Abstract: This article studies the influence of biopolymeric viscosity-modifying admixtures with water-retentive function on the physico-mechanical properties of natural hydraulic lime-based mortars and their adherence to the traditional fired-clay brick substrate. The use of admixtures increases the water/binder ratio, which in turn leads to a decrease in the strength of the mortars. The viscosity-modifying function improves the adhesive strength between mortar and pre-wetter brick by increasing the binder paste viscosity, while the water-retentive function along with increased water content may lead to a decrease in adhesive strength. On the contrary, water retention and increased water content are beneficial on a dry surface, while paste viscosity plays only a minor role. When subjected to temperature-varying cycles, the mortars are more prone to in-mortar failure during the pull-off test. The air-entraining function of some admixtures improves the frost resistance of the mortars; however, it would negatively affect the adhesive strength by incorporating pores into the contact zone between the mortar and brick substrate. This study showed that the use of some of the studied admixtures may improve the adhesion of mortar to the brick substrate.

Keywords: NHL-based mortar; viscosity-modifying admixture; water retention; air content; adhesive strength; flexural strength; compressive strength; porosity; hygric properties; contact zone

1. Introduction

Durability and longevity are desired characteristics for most products of mankind, especially for civil engineering structures, where the designed lifetime expectancy is rarely less than half a century, and this is usually affected by moral obsolescence and not the degradation of the main structural elements. Buildings comprise multiple components, each with its own lifetime expectancy, from several decades for the most exposed and/or least durable materials, e.g., paint finishes on wooden elements, up to several centuries for the main load-bearing structures such as walls. It is obvious that during the lifetime of the building, some of the components need to be changed/repaired/renewed in order to maintain the functionality of the system (even if only aesthetical). The philosophies of different approaches addressing the repairs of historical buildings are summarised in a two-part paper by A.M. Forster [1,2]. From the material point of view, the like-for-like performance-wise approach, along with the reversibility principle and undesirable performance of cementitious materials [3], is the main stimulus behind the renaissance of lime-based technologies in the last 50 years.

The lifetime expectancy of the protective plastering layer is about 50 years, so during the building’s lifetime, repair work is anticipated. The frequency and the extent of repair may be influenced during the design and construction period and then again during any of the forthcoming repair periods by choosing the best-possible combination of materials. The course of durability is often approached on the basis of separate materials [4–7] and not the complex plaster–substrate system as recommended by several RILEM technical papers [8,9], whereas the separate material methods are widely accepted while studying the effects of specific mixture constituents, e.g., aggregate grading [9].
In particular, but not only for lime-based mortars, durability is closely linked to the water absorption capacity, and therefore the microstructure of the mortar [4,9]. Apart from binder type, the microstructure is mainly influenced by the water/binder ratio (w/b) and the aggregate properties. Growing w/b leads to an increase in the mean pore diameter, and thus the size of voids between the particles, and mainly to an increase in the capillary water coefficient, one of the properties detrimental for durability [9,10].

Mortar–substrate bonding properties, which are considered to be predominantly mechanical [11], are influenced by a number of factors, which can be divided into three main categories: mortar properties (workability, water retention, air content, drying shrinkage), substrate properties (water absorption, surface properties such as texture, roughness, etc.), and workmanship [11]. Appropriate fluidity of the mortar contributes to the quality of bonding by filling open pores and voids in the structure, increasing the contact area, and so the mortars with the highest possible flow value are preferred [12–17]. The air content reduces the bond strength with water-absorbing materials (e.g., bricks) by inappropriately affecting the water transport in the contact layer [17] (pp. 55–60, 78), while excessive drying shrinkage preloads the joint with tangential stresses, sometimes resulting in mortar cracking and delamination [18–21]. The excessive drying in hydraulic materials hinders the hydration of the binder, strongly reducing the mechanical properties of the mortar [22,23]. The water-retentive properties of the mortar are, regarding the bond characteristics, closely related to the water absorption properties of the substrate. The more absorptive the substrate, the more water-retentive mortar should be used to eliminate the excessive drying of the mortar, which may result in the above-mentioned effects, and vice versa [21].

The water-retentive function of mortar can be modified by an appropriate admixture. Thorough history, the most common admixture used to improve cementitious mortars has been hydrated lime in notorious volumetric mix designs of 1:1.6 or 1:2.9 (cement:lime:aggregate) [12,14,15,20,21,24,25]. With the growth of the chemical industry in the 20th century, a wide range of chemical admixtures for cementitious mixes occurred. Cellulose ethers (CEs) have been used since the 1970s [26] as water-retaining and viscosity-modifying admixtures (VMA) in concrete and cementitious mortars [22,23,25–28]. Other types of polymers are still being developed, which may have properties similar to the currently dominant CE, but with possibly different side effects (e.g., not having such a significant retarding effect on the hydration of cement particles [29–32]).

