatai, be to nedaug dėmesio skirta biopolimero paruošimo technologiniams aspektams.

2. Eksperimentiniai ir tyrimo metodai

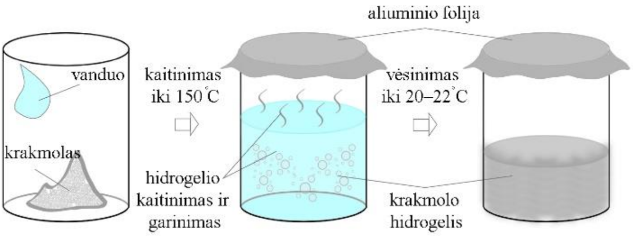
Šiame tyrime naudojamas molis yra Lietuvos vietovei būdingas hidrožėrutinis molis. Molyje yra 48,76 % SiO_2, 17,43 % Al_2O_3+TiO_2, 9,87 % CaO, 5,53 % Fe_2O_3, 4,57 % MgO ir mažesni kiekiai 2,24 % K_2O bei 0,42 % Na_2O. Nustatyta, kad molis sudarytas iš kvarco (17 %), ilito (62 %), lauko špato (12 %) ir kaolinito (9 %) mineralų. Molio mišiniams modifikuoti buvo panaudojami krakmolo, alginato ir chitozano biopolimerų tirpalai. Pagrindinis tokio modifikavimo principas – molio kompozitų gamybos proceso metu vanduo, reikalingas molio tam tikram plastiškumui užtikrinti, buvo pakeičiamas biopolimero tirpalu. Molio kompozitų su biopolimerais paruošimas pateiktas 1S lentelėje.

1S lentelė. Biopolimerų tirpalų ir molio kompozitų paruošimas

Step	**Apdorojimas karštu vandeniu**	**Apdorojimas šaltu vandeniu**	**Apdorojimas rūgšties tirpalu**
	Krakmolas	**Alginatas**	**Chitozanas**
1	Biopolimero sijojimas per sietą (d = 0,315 mm), kad būtų išvengta granulių susišokimo		
2	Krakmolas + karštas vanduo (temperatūra 90 °C) → maišymas (ne mažiau 2 min) → krakmolo gelio tirpalas (GSS)	Alginatas + šaltas vanduo (temperatūra 20 °C) → maišymas (ne mažiau 2 min) → alginato gelio tirpalas (GAS)	Chitozanas + 1M HCl vandens tirpalas (temperatūra 20 °C) → maišymas (ne mažiau 2 min) → chitozano gelio tirpalas (GCS)
	Pastaba: maišant neapdorotą biopolimerą su tirpikliu (vandeniu arba 1M HCl tirpalu), turi būti pasiektas didžiausias gauto tirpalo homogeniškumas		
3	GSS, GAS, GCS + molis → maišymas (ne mažiau 3 min) → → išlaikymas kambario sąlygomis 20-22 °C temperatūroje 24 h		
	Pastaba: vietoj vandens į molį įvedami GSS, GAS ir GCS tirpalai		
4	Prizminių/cilindrinių molio bandinių paruošimas		
5	Molio bandinių džiovinimas 20–22 °C temperatūroje 7–10 dienų, drėgmė 50–55 %		

Retrograduoto krakmolo hidrogelio (RSH) paruošimo technologija pateikta 1S pav. RSH buvo paruoštas naudojant tokią technologiją: tam tikros (2,5 %, 5 %, 7,5 % ir 10 %) koncentracijos krakmolas maišomas su karštu vandeniu (90 °C). Vėliau gautas krakmolo tirpalas buvo laikomas orkaitėje 150 °C temperatūroje 3 ar 5 valandas. Kai krakmolo hidrogelis kaitinamas ir vėliau atšaldomas, suardytos amilozės ir amilopektino grandinės vėl susijungia į labiau tvarkingą struktūrą (Wang ir kt., 2015). Retrograduoto krakmolo dalelės turi stambesnę struktūrą, dalelės „sluoksniuojasi“ ir skyla į mažesnes frakcijas (Lian ir kt., 2014). Retrogradacijos procese susidarius papildomiems vandeniliniams ryšiams, jungiasi daug krakmolo molekulių, dėl to susidaro sluoksniuotą struktūrą ir dėl to padidėja hidrogelio klampumas.

