New Generation of Clay Plasters Stabilized by Polymers

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Abstract. This article is dedicated to the use of unburnt clay, specifically as a material to produce clay plaster and they stabilization via polymers. The main goal is to enhance the attributes of a clay plaster through the stabilization of various polymers, alternatively by combining the polymer with hydrophobization in different ratios. Stabilization is particularly important for exterior plasters, as they are the most exposed to water. To compare the characteristics, the mixtures were tested for water resistance, water vapor permeability, flexural tensile strength and compressive strength.

1. Introduction

Unburnt clay had been widely used as a building material in the past around the world. “The history of buildings made of unburnt clay is very rich. Clay building can be observed and studied in all nations and all historical epochs. Till now, there are more clay buildings in the world than bricks and other industrially processed materials.” [1]

In the last century, this material was rather despised. Nowadays, however, this trend is reversing, and unburnt clay is experiencing a renaissance. More and more people emphasize ecology, a healthy and balanced indoor climate and demand buildings with low operational and energy intensity. All this can be offered by unburnt clay, because it is energy-efficient in production, easily accessible in almost all parts of the world, harmless and beneficial to human health, as clay can contribute to the improvement of the internal microclimate to a much greater extent than other building materials, as confirmed by many scientific findings.

Unfired clay has many advantages and only a few disadvantages, but they are all the more essential. However, these disadvantages can be reduced or perhaps eliminated in some ways, and this is the main topic of this article. The biggest obstacle for clay is the action of water and our effort is to improve its resistance to this natural element. At the moment, we can deal relatively well with large shrinkage of clay, which is another disadvantage, but the topic of improving water resistance seems to be insufficiently researched. As the title suggests, the improvement of the properties of clay will take place through the stabilization of polymers, where some types seem to target both of these major disadvantages.

2. Theoretical background

2.1. Loam
The clay is formed as a product of weathering of the rock surface. The finding location of clay plays role in its composition. Clay originating from a certain deposit has a certain specific composition which can have an impact on its properties.
Loam consists of clay, dust and sand. It can also contains coarser particles, such as gravel, rubble, stones, but also previously mentioned organic material. In civil engineering, the components of clay are sorted according to the size of the grains (particles).

The clay in the loam acts as a binder for the other coarser particles and keeps them together. Dust, sand and gravel therefore only work as a "filler". We divide the clay into clayey, dusty or sandy according to which of the components predominates. Clay consists of clay minerals, which are formed by weathering of feldspar-rich rocks (granite, gneiss, arkose, …) and other minerals.

2.2. Characteristics of clay plasters

Structure: According to PUV 2018-34801 unfired clay with controlled shrinkage contains plaster 2.5 to 30 wt. of primary binder consisting of clay particles up to 0.002 mm from the fine-grained fraction of soils, 50 to 97.5 % wt. fillers containing trace amounts of dust particles from 0.002 to 0.063 mm of fine-grained soil fraction, sandy soil fraction from 0.063 to 2 mm and optionally gravel soil fraction from 2 to 63 mm and optionally loose admixtures, up to 30% by weight. dispersed reinforcements formed by fibrous admixtures, up to 30 wt. dyes, up to 30 wt. aroma consisted by parts of plants, up to 30 wt. natural and chemical additives, up to 10 wt. of secondary binder, up to 10 wt. stabilizers. At the same time, the unfired clay for plasters with reduced shrinkage most preferably contains from 7.5% to 20% by weight. clay, 66.7 to 90 wt. of the above-mentioned dry mixture and further 10 to 33.3 wt. water. [2]

The most common clay minerals are kaolinite, illite and montmorillonite. In this order, binding, as well as swelling are increasing. The clay should be formed neither by too much montmorillonite due to swelling, nor by too much of kaolinite due to insufficient binding. Amount of clay minerals affects behavior of clay during its processing and subsequent drying.

Proportion of particular components determines final characteristics of the plaster, primarily binding and shrinkage, but also adhesion to underlay, or resistance to abrasion. It is possible to add different additives to improve the characteristics.

Effects of water Clay is not very resistant to water. First, it starts to swell in direct contact with water; this happens only after absorption of that big amount of water that it becomes plastically malleable. Also, the particles of the clay get surfaced when immersing the clay to water. During the long-lasting rain, particles get washed away from surface of construction.

Rain erosion has a dual form and is always related to the supersaturation of the clay with water. When the surface layer is supersaturated with water, the clay particles are washed away. However, if the inner layer of the plaster (core) is supersaturated, the electromagnetic forces will decrease, the strength will decrease, and the clay plaster will collapse.