The article deals with the influence of several biopolymers on the properties and durability of the bond between natural hydraulic lime (NHL)-based mortar and brick substrate. The following biopolymers have been used: Hydroxypropylmethyl cellulose (HPMC)—a representative of CE, used in various applications as water retainer [22,27]. The derivative containing hydroxypropyl (HP) group was chosen to minimise the effect of the different types of substituent groups [33] because two other HP derivatives are being studied. Hydroxypropyl guar gum (HPG)—an HP derivative of guar gum (also guaran), a galactomannan derived from the endosperm of guar gum (Cyamopsis tetragonoloba) beans. In cementitious composites, HPG is less effective in its water-retentive function compared to CE [34,35]. For lime-based materials, the air-entraining function of the HP group is reported, influencing the pore and capillary structure of the hardened mortar, contributing to durability [4,36–39]. Hydroxypropyl chitosan (HPCH)—an HP derivative of chitosan, which is prepared by deacetylation of chitin, the second-most abundant polysaccharide on Earth that is widely found, e.g., in the shells of marine crustaceans. While used in cementitious materials, HPCH increases viscosity and water retention value (WRV) [40,41]. In lime mortars, it has similar effects as HPG, but with lower efficiency [39,42]. The durability of NHL-based mortar is enhanced in a similar way as in the case of HPG [39]. Sodium alginate (ALGNA) is obtained by boiling brown seaweed (e.g., giant kelp (Macrocystis pyrifera)). As well as other VMAs, ALGNA is used in self-consolidating concrete (SCC) to reduce segregation and bleeding [43,44]. In lime mortar, ALGNA has only minor effects on the fresh-state properties studied (workability, WRV); however, the viscosity-modifying function leads to altered rheological properties of the binder paste, which should affect the bonding.
between mortar and substrate \[23,45,46\]. With growing dosage of ALGNA, the hygric properties and pore structure are significantly altered, which can have a notable impact on the durability of final application \[47,48\]. Diutan gum (DG) is an artificial biopolymer, prepared in the beginning of the 1990s in the CP Kelco laboratories as heteropolysaccharide S-657 \[49\]. Compared to a similar natural biopolymer—xanthan gum—DG is much less affected by the temperature and concentration of mono- and bivalent ions (e.g., Na\(^+\), Ca\(^{2+}\)) in a solution. DG is used in SCC to improve the fresh-state properties of a mixture \[44,50,51\], resulting in highly altered rheological properties (despite the same flow table value). These properties (thixotropy, low yield stress, and modulus of elasticity) lead to a more fluid mortar, which should ensure better contact with rough brick surface \[12–17\].

2. Materials and Methods

The mortars were prepared by mixing natural hydraulic lime of NHL 3.5 class according to EN 459 (Zement- und Kalkwerke Otterbein GmbH & Co. KG, Großenlüder, Germany) and siliceous sand of 0–4 mm grain size (Českomoravský štěrk, a.s., Hulín, Czech Republic), using 1:1 volumetric ratio. The aforementioned admixtures, which are further summarised in Table 1, were added in the doses of 0.1%, 0.5%, and 1.0% of binder weight. Traditional fired-clay bricks (Zlínské cihelný s.r.o., Žopy, Czech Republic), with 21% water absorption according to EN 771-1:2005, annex C (provided by the manufacturer), were used as a substrate for the adherence tests.

### Table 1. Admixtures and w/b used during the preparation of mortars.

| Abbrev. | Chemical Composition | Dosage (%) | Water/Binder Ratio (–) | Manufacturer |
|---------|----------------------|------------|------------------------|--------------|
| REF     | –                    | –          | 0.600                  | –            |
| HPCH    | hydroxypropyl chitosan | 0.1        | 0.725                  | Kraeber & Co. GmbH |
|         |                      | 0.5        | 0.850                  |
|         |                      | 1.0        | 0.900                  |
| HPMC    | hydroxypropylmethyl cellulose | 0.1        | 0.725                  | Lotte Fine Chemical |
|         |                      | 0.5        | 0.850                  |
|         |                      | 1.0        | 1.000                  |
| HPG     | hydroxypropyl guar gum | 0.1        | 0.650                  | Lamberti s.p.a. |
|         |                      | 0.5        | 0.800                  |
|         |                      | 1.0        | 0.925                  |
| ALGNA   | sodium alginate     | 0.1        | 0.675                  | Sigma-Aldrich, Co |
|         |                      | 0.5        | 0.700                  |
|         |                      | 1.0        | 0.875                  |
| DG      | diutan gum          | 0.1        | 0.800                  | CP Kelco     |
|         |                      | 0.5        | 0.950                  |
|         |                      | 1.0        | 1.100                  |