Molio mišinių su biopolimerų tirpalais charakteristikos pateiktos 2S lentelėje.



1S pav. Retrograduoto krakmolo hidrogelio paruošimas

2S lentelė. Molio mišinių su biopolimerų tirpalais charakteristikos

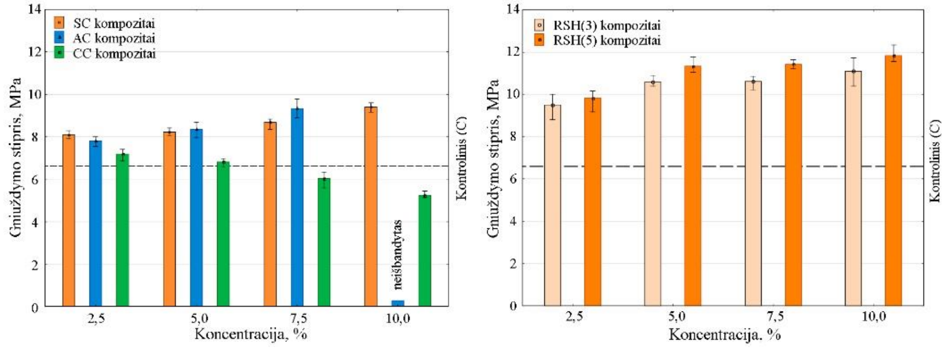
Mišinių kodas	Tirpalų charakteristikos			Molio mišinių charakteristikos	
	Biopolimerai	**Apdorojimas**	**Koncentracija, %**	**Skysčio kiekis, %**	**Mišinio plastiškumas**
Kontrolinis (C)	–	–	–	20,0	17,0–18,0
SC-2.5	Krakmolas	Apdorojimas karštu vandeniu	2,5		
SC-5			5	22,5	
SC-7.5			7,5		
SC-10			10		
AC-2.5	Alginatas	Apdorojimas šaltu vandeniu	2,5	20,0	
AC-5			5	22,5	
AC-7.5			7,5		
AC-10			10	25,0	
CC-2.5	Chitozanas	Apdorojimas rūgšties tirpalu	2,5	20,0	
CC-5			5	22,5	
CC-7.5			7,5		
CC-10			10		
RSH-2.5 (3)	Krakmolas	Retrogradacijos procesas (3 arba 5 val.)	2,5	20,0	
RSH-5 (3)			5	22,5	
RSH-7.5 (3)			7,5		
RSH-10 (3)			10		
RSH-2.5 (5)			2,5	20,0	
RSH-5 (5)			5	22,5	
RSH-7.5 (5)			7,5		
RSH-10 (5)			10		

Biopolimerų poveikis molio kompozito savybėms ištirtas taikant standartinius metodus, nurodytus tarptautiniuose ir nacionaliniuose standartuose (ASTM, ISO, LST EN, DIN ir kt.). Fizinės ir mechaninės savybės buvo įvertintos pagal LST EN 772-13:2003, LST EN 826:2013 ir ASTM C326-09:2014 standartus. Molio kompozito ilgaamžiškumas (atsparumas vandens erozijai) nustatytas remiantis *Geelong* metodu, nurodytu UNE R41410:2008 ir NZS 4298:1998 standartuose. Molio kompozitų higroskopiškumas nustatytas pagal ISO 24353:2008 ir ISO 12571:2013 standartus. Medžiagų struktūra ištirta naudojant skenuojančią elektronų mikroskopiją (SEM) ir rentgeno kompiuterinę tomografiją (XCT).

