Natural and Synthetic Polymers Used in the Preservation of Historical Stone Buildings

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Abstract. In this review, the rules applicable to the preservation of stone monuments, referring both to the selection of appropriate materials (compatibility principle) as well as the repair process itself was discussed. A wide range of natural and synthetic polymers used for reconstruction purposes has been described. An example of the use of polymers for hydrophobization treatment of historic stone structures at one of the archaeological sites in Tyritake, Russia, carried out by Civil Engineering Faculty of the Warsaw University of Technology is also presented.

1. Introduction

Preservation of stone masonry monuments, a part of the architectural and structural heritage, is frequently focused on protection or, in case of severe damaged materials, recovery actions. Such a treatment is particularly necessary for structures that are a part of archaeological excavations or of archaeological open-air museums. Those monuments usually require strengthening of an internal structure of individual stones, as well as a whole masonry components (such as walls, vaults, etc.). The main issue that the treatment addresses is a protection against the degradation that may come from several origins, such as natural environment or nature of service. The most common structures and materials that appear in archaeological tranches are highly degraded due to their age and long-term influence of destructive agents, such as: environment or climate impact, biological or mechanical deterioration or, in case of better preserved structures, an inadequate maintenance. In all of this actions, both strengthening and protection of masonry monuments, polymers have some important auxiliary function. They are not only ingredients that improve the properties of repair mortars but also materials that are used for consolidation of deteriorated stone as well as hydrofobization.

Masonry is a structure that is composed of masonry units (e.g. sorted or unsorted stones, semiregular units or regular units - ashlars or blocks) that originate from different rocks with various physical, chemical and mechanical characteristics. The units are assembled in a proper way (in a specific pattern called masonry bond) and, usually but not necessarily, joined together with mortar. Taking into consideration that the ancient masonry is usually in severely damaged conditions, the given definition of masonry implicates a complexity of conservation. Based on the type of masonry and the masonry bond, the degradation can refer to overall structure, its internal or external composition, the failure of a mortar’s adhesion or even failure of each masonry units (in case of an ancient masonry a frequently observed phenomenon is a granular disintegration of masonry units). An
irregular or semiregular masonry, that consists of small unsorted stone units, are usually internally consolidated with a low strength mortar, in which an easily accessible material (such as lime, clay or gypsum) is used as a binder. The mortar is the masonry component that features the biggest influence on structural durability. The above mentioned, low strength mortars have also low durability and internal integrity. Hence, the irregular masonry is vulnerable to the weather influence, such as rainfalls, snowfalls or subzero temperatures. The regular masonry (e.g. ashlar masonry) is usually more durable since its integrity mostly depends on physical and chemical characteristics of stones that were used for masonry units.

The conservation work should be preceded by a proper diagnostic phase. It should result not only from the assessment of the technical conditions of the structure and its components (mortar and masonry units), but also from the analysis of the physical, chemical and mechanical characteristics, as well as from the identification of the bricklaying technique and the masonry bonds. Then the proper conservation technique can be applied. Those interventions can address one or more of three different aspects – repair, strengthening or protection. Among those actions, the following could be specified:

- reprofiling - reprofiling of existing masonry parts with the anastylosis method (recreation of a structure with all original elements and identical to its original shape). Masonry reprofiling should be carried out in four main stages. First, the top layer of the structure is rebuilt. In the next two steps, a finishing mortar is placed to a fresh grout (pointing) and, after hardening, the joints are again complimented with a finishing mortar. The final action is mechanical cleaning.
- bonding - integration of internal wall structure by injection method;
- reconstruction using anastylosis or semianastylosis method (recreation of a structure with all original elements but not identical to its original shape);
- hydrophobization. [1,2,3]

In the preservation of stone masonry monuments the following principles must be applied:

- compatibility of materials – all materials used in conservation activities should have the same (or similar) mechanical and physical properties as the original one;
- reversibility of methods and materials - all conservation activities should be carried out in such a way and using such materials that can be removed in the future, restoring the original state;
- distinctiveness - not original materials cannot dominate over the original one and have to be clearly distinguished. [4,5]

2. Natural Polymers

Since ancient times, a range of natural additives has been used to improve the properties of mortars. The simplest were chopped straw and various types of plant fibers [6], which increased mortar resistance to shrinkage cracking and mechanical damage. The reinforcement material was cellulose, composed of polysaccharide chains, which form microfibrils bound together by amorphous lignin and hemicellulose. The individual cellulose microfibrils are few nanometers in diameter being aggregated into bundles and macrofibrils that constitute complex multilayered structure of plant cell wall [7]. Accordingly to results described in [6] the addition of a nopal, both as powder and as mucilage, results in an increase of the mechanical resistance by a factor of 1.5 in comparison to the reference sample.