The dry constituents (lime, sand, and admixture) were mixed together to form a homogenous mix, which was then introduced into the specified amount of water to achieve a flow table value of 160 ± 5 mm according to the flow table test (EN 1015-3; for the specific water contents, see Table 1) and mixed for 5 min using a planetary mixer. Then the following properties of the fresh mortar were determined: flow table value (EN 1015-3), water retention value (EN 1015-8), air content (EN 1015-7), and density (\(D_{fm}\)) (EN 1015-6). Two types of samples were prepared for testing the hardened properties: standardised 40 × 40 × 160 mm beams, which were then used to study the compressive and flexural strength (EN 1015-11), hardened bulk density (EN 1015-10), capillary water coefficient (\(C_m\)) (EN 1015-18), measured using an automatic setup as proposed by Courard and Dari-
mont [52]), and porosity of the mortar by the high-pressure mercury intrusion porosimetry (MIP) principle using PoreSizer 9310 (Micromeritics Instrument) at the age of 90 days. Each mortar was also applied onto two groups of bricks (290 × 140 × 65 mm), dry (D) and water-saturated (W). The rendered bricks were cured under laboratory conditions (21 ± 2 °C, 55 ± 5% RH) for 90 days. They were then divided into two subgroups; one was subdued to 15 temperature-variating cycles from −20 °C to 20 °C in a highly humid environment with a hold of 4 h at −20 °C, and 6 h at 20 °C, respectively, one cycle lasting 24 h, and the second subgroup was stored in a container with relative humidity close to 100% for the cycling duration. After the durability testing, the bricks were allowed to stabilise their humidity under laboratory conditions for one day. The samples with 50 mm diameter were then drilled out and tested for adhesive strength by the pull-off test using devices and methodologies in accordance with EN 1015-12. After the pull-off test, a sample from the unviolated part was cut out, cast into epoxy resin, and broken in half perpendicularly to the contact surface to obtain samples with a fracture surface containing the contact zone between mortar and brick. These samples were then studied using a Leica DM4000 optical microscope.

3. Results and Discussion

3.1. Fresh-State Properties

Most of the fresh-state properties, summarised in Table 2, showed a clear dependency between the dosage of admixture and the variable studied. The $D_{fm}$ decreases with growing admixture dosage. The decrease is driven by two complementary factors: the water content (w/b), which is prevailing within mortars with lower air content (HPCH, ALGNA, DG), and the air content, which (significantly increased by the air-entraining function of HPG and HPMC) leads to a more pronounced drop in the density. The decrease in the fresh mortar density with growing water content, as well as with incorporation of a biopolymeric admixture (mainly HPMC), has been documented by several authors for lime and cementitious mixes [36,39,48,53,54].

| Sample | $D_{fm}$ (kg m$^{-3}$) | Air Content (%) | WRV (%) | $C_m$ (kg m$^{-2}$ min$^{-1}$) | Total Open Porosity (%) |
|--------|------------------------|-----------------|---------|---------------------------|------------------------|
| REF    | 1920                   | 4.80            | 90.5    | 1.727                     | 29.75                  |
| HPCH 0.1 | 1895              | 4.20            | 90.4    | 1.938                     | 31.04                  |
| HPCH 0.5 | 1810              | 5.50            | 91.4    | 2.117                     | 37.03                  |
| HPCH 1.0 | 1810              | 5.00            | 89.5    | 2.363                     | 37.92                  |
| HPMC 0.1 | 1835              | 7.25            | 91.8    | 2.287                     | 33.45                  |
| HPMC 0.5 | 1485              | 17.25           | 96.8    | 1.012                     | 42.85                  |
| HPMC 1.0 | 1355              | 22.50           | 98.4    | 0.611                     | 50.69                  |
| HPG 0.1 | 1895               | 5.70            | 88.5    | 2.424                     | 29.74                  |
| HPG 0.5 | 1760               | 12.40           | 95.8    | 2.030                     | 36.34                  |
| HPG 1.0 | 1425               | 18.50           | 98.3    | 1.322                     | 41.25                  |
| ALGNA 0.1 | 1900             | 5.40            | 85.7    | 1.808                     | 31.35                  |
| ALGNA 0.5 | 1890             | 5.60            | 92.8    | 1.901                     | 34.47                  |
| ALGNA 1.0 | 1810             | 6.50            | 91.6    | 1.955                     | 37.70                  |
| DG 0.1 | 1870             | 3.60            | 86.6    | 3.072                     | 35.37                  |
| DG 0.5 | 1840             | 1.80            | 98.2    | 2.701                     | 33.02                  |
| DG 1.0 | 1755             | 2.85            | 97.5    | 1.554                     | 38.76                  |