3. Biopolimerų poveikio molio kompozitams tyrimai

Atlikus tyrimus nustatyta, kad padidėjus bioplimerų (krakmolo, alginato ir chitozano) koncentracijai tirpaluose nuo 2,5 % iki 10 % (geliavimo procesas) molio kompozitų tankis sumažėjo nuo 1 % iki 9 %. SC molio kompozitų tankis sumažėjo nuo 2030 kg/m^3 iki 1940 kg/m^3, AC molio kompozitų tankis sumažėjo nuo 1970 kg/m^3 iki 1855 kg/m^3 ir CC kompozitų tankis sumažėjo nuo 1940 kg/m^3 iki 1810 kg/m^3. Tačiau, panaudojant retrograduotą krakmolo hidrogelį (RSH, retrogradacijos procesas), molio kompozitų tankis padidėjo iki 2,5 %, nuo 1990 kg/m^3 iki 2040 kg/m^3. Molio kompozitų, panaudojant RSH, tankio padidėjimą galima paaiškinti krakmolo struktūros „šiurkštumu“ po retrogradacijos proceso. Retrogradacijos procesas yra susijęs su krakmolo grūdelių kietumo, rišlumo ir lipnumo didėjimu, nes keičiasi jo molekulinė struktūra (Anbarani et al., 2021). Taip pat pagerėja sukibimas tarp molio dalelių ir RSH, nes RSH yra linkęs užpildyti kai kurias molio kompozito poras, dėl to padidėja RSH 2,5 – RSH 10 molio kompozitų tankis.

Molio gaminiai yra labai jautrūs susitraukimui ir tai gali būti problema gaminant nedegto molio medžiagas. Kontrolinio molio kompozito susitraukimas (*C-sample*) yra 6,2 %. Biopolimero (krakmolo), panaudojant skirtingas paruošimo technologijas (geliavimo ir retrogradacijos procesai), įterpimas sumažina molio kompozitų susitraukimą nuo 5,4 % iki 3,7 %. Taip pat, biopolimero koncentracijai tirpale padidėjus nuo 2,5 % iki 10 % (geliavimo procesas) AC molio kompozitų susitraukimas sumažėjo nuo 6,1 % iki 4,3 %, CC molio kompozitų susitraukimas sumažėjo nuo 5,6 % iki 5,1 %. Nustatyta, kad panaudojant skirtingus biopolimerus ir jų paruošimo technologijas, visų gautų molio kompozitų susitraukimas yra mažesnis nei kontrolinio molio kompozito. Savybių, tokių kaip tankis ir susitraukimas, kitimas gali būti siejamas su optimaliu drėgmės kiekiu formavimo mišiniuose. Didėjant biopolimero koncentracijai tirpale, sumažėja laisvo vandens kiekis, tai lemia molio mišinių plastiškumą formavimo etape. Taigi, norint pasiekti optimalų plastiškumą, skysčio (biopolimero tirpalo) kiekį molio mišiniuose reikia keisti, tą patvirtina molio mišinio charakteristikos, pateiktos 2S lentelėje.

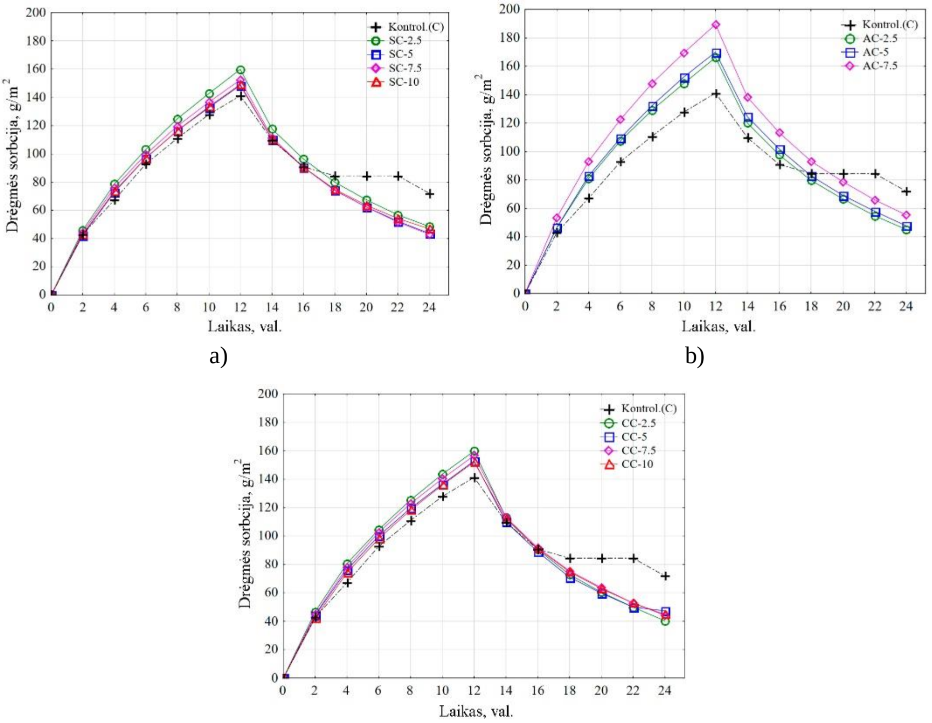


a) b)