2.3. Stabilization methods for outdoor use

The phenomena described in the previous chapter can be partially prevented by construction solutions, either by overlapping the roof or waterproof coating. Another variant is compaction, selection of suitable clays, dispersed reinforcement, use of additives, i.e. stabilizers or binders, hereinafter only stabilizing binders, or combinations of the above. Lime and / or cement, resins, i.e. asphalts, and tars, are most often used as stabilizing binders in doses of 3 to 6% by weight of unfired clay. However, these stabilizing binders reduce the strength, increase the diffusion resistance, and change the colour of the final product.

Lime and / or cement are mainly used for bricks, blocks, and formwork. Resin is used as a stabilizing binder or coating for exterior plasters. Nonetheless, increase in diffusion resistance is unsuitable for the application of unfired clay as an outdoor plaster on straw isolation, where it causes condensation of moisture at the straw-outdoor plaster contact. [3] Another stabilizing binder is substances of organic origin. These appear to be a suitable stabilizer with regard to ecology. In most cases, however, larger amounts of these substances are required for at least partial stabilization. Their use carries certain risks regarding aesthetics or increase of diffusion resistance or deterioration of strength characteristics.
2.4. Stabilization of clay plasters with polymers
The Polymer powder dispersion is used to stabilize clay plasters. These are two-phase water-soluble systems. The stabilization of clay plasters belongs to the group of vinyl acetate-ethene (so-called VAE) polymers and vinyl chloride co- and terpolymers (so-called VC).

“The principle of stabilization is based on double protection - increased tensile strength (captures forces from the swelling of clays, especially in the surface layer) and hydrophobization (prevents the penetration of water into the depth). Unlike lime and cement, polymeric stabilizing binders significantly increase the tensile strength, without a significant increase in the diffusion resistance compared to resins. The carrier of hydrophobic effects can advantageously be directly a polymeric stabilizing binder or can be provided by another substance / composition with a hydrophobic effect. The hydrophobic agent, as well as the polymeric stabilizing binder, must be selected and dosed to prevent the ingress of water in the liquid phase while allowing water vapor to pass through. This stabilization then preserves the required properties - it does not significantly increase the diffusion resistance, prevents the penetration of water, does not change the color of the product, does not bring dangerous properties, allows recycling. If suitable polymeric stabilizing binders with a hydrophobic effect are used, dosing is possible from as little as 0.125% by weight of unfired clay to achieve a slight stabilization against the effects of water. Sufficient stabilization against the effects of water is achieved from about 1 to 2% by weight of unfired clay.” [3]

The aim is to find a polymer that will act as a flexible secondary binder cooperating with the clay and having hydrophobic properties, which will prevent that water enter the plaster core and therefore will not swell the clays, will not lose their binding ability and will maintain their strength and function as a primary binder, thus better protecting the core. The function of the secondary binder is used in the surface zone, where when the surface is saturated with water, it takes over the function of the primary binder, absorbs forces from the swelling of clays and prevents surface erosion. The sample will be protected by two principles. The polymer should not change the color or rheological properties of the clay.

3. The process of tests and own results
3.1. Stabilization of clay plasters with polymers
The mixture for the test specimens was consisted of a dry mixture of coarse clay plaster without cuttings and various dispersion polymers with a hydrophobic effect (so-called H type) or a combination of a polymer without a hydrophobic effect (so-called N type) and a hydrophobizing agent. The resulting mixture is first mixed in the dry state.

The plaster from the supplied mixture has a maximum shrinkage of 2% and is prepared from clays, where an ilitic clay mineral with a small content of montmorillonite and mortar sand predominates. According to the technical sheet, the grain size is 0-4 mm and the bulk density of the hardened mortar is 1760 kg / m³. [4]

The types of mixtures are listed below:

- **Without** - the mixture consists of the rough clay plaster itself without cuttings
- **Polymer A** - a mixture of plaster and dispersion polymer with a strong hydrophobic effect based on vinyl acetate, vinyl ester and ethene.
- **Polymer B** - a mixture of plaster and dispersion polymer with hydrophobic effect based on ethene, vinyl laurate and vinyl chloride.
- **Polymer C** - a mixture consisting of plaster and dispersion polymer with a strong hydrophobic effect on the composition of vinyl chloride, ethene, vinyl laurate.
3.2. The process of tests

Resistance of clay to water actions: The test was performed sequentially on all samples with the same amount of polymer. The test specimens were hung evenly next to each other and immersed 5 cm in water at once. Then photographs were taken every 5 minutes and after an hour the samples were taken out and placed carefully next to each other on the table. All the wet material was scraped from the samples to divide as far as the water had penetrated, which will indicate how hydrophobic the sample is. In the first figure, the rise of water and how the secondary binder acts on the surface of the sample will be monitored, in the second figure the hydrophobization and how the core of the sample is protected from water. One sample from each mixture was tested.