The air-entraining function of the HP derivatives of cellulose and guaran has been demonstrated, in accordance with the literature research [27,36,39,53,54], by significantly increasing the air content in fresh mortar; however, HPCH has shown, contrary to previous results of authors [39,42,48], an inefficiency in this mix setup, acting more like the VMA, as
observed by Y. Ustinova and T. Nikoforova [41], for chitosan in the cementitious mixture. The significant alteration to mortar rheology by incorporation of DG led to a decrease in the air entrained.

The relatively high WRV of unmodified NHL-based mortar was further improved by water-retentive admixtures. The behaviour of the HP derivatives is closer to the one in the cementitious material [22,34,40,53,55] than in the aerial lime [36,38,42,56], where HPMC influence is inferior to HPG and HPCH. DG proves to be similarly efficient to HPG and HPCH, having slightly different dosage dependency, with the optimal dosage for maximal WRV being in the interval of tested dosages.

3.2. Hygric Properties

The transport of liquid water in mortar is characterised by the capillary water coefficient (Table 2), a gradient of the capillary water uptake curve. The values for the reference and slightly modified mortars are well comparable to the ones reported by several authors in the literature on aerial lime- and NHL-based materials [3,4,36,39,48,53,57]. For air-entraining admixtures (HPG and HPMC), there is a clear dosage dependency. After an initial increase in the water transport speed, caused by an increase in the number of capillary pores (Figure 1) due to higher w/b, the water transport is gradually hindered with growing dosage, and thus the air content that acts by interrupting capillaries with large aerial pores [48,53]. The different dosage dependency between HPMC and HPG correlates with the differences in the amount of air entrained. HPCH and ALGNA, which did not show a significant increase in air content, with growing dosage, further support the water transport through the mortar matrix in intensity corresponding to the w/b of mortar. This is caused by the growing volume of capillary pores, as discussed in Section 3.3. DG in doses of 0.1% and 0.5% significantly supports the water transport according to increased w/b and pore size distribution; however, it hinders it at the highest dosage (with the highest w/b) without significant support in the porosimetry study (Section 3.3, Figures 1 and 2).

Figure 1. Pore size distribution of the mortars modified by 0.1% (dotted lines), 0.5% (dashed lines), and 1% (full lines) addition of a biopolymeric admixture.
differences in the mortar properties, mainly a lower dosage of 0.3% and a significantly lower air content in either unmodified or modified mortar. The increase in the large pore volume is more intense than in the authors’ previous studies on NHL-based modified mortars with a constant w/b [39] or aerial lime-based modified mortars with constant workability [48], which, however, showed significantly lower air content.

The total open porosity expressed either as a complement to the bulk/skeletal density ratio obtained by MIP (Table 2) or as total intruded volume seen as the end of the curve in Figure 1 is for most mortars (with the exception of highly air-entrained HPMC 1.0 and 0.5 and HPG 1.0) influenced by an increase in the volume of pores by 0.5 to 2 μm (Figures 1 and 2). In some cases, the growing amount of small (<0.1 μm) pores is responsible for the higher total porosity (slightly higher slope of the curve in this area), which is most apparent in the comparison of DG, ALGNA, and HPCH mortars with 1% of admixture (Figure 1). However, this effect is less pronounced in NHL than in modified aerial lime-based mortars [4,36,48]. The increased total open porosity often leads to a decrease in the strength of the material [4,36,53].