2S pav. Molio kompozitų gniuždymo stipris: a) modifikuotas krakmolo, alginato ir chitozano tirpalais; b) modifikuotas retrograduotu krakmolo hidrogeliu

Atlikti tyrimai parodė, kad molio kompozitų gniuždymo stipris, padidinus krakmolo ir alginato koncentraciją biopolimerų tirpaluose nuo 2,5 % iki 10 %, didėja. SC kompozitų gniuždymo stipris padidėjo nuo 21 % iki 42 %, AC kompozitų gniuždymo stipris padidėjo nuo 18 % iki 40 %, palyginti su kontroliniu molio mišiniu. Padidinus chitozano koncentraciją biopolimero tirpale, CC molio kompozitų stiprumas sumažėjo 19,7 %, palyginti su kontroliniu mėginiu (2S pav., a). CC molio kompozitų stipruminių savybių sumažėjimas siejamas su silpna biopolimero bei molio dalelių sąveika, tą patvirtina atlikti molio kompozito mikrostruktūros tyrimai (6S pav.) Pridėjus retrograduoto krakmolo hidrogelio RSH (3), RSH (5) molio kompozitų gniuždymo stipris žymiai padidėjo nuo 40 % iki 72 % (2S pav., b). Gniuždymo stiprio padidėjimą gali lemti homogeniškesnė molio kompozitų struktūra (7S pav.), naujų vandenilinių jungčių susidarymas molio/RSH struktūroje, taip pat pusiau kristalinės krakmolo struktūros susidarymas retrogradacijos proceso metu, ką patvirtina ir kitų autorių atlikti darbai (Soni et al., 2020; Lian et al., 2014; Zhang et al., 2007; Buleon et al., 1998; Cornejo-Ramirez et al., 2018; Wang et al., 2015).

Molio kompozitų drėgmės buferinis pajėgumas buvo išreikštas sorbcijos izotermomis parodytomis 3S pav., a–c. Didžiausioji kontrolinio mėginio adsorbcijos vertė lygi 141,1 g/m^2 (3S pav., a–c).



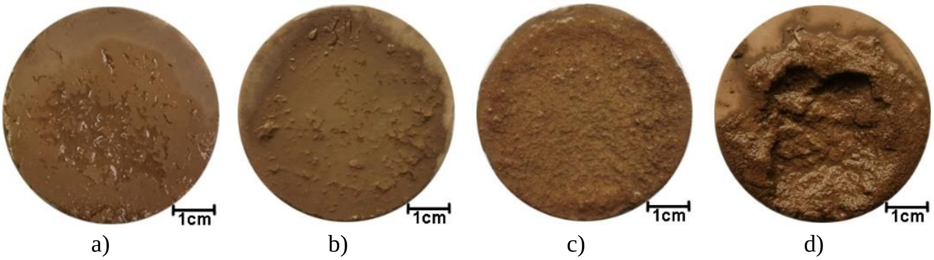
a) b)

c)

3S pav. Higroskopinė molio kompozitų buferinė talpa: a) SC kompozitai; b) AC kompozitai; c) CC kompozitai