A) Polymer samples 0.1 %
Samples containing polymer, even in such small amounts, have a much higher resistance to water than an unstabilized sample. The polymer acted as a flexible secondary binder, but the hydrophobic properties at these ratios are insufficient and the sample core is thus not sufficiently protected against water. For comparison, it should be mentioned that most polymers at 0.1% are comparable in resistance to natural stabilization, concretely stabilization with horse and cow manure at 12.3%. [5]

B) Polymer samples 0.5 %
This amount increases the resistance of most samples already very satisfactorily. Clay did not fall out of any of the samples for the duration of the test, so the role of the secondary binder in this amount of polymer already appears to be sufficient. The second role of the polymer, hydrophobization, is still insufficient in some samples.

C) Polymer samples 1 %
The role of the secondary binder is still sufficient, see the previous part of the test (polymers 0.5%). Capillarity is minimal in most samples. Hydrophobization, and thus core protection, is improving but still insufficient in three of the five samples.

D) Polymer samples 2%
2 % polymer seems to be like visible sufficient, in some samples even not economical anymore.
In the test of the resistance of the clay to water, polymer A clearly shows the best results. In an imaginary second place, the E + F polymer mixture, which appeared worse than B and C in the last part of the test but was more durable at lower ratios. Particularly in this case, a better setting of the mixture is conceivable, since the two desired functions, the secondary binder and the hydrophobization, are divided into two additives. The amount of polymer E had a sufficient binding function to absorb the internal forces during the swelling of the clay, even at an amount of 0.1%. Hydrophobizing additive F showed sufficient resistance at 0.5%. From the above, it is therefore necessary to consider whether, at 0.1-0.3% polymer E and 0.3-0.6% hydrophobizant F, the polymer mixture E + F will be better than A, when comparing the properties resulting from the following tests.

Flexural and compressive strength: The test was carried out according to ČSN EN 1015-11 since June 2000 and the test was performed in the experimental center of ČVUT on November 6th, 2019.
The average values of flexural and compressive tensile strengths were determined for all test mixtures. These values are for guidance only. Flexural tensile strength are presented in the table 1 and figure 1 and compressive strength in the table 2 and figure 2.

### Table 1. Average flexural tensile strengths [6]

| Type of clay mixture | 0%       | 0.10%    | 0.50%    | 1%       | 2%       |
|----------------------|----------|----------|----------|----------|----------|
| Unstabilized mixture | 0.98     | X        | X        | X        | X        |
| Polymer A            | X        | 1.22     | 1.78     | 2.29     | 3.17     |
| Polymer B            | X        | 0.94     | 1.10     | 1.68     | 2.30     |
| Polymer C            | X        | 0.93     | 1.01     | 1.41     | 2.65     |
| Polymer D            | X        | 1.00     | 1.33     | 1.87     | 2.59     |
| Polymer E + 0.05 % F | X        | 0.94     | 1.33     | X        | X        |
| Polymer E + 0.10 % F | X        | X        | 1.36     | X        | X        |
| Polymer E + 0.25 % F | X        | X        | 1.49     | 2.03     | X        |
| Polymer E + 0.50 % F | X        | X        | 1.68     | X        | 4.81     |

### Figure 1. Average flexural tensile strengths [6]

From the above data, it can be seen that the polymers in an amount of 0.1% do not substantially affect the flexural tensile strength except for polymer A, for which an increase in strength is evident even at this dose. For some samples, we measured a lower average strength than for the unstabilized sample, but this does not mean that the polymer deteriorates the strength. This is a deviation that is caused by a smaller number of measured samples. When testing a larger number of samples, the average strength of the unstabilized sample would be lower.

At 0.5% by weight of polymer, the strengths have already increased markedly in most samples. Only with polymer C this change did not occur and the same could perhaps be said for polymer B.
polymers, as can be seen from the graph, the flexural tensile strength increases with increasing amount of polymer. An interesting finding is that hydrophobization F also increases this strength.