3.3. Porosity

The cumulative pore volume curves in Figure 1 show the shape typical for lime-based materials with a predominant pore diameter of around 1 μm [4,5,10,36,39,48,58–60], which is approximately an order of magnitude larger than the typical diameter of cementitious materials, e.g., [61]. In this area, the effect of the growing water content as observed by Arandigoyen et al. [10] can be seen as a shift of the steep part of the curve to the area of larger pores as well as an increase in the volume of the pores in the subjected interval. However, this effect is not only driven by water content but also affected by the admixtures in both positive (DG 0.5, ALGNA 1.0) and negative (e.g., HPG 0.5 or HPMC in general) ways. The admixture addition also leads to a narrowing of the main pore volume interval, promoting the development of the more similar-sized pores, as seen in Figure 2.

The large pores (5–30 μm), which occurred in HPMC 0.5, 1.0, and HPG 1.0 mortars, represent the air-entraining ability of these admixtures (Table 2). The HPG results are in opposition with the results reported by Izaguirre et al. [4] for aerial lime, where the HPG addition led to a reduction in the number of large pores; however, there are significant differences in the mortar properties, mainly a lower dosage of 0.3% and a significantly lower air content in either unmodified or modified mortar. The increase in the large pore volume is more intense than in the authors’ previous studies on NHL-based modified mortars with a constant w/b [39] or aerial lime-based modified mortars with constant workability [48], which, however, showed significantly lower air content.

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Figure 2. Pore size distribution of the studied mortars in the area of the typical pore size.
3.4. Strengths, Density

The hardened bulk density presented in Figure 3a shows the same trends as the density of fresh mortar (Table 2) for all admixtures and doses. The air-entraining function is the main cause in the case of HPMC and HPG, and capillaries left over by excessive water in the other cases [36].

Figure 3. Hardened properties of NHL-based mortars with biopolymeric admixtures: (a) dry bulk density, (b) flexural strength, and (c) compressive strength.

The effects of VMAs on the mortar strength, found in the literature, vary depending mainly on the test design (constant w/b vs. constant consistency) and the type of binder. The decrease in strength, which is more significant in the case of compressive strength, is in accordance with the effect of HPMC and HPG on aerial lime-based mortar with a constant consistency, as observed by Izaguirre et al. [4,36]. A decrease in the compressive strength was also observed in most binder types and admixtures in constant w/b tests [29,39,47,53,62,63], with the exception of ALGNA and DG in NHL-based mortars [6]. The strength reduction is often attributed to increased porosity either by increased water demand [4,36] or by the air-entraining function of the admixtures [39,53]. This theory is supported by the porosity study (Section 3.3), and it is the most probable reason for the strength reduction in this case, too. While comparing the pore structure (Figure 1, Table 2), air content in fresh mortar (Table 2), and w/b (Table 1), it can be assumed that w/b is the dominant factor responsible for most of the strength reduction, well in compliance with Abram’s law, which is accepted in the theory of concrete [64,65]. The further influence of
air content can be expressed by comparing the compressive strength results (Figure 3c) of air-entraining HPG and HPMC with non-air-entraining but water-demanding DG samples, especially in higher doses.

3.5. Adherence

The aforementioned mortars were applied to saturated (W) and dry (D) traditional fired-clay bricks to study the influence of the admixtures on the bond characteristics of NHL-based mortar applied to the substrate. Immediately after application, especially on dry bricks, the differences between the mixes occurred as the mortar was dried out at various rates, and the cracking due to drying shrinkage appeared. Figure 4 shows some of the mortars applied on bricks after 90 days of ageing to illustrate different types of behaviour. While applied on saturated bricks (Figure 4a,f), even the unmodified mortar showed no cracking, and the most notable difference between various mortars applied was the roughness of the texture, indicating the intensity of the viscosity-modifying function of the admixtures (compare Figure 4a–e to Figure 4f–j). In general, mortars modified by 0.1% addition of any admixture and by any dosage of less efficient admixture such as ALGNA and HPCH showed rougher texture than the mortars with more efficient admixtures, and thus with higher water content and more pronounced thixotropy of the mixture. There were three main ways to the mortars cracking on the dry bricks: two induced by initial shrinkage due to the rapid drying [17] (p. 64) and the third that developed during the curing period. The first type, shown in Figure 4b,c, consisted of two cracks perpendicular to the longer side of the brick dividing the applied mortar into three approximately same-sized segments. This was the common case for the mortars modified by 0.1% addition of admixtures. With growing dosage (thus also water content), the longitudinal crack with several branches started to appear, dividing the mortar into smaller fragments with different crack widths depending on the efficiency of the admixture (Figure 4d,e,h,i). By comparison of two approximately similar mixtures of HPG 0.5 (Figure 4h) and HPMC 0.5 (Figure 4i), it can be assumed that the high WRV is not the only prerequisite for a less cracking mortar. The slightly higher water content, ensured by the viscosity-modifying function of the admixture, makes a noticeable difference in the structure of cracks. During the first few days after application, smaller solitary cracks appeared on some either D or W, previously intact specimens, probably indicating the local imperfections in the substrate, which lead to different thicknesses of the mortar. During this time, the diametrically different behaviour of DG-modified mortars occurred, while, instead of a few large cracks, the network of small (less than 1 mm wide) hair-like cracks developed on the surface, not permeating the whole thickness of the mortar (Figure 4j; detail in Figure 5).