Krakmolo ir chitozano tirpalais modifikuotų molio kompozitų didžiausios adsorbcijos vertės yra panašios ir siekia 159,8 g/m^2 (SC−2,5 ir CC−2,5 molio kompozitai). Molio kompozitų, modifikuotų alginato biopolimero tirpalais, sorbcijos izotermos pateiktos 3S pav., b. Didžiausioji adsorbcijos vertė siekia 189,4 g/m^2 (AC−7,5 kompozitas). Molio kompozitų AC−2,5 ir AC−5 adsorbcijos vertės yra 166,1 g/m^2 ir 169,9 g/m^2, šios vertės yra didesnės nei SC ir CC molio kompozitų adsorbcijos vertės. Didesnės alginatu modifikuotų molio kompozitų padidėjusio adsorbcijos vertės įrodo molio kompozitų padidėjusį paviršiaus hidrofiliškumą. Molio kompozitų, stabilizuotų retrograduotu krakmolo hidrogeliu (RSH), adsorbcijos vertės yra 141,11−180,00 g/m^2 ribose. Didžiausioji adsorbcijos vertė nustatyta RSH 2,5(3) molio kompozitui ir siekia 180,00 g/m^2. Gauta vertė 27 % didesnė palyginti su kontroliniu molio kompozitu. Visi molio kompozitai modifikuoti RSH parodė geresnes higroskopines savybes nei kontrolinis mėginys, nes RSH priedas iš dalies užpildo molio kompozito poras ir kapiliarus (7S pav.), o mažesnės, priešingai nei didelės, poros daro įtaką didesnei sorbcijai ir higroskopiškumui (Rode & Grau, 2008; McGregor et al., 2016). Pagal DIN 18947:2013 standartą, visi tirti molio kompozitai atitinka WC−3 adsorbcijos klasę, jų adsorbcijos pajėgumas didesnis nei 60 g/m^2 per 12 val. Atlikti tyrimai įrodo, kad visi tirti molio kompozitai gali būti naudojami uždarose patalpose, nes pasižymi puikiomis higroskopinėmis savybėmis ir gali puikiai reguliuoti vidaus patalpų mikroklimatą.

Atlikus molio kompozitų ilgaamžiškumo (vandens erozijos bandymas) tyrimus (4S pav., a−d), nustatyta, kad kontrolinio molio bandinio paviršius turi tam tikrus atsiradusius defektus (4S pav., a), t. y. tiesioginio vandens poveikio bandinio paviršiuje matomas medžiagos atsisluoksniavimas, tačiau vis dėlto mėginio struktūra išlieka nežymiai pakitusi, didelių erozijos defektų (≥ 0,5−1 mm gylio duobučių) nėra. SC−2,5 molio kompozito paviršiuje nežymių defektių atsiranda dėl molio „dribsnių“ atsisluoksniavimo proceso, tačiau šie defektai nėra dideli (≥ 0,1 mm gylio), struktūra išlieka nežymiai pakitusi (4S pav., b). Nustatyta, kad po vandens erozijos tyrimo AC−2,5 molio kompozito paviršiuje atsiranda didesnė paviršiaus erozija, palyginti su kontroliniu bandiniu, matomas didelis bandinio paviršiaus „pleiskanojimas“ (4S pav., c). Šiuo atveju paviršiaus erozijos padidėjimas gali būti siejamas su molio kompozito, panaudojant alginato ir biopolimero tirpalą, hidrofiliškumo padidėjimu. Mažiausią ilgaamžiškumą, atsparumą vandens erozijai turi kompozitas, modifikuotas chitozano tirpalu (CC−2,5 kompozitas). Ant bandinio paviršiaus susidaro 0,5–2,5 mm gylio duobutės, kurios užima apie 40 % bandinio ploto, o tai labiausiai atitinka NZS 4298:1998 standarto aprašą, apibūdinantį „gilios duobės“ formavimąsi (4S pav., d).



a) b) c) d)

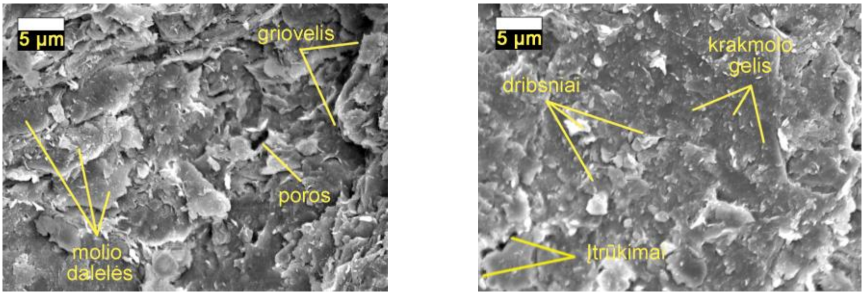
4S pav. Molio kompozito paviršius po vandens erozijos bandymo: a) kontrolinis molio kompozitas; b) SC-2,5 kompozitas; c) AC-2,5 kompozitas; d) CC-2,5 kompozitas

Didžiausią atsparumą vandens erozijai parodė molio kompozitai, modifikuoti retrograduoto krakmolo hidrogeliu RSH (3) ir RSH (5), nes krakmolo restruktūrizavimo retrogradacijos procese biopolimeras tapo hidrofobinis, todėl molio kompozito ilgaamžiškumas (atsparumas vandens erozijai) itin didėja, paviršiuje nesimato jokių erozijos požymių (5S pav.).