The polymer E 2% + F 0.5% performed best, in which we measured an almost five-fold increase in strength compared to the unstabilized sample. In the second place, polymer A 2%, which, however, showed higher strengths in smaller quantities compared to other samples of the same series.

| Type of clay mixture         | 0%          | 0,10% | 0,50% | 1%          | 2%          |
|-----------------------------|-------------|-------|-------|-------------|-------------|
| Unstabilized mixture        | 2.27        | X     | X     | X           | X           |
| Polymer A                   | X           | 2.31  | 4.05  | 6.01        | 7.64        |
| Polymer B                   | X           | 2.30  | 2.95  | 4.19        | 5.69        |
| Polymer C                   | X           | 2.12  | 2.81  | 3.51        | 6.39        |
| Polymer D                   | X           | 2.73  | 3.96  | 5.18        | 6.47        |
| Polymer E + 0.05% F        | X           | 2.43  | 3.95  | X           | X           |
| Polymer E + 0.10% F        | X           | X     | 3.79  | X           | X           |
| Polymer E + 0.25% F        | X           | X     | 4.21  | 4.50        | X           |
| Polymer E + 0.50% F        | X           | X     | 3.73  | X           | 9.12        |

As with the previous flexural tensile strength test, it can be seen that 0.1% polymers do not affect the compressive strength. Only polymer D can be said to increase. Almost the same applies as in the previous test, the more polymer, the higher the strength, but the hydrophobization F no longer improves the compressive strength.

The polymer E 2% + F 0.5% again performed best, in which the increase in compressive strength is fourfold compared to the unstabilized sample. In second place was also polymer A 2%, which again showed higher strengths in smaller quantities in comparison to other samples of the same series.
Determination of water vapor transmission properties: The test was carried out according to ČSN ISO 12572. It was performed in the experimental center in the period of 11th – 19th November 2019. The water vapor permeability values were tested only for the polymers that performed best in previous tests and can be seen in the table 3 and figure 3.

Table 3. Result values of the diffusion resistance factor [6]

| Type of mixture          | $\mu$ [-] (dry) | $\mu$ [-] (wet) | $\varnothing$ $\mu$ [-] |
|--------------------------|----------------|----------------|-------------------------|
| Without                  | 12.1           | 7.1            | 9.6                     |
| Polymer A 2.00%          | 26.6           | 14.7           | 20.6                    |
| Polymer B 2.00%          | 21.1           | 14.4           | 17.7                    |
| Polymer C 2.00%          | 24.3           | 12.4           | 18.4                    |
| Polymer D 2.00%          | 24.0           | 13.7           | 18.9                    |
| Polymer E 0.50% + F 0.10%| 16.2           | 13.3           | 14.8                    |
| Polymer E 0.50% + F 0.25%| 15.1           | 12.6           | 13.9                    |
| Polymer E 0.50% + F 0.50%| 12.4           | 10.0           | 11.2                    |
| Polymer E 2.00% + F 0.50%| 20.7           | 8.60           | 14.6                    |

Figure 3. Average values of the diffusion resistance factor [6]

The test results show that the polymers aggravate the water vapor permeability. Polymer E + F performed best. Polymer E alone can be seen to impair diffusion. On the contrary, hydrophobization F improves the water vapor permeability, as it seems at first glance. The second best in this test performed polymer B.

4. Discussion of results
Unburnt As already mentioned, the most important aspect for us in regard to clay exterior plasters is resistance to the effects of water and at the same time good permeability to water vapor. These
requirements, according to the results of previous tests, are best met by a mixture of polymer E + F. In the water resistance test, although it does not have the best results at the ratios of polymer E and hydrophobizant F used, the more suitable setting of the mixture could the diffusion resistance factor works best for the E + F mixture.

With regard to these results of the water vapor permeability test, it is necessary to adhere to the scientific principle "correlation does not imply causality" that the fact that increasing diffusion improves the amount of F does not mean that hydrophobizant F is the cause. It could be caused by a consistence, which in the case of E + F mixtures significantly liquefied with increasing amount of additive. The manufacturer of the additive states that the hydrophobization F is completely permeable to steam, so it is very likely that it is the hydrophobizant that can improve the permeability to water vapor. It is necessary to reveal a causal relationship, and therefore what can improve diffusion? At the same time, the samples of the E + F mixture performed very well during the flexural and compressive tensile strength test.

In the figure 4 can we see all the samples soaked in water after 60 minutes.