In addition to fibrous reinforcing materials, naturally occurring polysaccharides, proteins and fats were also used, such as dairy products, eggs, cereals, animal blood, glutinous rice, oils and fruit pulp [8]. Proteins contained in the blood could control the crystal growth and form a compact skin layer on the surface of hardening render. They might act as setting retarders through a complexation of calcium ions. Also, proteins played a role of air-entraining agents and improved the adhesiveness as well as hydrophobic properties of cement mortar [9,10].

Dairy products such as milk, curd and whey have been added to mortars since ancient times. Casein, the main phosphoprotein of bovine milk, may act as plasticizer or stiffening agent, improving the workability and consistency of cementitious mortars [11].
Egg white was detected in the ancient traditional mortar, widely used in different areas in China [12]. The study of Mydin showed that the addition of up to 6 % egg white increases the workability, compressive and flexural strength of lime mortar. This was attributed to the acting of egg proteins as a lubricant making the mortar easier to compact and filling the smaller voids inside the mortar [13].

The types of natural additives containing polysaccharides used in mortars are mainly the result of their availability in a given region. An example of some additive used as architectural material in ancient China was sticky rice [14]. By its introduction the physical properties, mechanical strength, and compatibility of lime mortar were significantly improved. An analytical study showed that amylopectin, highly branched polymer of glucose, was the rice ingredient responsible for the strength and durability of the mortar used to build the Great Wall and Tomb of Deng Count from the Southern and Northern Dynasty (420–589 AD). Amylopectin acted as an inhibitor, resulting in controlled growth of the calcium carbonate crystal with formation of microporous structure. The advantage of using sticky rice compared with other natural additives (brown sugar, tung oil) was its lower cost, easier transport and storage [15].

Other natural additive used regionally in Mexico is cactus juice extracted from the Opuntia ficus-indica. The advantage of cactus based admixtures is their biodegradability, non-toxicity and high availability in different parts of the world. Using the mucilage from cactus as additive allows to improve mechanical, physical and strength properties of lime, especially compressive and bending strength as well as hydrophobicity [16].

In India leaves, previously left to rot, were mixed with clay and lime. They contained a number of ingredients beneficial from the viewpoint of the mortar properties, including wax, increasing the resistance to water sorption and fibers protecting the matrix from cracking. As a result, a material with increased strength and durability was obtained [17]. Another studies were performed to investigate the influence of incorporation of Cissus glauca Roxb, a trailing herb that was historically used also in several regions of India [18]. The results of the investigation show the increase of the compressive and flexural strength. Due to hydrophobicity offered by the admixture, the water absorption was reduced by almost 20%. It also resulted in the blockade of the capillary pores, which reduce the capillarity suction and can protect structures from the damage due to rain or the other weathering agents. Moreover, the hydrophobic properties result in a reduction of salts penetration and the associated damages.

Natural oils and fats were among the most common types of water-repellent additives used in mortars in the antiquity. As it was shown in [6], olive oil used as additive reduces the pore size and results in a hydrophobic mortar with significantly improved water resistance. The mortar with added tung oil was often used to fill gaps in wells, tombs or wooden boats, protecting them against water leakage. Beeswax, vegetable oils, paraffin or ceresin are often used in conservation practice, providing the hydrophobic properties to protected stone elements. Because of high elasticity and low mechanical resistance, they do not have a destructive effect on the stone (different coefficient of thermal expansion) [19].