a) b)

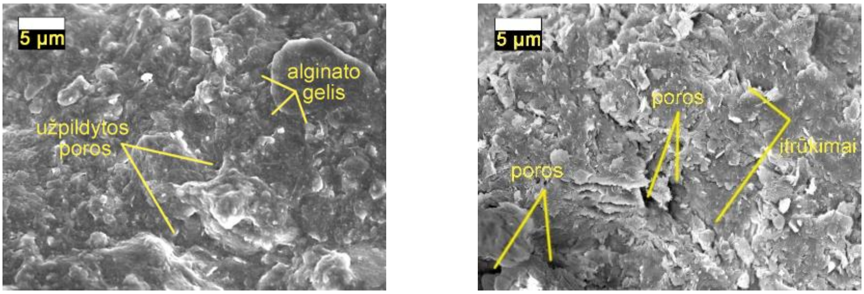
5S pav. Molio kompozito paviršius po vandens erozijos bandymo:
a) RSH-2,5(3) kompozitas; b) RSH-2,5(5) kompozitas

6S pav., a–d, parodyta molio kompozitų, modifikuotų maksimalios koncentracijos biopolimeriniais tirpalais (SC–10, AC–10, CC–10 molio kompozitais), bei kontrolinio molio mėginio mikrostruktūra. Kontrolinio bandinio struktūroje matoma (6S pav., a), kad ilito plokštelės išsidėstė chaotiškai tarp jų matomos mikroporos, kurių dydis svyruoja nuo 1 μm iki 5 μm. Krakmolo tirpalu modifikuoto kompozito paviršiaus struktūra (6S pav., b) yra lygesnė, homogeniškesnė nei kontrolinio bandinio, mikrostruktūroje nėra gilesnių, didesnių porų, griovelių ar duobučių, matomos poros tolygiai pasiskirsčiusios, jų dydis yra apie 1–3 μm. 6S pav., c, parodyta molio kompozito modifikuoto 10 % alginato tirpalu mikrostruktūra. Alginato tirpalas puikiai padengia molio plokšteles, užpildo visus struktūros nelygumus, poras ir tarpus, struktūra tampa daug homogeniškesnė, palyginti su kontrolinio bandinio struktūra. Molio kompozito struktūra, modifikuota chitozano tirpalu, yra grubesnė, mažiau homogeniška, palyginti su SC ir AC molio kompozitų struktūromis, taip pat matomos didesnės poros bei defektinės vietos.



a) b)

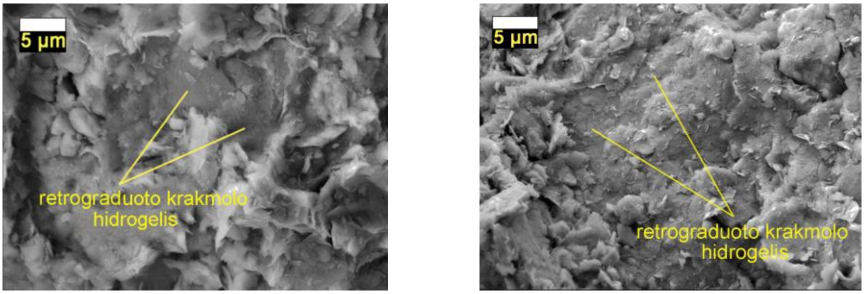
6S pav. tęsinys kitame puslapyje



c) d)

6S pav. Molio kompozitų mikrostruktūra (x3000): a) kontrolinis molio kompozitas; b) SC-10 kompozitas; c) AC-10 kompozitas; d) CC-10 kompozitas