![Figure 4. All test samples in the clay water resistance test after 60 minutes [6]](image)

Polymer A passed the water resistance best, in the flexural and compressive tensile strength test also essentially because it was actually less by weight than the E + F blends. For example, polymer E 2% + F 0.5% was combined 2.5% of the total weight of the additive, while polymer A was in the same row 2%. However, in the test of determining the properties of water vapor transmission, it turned out the worst. At 2%, it worsened the diffusion twofold, to a value similar to lime-cement plaster. That's the reason why we would put him in second place.

The third place would be taken by polymer B, which did not have very good flexural and compressive tensile strength, but in terms of water resistance it was third and the diffusion resistance factor has the second best.

There is a question which need to be asked. Are the values of the diffusion resistance factor for all samples really high? If we think about it, we can come to the conclusion that even the average value of
20.6 for polymer A 2%, which was the highest, is still relatively small and negligible compared to the mixture without stabilization. However, we must consider if the higher values can also tell us that the given polymer can influence more and other properties of the clay, which are important for us? If we use a polymer-stabilized plaster in interiors with increased humidity and the threat of splashing water, such as a bathroom, will this plaster still be able to balance the indoor microclimate? Will it absorb odors? These are questions we are unable to answer at this time.

Due to the amount of polymers used, this stabilizer also appears to be economically effective. Firstly, because a small amount is used, and secondly, even thinner layers of plaster can be applied due to the good properties of the stabilized clay plaster with polymers.

In the figure 5 can we see all samples scraped to the dry part of the sample after testing the resistance of the clay to water.

![Figure 5](image_url)

**Figure 5.** All test samples scraped to the dry part. [6]

5. Conclusion
In conclusion, we can confirm that the main goal of improving the properties of clay plaster by stabilizing various polymers, alternatively by combining the polymer with hydrophobization in various proportions, was met.

Another direction of research offers particular the mixture of polymer E and hydrophobizant F, for which it is necessary to better adjust the mixture. The ideal amounts are 0.1-0.3% of polymer E and 0.3-0.6% of hydrophobizant F. These mixtures should certainly be compared with polymer A and possibly also polymer B. Of course, this comparison should be run with correct consistency and comparing a range of ratios.

It is proposed to use a hydrophobizing agent in combination with a polymer which belongs to type H and thus has hydrophobizing properties, and thus to improve these properties.

Another important aspect is the ecological comparison, which is closely related to clay plasters. In this regard a comparison of the carbon footprint of the additives is offered, but also the disposal or recycling
of stabilized plasters with polymers. We are aware that most polymers decompose by UV radiation, so it is offered to grind the plaster during disposal and let it rest on a surface with direct sunlight. Recycling can take place by mixing part of the old plaster into the new one or by using all the old plaster. It would be necessary to compare the properties of the samples of the new plaster itself compared to the samples with reused plaster in a mixture with the new one in amounts of e.g. 20%, 50%, 100% of the old plaster.

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References
[1] V. Havlíček, and K. Souček. *Stavby z nepálené hliny*. Praha: Státní zemědělské nakladatelství, 1958 (in Czech).
[2] M. Procházka, and P. Znamenáčková. *Nepálená hlína s regulovaným smrštěním*. IPC: C04B 14/10, C04B 24/12, C04B 24/18. Česká republika. Utility model, CZ 32396 U1. [Online] 2018-11-30. Available from: https://isdv.upv.cz/doc/FullFiles/UtilityModels/FullDocuments/FDUM 0032/uv032396.pdf (in Czech).
[3] M. Procházka, *Nepálená hlína stabilizovaná polymery*. IPC: B28C 1/04, C04B 14/10, C04B 24/24. Česká republika. Utility model, CZ 19563 U1. [Online] 2009-04-27. Available from: https://isdv.upv.cz/doc/FullFiles/UtilityModels/FullDocuments/FDUM0019/uv019563.pdf (in Czech).
[4] Picas. *Technický list výrobku, hliněné omítky série ECONOM*. [online] 2012 [Accessed 2020-01-01] Available from: https://www.picas.cz/images/import/files/Technicky_list-Eco.hruba_8.5.2013.pdf (in Czech).
[5] P. Vacková, *Porovnání venkovních hliněných omítok*. Prague. Diploma thesis. Czech Technical University in Prague Faculty of Civil Engineering, Department of Construction Technology, 2012 (in Czech).
[6] Z. Zušťák, *Nová generace hliněných omítok stabilizovaných polymery*. Prague. Diploma thesis. Czech Technical University in Prague Faculty of Civil Engineering, Department of Construction Technology, 2020 (in Czech).