3. Synthetic Polymers
Among the synthetic polymers used for conservation, the most employed are epoxy and acrylic polymers, organic silicones as well as fluoropolymers, differing in their properties and their impact on treated objects. [20]

Epoxy resins can effectively penetrate and seal porous substrates, when polymerized they form a crosslinked network with outstanding mechanical strength. The first reports on the use of epoxy-amine systems for the consolidation of deteriorated stone were published in 1960s [21]. Since then, various epoxy systems in the form of solutions or dispersions, containing plasticizers, fillers and pigments have been applied to in the conservation of stone materials [22,23]. The most extensively used epoxy resins are based on aromatic monomers such as bisphenol A (dian) and its oligomers, which are characterized by a favorable ratio of strength to the amount of introduced resin. However, the use of
dian resins is limited due to their low resistance to light exposure. Aliphatic and cycloaliphatic resins as well as polyglycidyl esters of cyclic alcohols and acids do not exhibit this drawback. Polyglycidyl esters have lower viscosities compared to the dian resins, which is related to the ease of penetration into the porous material for comparable reinforcing efficiency. Although not containing UV-sensitive aromatic groups, cycloaliphatic epoxy polymers may suffer gradual photodegradation, discoloration and cracking as it was shown both in natural and artificial aging investigations. FTIR analyses indicated that a degradation mechanism involves the opening of cyclic structures, chain scissions, and hydrogen abstractions from the polymer backbone [24]. Another way to overcome the limitations of epoxy resins are hybrid systems such as epoxy-silica materials based on glycidoxy functional silanes [25] or tetraethoxysilane (TEOS) added to polysiloxane epoxy resin [26]. TEOS plays a dual role, reducing the viscosity of the formulation and contributing to the mechanical properties of the film without causing cracking.

Acrylic polymers are frequently used for the preservation of monuments, primarily for strengthening stone elements and filling cavities [27,28]. The most important are copolymers of acrylic and methacrylic acid esters as well as polymethyl methacrylate and butyl polymethacrylate, i.e. thermoplastic polyacrylates. They are characterized by good solubility in organic liquids, excellent transparency, resistance to light, moisture and microorganisms. A biodegradable polyester, high molecular weight poly(lactide) was used as protective coating on marble reducing gypsum formation on marble surfaces in the polluted environment [29]. A very promising direction of research is application of hybrid coatings containing nanoparticles mixed with commercial polymers, that can produce superhydrophobic surfaces [28]. Amphiphilic block copolymers synthesized from acrylic monomers by means of the RAFT controlled polymerization method are combined with inorganic nanoparticles, (including UV-blocking titania and zinc oxide) resulting in hybrid nanocomposite materials for either protective or consolidating treatments of stone. The preliminary tests of colloidal polymer dispersions applied onto sandstone and marble surfaces showed that very low amounts of the applied polymer are sufficient to make the stone surface hydrophobic [29].

Among the silane derivatives, the most important are alkylsilanes, more specifically tetraalkoxysilane and the products of its partial condensation. They are basic components of the compositions for reinforcing porous materials, on the other hand they are not able to provide any hydrophobic properties (the resulting silica is hydrophilic). The effect of hydrophobization can be obtained using alkyltriethoxysilanes, e.g. methyltriethoxysilane. The resulting polysiloxane is bound with the inorganic substrate in such a way that the alkyl groups are directed upwards [30].

In the conservation practice, silicone microemulsions based on alkoxy and alkyl alkoxy silanes as active substances are often used, especially for hydrophobization. An additional effect of material strengthening may occur when using some emulsions, however, this is not the main goal of their application. Recent advances in alkoxy silane-based consolidants for stone were reviewed by Xu et coworkers. [31]. Many studies have been devoted to preventing the cracking of silica gel formed by the hydrolysis of silane. One of the successful approaches was introducing elastic segments by incorporation of low molecular weight hydroxyl-terminated polydimethylsiloxane (PMDS-OH). Other solutions include reducing capillary pressure by adding a surfactant or using nanoparticles to increase gel pore diameter.

Also, silicone resins are used in the conservation of stone buildings, primarily for the hydrophobization of porous materials. Usually, these are modified poly (dimethyl-siloxanes), soluble in aliphatic hydrocarbons, and their cross-linking takes place under the influence of moisture, due to the presence of groups reacting easily with water. Siliconates were also used to preserve monuments, but the problem was a large amount of by-products in the form of sodium and potassium carbonate, which damages the stone [32].

Fluoropolymers are organic polymers containing carbon-fluorine bonds, which results in increased resistance to decay factors. For conservation of stone elements, fluorinated oils, i.e. perfluorovinylether polyethers with low degree of polymerization are of the largest importance. They are characterized by significant chemical and biological resistance as well as hydrophobicity. For
some time, fluorinated polyamides and polyurethanes were also used, which in addition to hydrophobicity and oxidation resistance, have good adhesion to stone substrates [33].