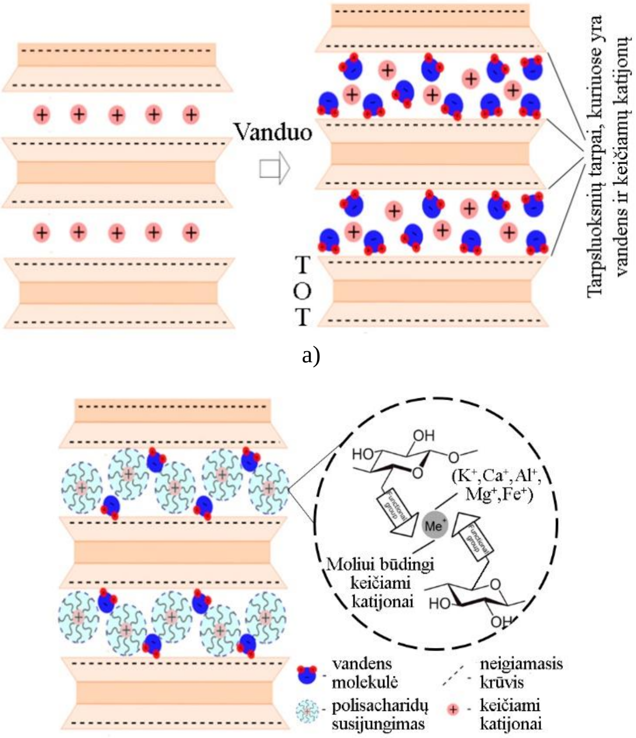
RSH 10(3) molio kompozito struktūros paviršiuje (7S pav.) yra plonas smulkiai dispersinis RSH sluoksnis, kuris išlygina struktūrą, padengia molio daleles, todėl struktūra tampa homogeniška, be matomų didelių ar gilių porų. Dėl koloidinių molio ir RSH savybių hidrogelis gali užtikrinti geresnę molio dalelių sanglaudą (Shaikh et al., 2017) bei iš dalies užpildyti poras ir struktūrinius defektus, nes paprastai polisacharidai turi geras sorbcines savybes, tą patvirtino gauti tyrimų rezultatai, ir stiprią mikrostruktūrinę sąveiką su moliu (Chenu, 1993; Shaikh et al., 2017). Ilgesnės molekulinės biopolimerų grandinės gali apsivynioti aplink molio daleles, taip koaguliuodamos jo struktūrą (Chang et al., 2015). Ši prielaida iš dalies paaiškina gautus molio kompozitų, modifikuotų biopolimerais, panaudojant skirtingas paruošimo technologijas, mikrostruktūros tyrimus (6S pav., 7S pav.).



a) b)

7S pav. Molio kompozitų mikrostruktūra (×3000): a) RSH-2,5(3) kompozitas; b) RSH-10(3) kompozitas

Atlikus šį mokslinį darbą nustatyta, kad molio modifikavimas biopolimerais turi įtakos molio kompozito struktūrai ir savybėms. Gautas efektas gali būti siejamas su naujų vandenilinių jungčių formavimusi molio kompozitų struktūroje, taip pat su Van der Valso jėgų, užtikrinančių stabilias „molio ir biopolimero“ sąveikas, susidarymu. Molio modifikavimo biopolimerais (krakmolu, alginatu, chitozanu), priklausomai nuo paruošimo technologijos, mechanizmas pateiktas 8S pav.



a)

b)

8S pav. Hidrožėrutinio molio struktūros modifikavimas biopolimeriniais tirpalais:
a) klasikinė hidrožėrutinio molio struktūra (pagal Brigatti et al., 2013);
b) molio ir polisacharido sąveikos principas (remiantis dabartiniu tyrimu)

Kairėje yra tipiška 2:1 ilitinio molio struktūra, kai vienas oktaedrinis sluoksnis (O) įsiterpia tarp dviejų tetraedrinių sluoksnių (T) (Brigatti et al., 2013). Keičiami katijonai ir vandens molekulės yra tarpsluoksnio erdvėje (8S pav., a). Pagrindinis molio modifikavimo principas šiame darbe reiškia visišką vandens pakeitimą biopolimerų geliniais (krakmolo, alginato ir chitozano) tirpalais arba retrograduotu krakmolo hidrogeliu (RSH). Taigi, galima daryti prielaidą, kad molio ir biopolimerų vandeninio tirpalo pavidalu sąveika gali atsirasti tarpsluoksnyje, kuriame yra keičiamų katijonų, būdingų naudojamam moliui (8S pav., b).

Remiantis literatūros šaltiniais ir atlikta analitine analize, galima daryti prielaidą, kad krakmolo ir alginato biopolimerai gerai sąveikauja su Ca^{2+} ir Mg^{2+} katijonais, chitozanas gali sąveikauti su Fe^{2+} katijonais. Taip pat biopolimerų poveikis molio modifikavimui gali priklausyti nuo molio žaliavų cheminės ir mineraloginės sudėties. Pagal cheminę sudėtį tirtame molyje yra iki 15 % kalcio ir magnio turinčių oksidų (CaO − 9,87 %, MgO − 4,57 %), kurie gali teigiamai paveikti molio ir krakmolo bei alginato tirpalų sąveiką. Tuo pačiu metu bendras geležies turinčių oksidų (Fe_2O_3) kiekis nėra pakankamas, kad užtikrintų tinkamą molio ir chitozano tirpalo sąveiką.

Bendrosios išvados

1. Sąveikaudami su hidrožėrutiniu moliu biopolimerai (polisacharidai − krakmolas, alginatas, chitozanas), priklausomai nuo jų paruošimo technologijos (biopolimerų geliavimo, krakmolo retrogradacijos procesai), gali sudaryti naujus vandenilinius ir elektrostatinius ryšius su tirto molio paviršiais. Biopolimerai, tokie kaip krakmolas ir alginatas, gerai sąveikauja su Ca^{2+} ir Mg^{2+} katijonais, kurie būdingi tirtam hidrožėrutiniam moliui. Chitozanas parodė mažiau veiksmingą sąveiką su tirtu moliu dėl riboto geležies turinčių oksidų buvimo molio sudėtyje. Adsorbuoti biopolimerai (krakmolas ir alginatas) modifikuoja ir keičia molio paviršiaus struktūrą, taip paveikdami molio kompozitų savybes.
2. Molio kompozitams modifikuoti panaudojant krakmolo ir alginato (koncentracija tirpale atitinkamai 10 % ir 7,5 %) biopolimerus (geliavimo procesas), molio kompozitų gniuždymo stipris padidėjo 40 %, palyginti su kontroliniu molio kompozitu; 2,5−10 % retrograduotas krakmolo hidrogelis (retrogradacijos procesas) molio kompozitų stiprumą gniuždant padidina 40−74 %. Todėl minėti kompozitai pagal DIN 18945:2013-08 standartą gali būti priskirti 5 klasei (laikančiosios sienos, vidinės sienos), nes jų gniuždymo stiprio vertė viršija 6,3 MPa.
3. Biopolimerų (polisacharidų – krakmolo, alginato, chitozano), panaudojant skirtingas paruošimo technologijas (biopolimerų geliavimo, krakmolo retrogradacijos procesas), naudojimas padidina molio kompozitų paviršiaus drėgmės adsorbciją nuo 13% iki 34%. Drėgmės adsorbcijos padidėjimą gali lemti naujos vandenilinės jungtys molio medžiagų struktūroje. Pagal DIN 18947:2013 standartą visi tirti molio kompozitai atitinka WC−3 adsorbcijos klasę (t. y. „puiki“ drėgmės adsorbcija), nes adsorbcijos greitis didesnis nei 60 g/m^2 per 12 val. (gauti molio mišiniai tinka apdailos medžiagoms gaminti, pvz., molio tinkas).
4. Biopolimero tipas ir skirtinga paruošimo technologija stipriai veikia molio kompozito atsparumą vandens erozijai, nes adsorbuotos biopolimero molekulės gali padaryti molio paviršių labiau hidrofilinį arba hidrofobinį. Alginato ir chitozano panaudojimas sumažino molio kompozito atsparumą vandens erozijai dėl tokių biopolimerų hidrofiliškumo. Retrograduoto krakmolo hidrogelio įterpimas žymiai padidino molio kompozito ilgaamžiškumą dėl biopolimero hidrofobinio pobūdžio po retrogradacijos proceso.

Yahor TRAMBITSKI

RESEARCH OF STRUCTURE AND DURABILITY OF NATURAL POLYMER MODIFIED CLAYS

Doctoral Dissertation

Technological Sciences,
Materials Engineering (T 008)

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NATŪRALIAIS POLIMERAIS MODIFIKUOTO MOLIO STRUKTŪROS IR ILGAAMŽIŠKUMO TYRIMAI

Daktaro disertacija

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Lietuvių kalbos redaktorė Dalia Markevičiūtė
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Vilniaus Gedimino technikos universitetas
Saulėtekio al. 11, 10223 Vilnius,
Spausdino UAB „Ciklonas“,
Žirmūnų g. 68, 09124 Vilnius