4. Example of application

As an example of an application of polymers in conservation of ancient masonry, we present hydrophobization treatment, that was applied in the Tyritake archaeological site in the city of Kerch (Crimea) (Figure ). The conservation works were conducted as a part of the international project “The Bosporan City Tyritake” which included not only the archaeological research but also a comprehensive geological, urban, paleozoological and paleobotanical analysis of the ancient city territory. The leading organization of the Polish Archeological Campaign was the National Museum in Warsaw and the conservation work was handled by the Civil Engineering Faculty of the Warsaw University of Technology in years from 2011 to 2013 [1,2,3].

Figure 1. View over the trench no. 27 at Tyritake archaeological site in Kerch (Crimea)

The conserved structures were irregular stone masonry walls constructed between 5th century BC and 5th century AD. As a result of the wide time spread and different functions of conserved masonry the applied technology varies from a single-leaf irregular masonry, through a double-leaf irregular masonry to a triple-leaf masonry with relatively massive stones in the facades and rubbles with mortar as an infill. The masonry were made mostly of crushed limestones bonded with a clay mortar. This kind of structures and materials are recognized for their low internal cohesion, hence a low durability and vulnerability to weather conditions. The maintenance and conservation work was mostly oriented on a consolidation of the existing structures with partial reconstructions by anastylosis or semi-anastylosis. Due to the severe weather conditions, such as heavy rains and temperatures below 0°C, the necessity of an external surface hydrophobization of the conserved structures was stated [1,2].

Prior to the wide-range application of the treatment, the preliminary tests were performed. The tests were composed of applications of various commercially available agents on the different types of masonry units used in the analysed structures. Such an approach can prevent from any damages or alteration that can occur on the surface of an authentic historical construction. The masonry units selected to the preliminary test differed in the shape, but most of all in the porosity, that was representing diversity of masonry units used in the analysed structures (Fig). The examined agents were two different siloxane solutions and water-alcohol solution of vinyl-versatate copolymers. The solutions were applied on the parts of selected masonry units and left at the exposure to the local weather condition for one year. After that period the results of the application were investigated. The two applied agents were excluded from the further tests due to the influence on the masonry units’
surface, such as a change of the surface colour. The reaming with oligomer siloxane solution was applied to the selected masonry walls in the archaeological site (Figure )

![Figure 2. Examples of samples for determination of the influence of hydrophobization treatment on masonry units and environmental durability.](image)

The performance of the hydrophobization treatment was measured by comparison of absorptivity of the impregnated masonry with the non-impregnated one. The measurement was performed with Karsten’s pipe (Figure ) and the results are presented in Figure . As it could be clearly seen on the graph, the water absorption of the impregnated masonry stopped after 30 minutes and was equal to 2.5 ml in contrary to the absorption of non-impregnated surface that was still active and equal to 12 ml after the same time.

![Figure 3. Masonry in trench no. 27 of Tyritake archaeological site in Kerch (Crimea) during: the hydrophobization treatment (on the left) and the performance measurement (on the right).](image)

![Figure 4. Water absorption of impregnated and nonimpregnated masonry.](image)
The performed test showed a good performance of the applied treatment. However, the durability of this solution should be examined in details. This kind of protection is considered as not permanent one and the losses of impregnation performance should be followed by repetition of treatment.

5. Conclusion
Conservation of ancient stone masonry structures is a complicated and complex issue due to the diverse structure of the walls and various properties of the materials from which they are made. It has a significant impact on the durability of the structure and degree of their preservation in archaeological parks. Natural polymers have been widely used in constructions, improving their physical and mechanical properties, thus their application for conservation is favourable. However, it requires understating of a process that drives the enhancement and that is why the studies of natural polymer additives should be continued. Nowadays, synthetic polymers are often used, mainly for reinforcing and hydrophobization activities, preserving the need for a limited and reversible effect on the structure of the primary material. The application at Tyritake archaeological site in Kerch has proved that the hydrophobization treatment is effective, but in order to ensure its durability some fixation treatments, most often by repetition of treatment, are necessary. The use of synthetic polymers in the preservation of stone masonry structures is a promising activity. The introduction of new materials and technologies requires further research, in which attention must be paid to the principles of selection of the materials with respect to the originally used, historical material.

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