The adhesive strength of the mortar to the substrate was determined by the pull-off test using pull-head plates of 50 mm diameter. The average values of the adherence are shown in Figure 6 and the typical ways of detachment in Figure 7. The best results of adhesive strength were obtained on the specimens applied on pre-wetted bricks (Figure 6a) for most of the mixtures supporting the generally accepted and applied practice of brick-wetting, also indicated in previous results [13,14,17,19,21]. Two distinctive trends can be observed regarding the amount of admixture added: improvement in adhesive strength after modification with a low dosage of admixture, followed by a decrease in adhesive strength with growing dosage (HPCH, ALGNA, and DG) or initial decrease in strength followed by growth with increasing dosage (HPMC and HPG). However, neither WRV nor w/b is in any correlation with most of the results on pre-wetted bricks. This is most obvious in the comparison of two pairs of samples with almost identical fresh-state properties—HPCH 0.1 and HPMC 0.1, which slightly vary in air content and WRV, and HPG 0.1 and ALGNA 0.1, which slightly vary only in w/b; however, there is more than 50% difference in adhesive strength within these pairs. This is caused by the various viscosity-modifying functions of the admixtures. The effects of viscosity on the adhesive strength are indicated in the report by Högberg [17] (pp. 60–63). Zhi et al. [23] reported that in cementitious thin-layer mortar, an increase in viscosity improves the tensile adhesive strength. The
The effects of the admixtures used in this study on the rheological properties of NHL paste can be found in the authors’ previous works [46,66], where it was seen that HPCH- and, mainly, ALGNA-modified pastes show significantly higher viscosity compared to their above-mentioned counterparts. The decrease in the adhesive strength of the HPMC 1.0 mortar is caused by a combination of the high air content (Table 1), which affects the contact zone (Figure 8) [11,15–17,20], and the excessively high w/b of pre-wetted (nonabsorptive-like) bricks [13,17,19,67], which is also responsible for the notably poor performance of highly modified DG mortar on wet bricks.

**Figure 4.** Examples of the various cracking of the modified mortars while applied on pre-wetted (W) and dry (D) bricks (140 × 290 mm): (a) REF W; (b) REF D; (c) ALGNA 0.1 D; (d) ALGNA 1.0 D; (e) HPCH 1.0 D; (f) DG 1.0 W; (g) HPG 1.0 D; (h) HPG 1.0 D; (i) HPMC 0.5 D; (j) DG 1.0 D.
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Figure 5. Detail of DG 1.0 D surface with microcracks.

Figure 6. Average adherence of the modified NHL mortar to wet (saturated) (a) and dry (c) bricks, and the respective values after temperature cycles ((b) wet and (d) dry bricks). The eggshell/honeycomb hatch (e.g., HPCH 0.5 on a)) was used to indicate the mortars where 50% of the failures occurred in the mortar. The slashed hatch (mostly HPMC) is used where all the failures occurred in the mortar. The dotted grid is used to highlight the failure in the mortar and in adhesion together in the testing zone (e.g., DG 1.0 on (c,d)). The failure modes are shown in detail in Figure 7.
Figure 7. Examples of failure modes: (a) failure in adhesion (contact zone) (HPCH 1.0 W); (b) failure in adhesion and in mortar together (DG 1.0 D); (c) shallow failure in mortar (HPMC 1.0 D weathered); and (d) deep failure in mortar (HPMC 1.0 W weathered).

Figure 8. Chosen microphotographs of the contact zone between brick and mortar (50× magnified): (a) REF W; (b) REF D; (c) DG 1.0 W; (d) HPMC 1.0 D; (e) HPMC 1.0 W; (f) HPCH 1.0 D.

For most of the admixtures applied to dry bricks, the trends in the adhesive strength regarding dosage dependency remained the same, with the notable exception of DG. The mortars with high WRV performed comparably well or better than while applied on W bricks, showing the positive effect of the admixtures with high water-retentive function. The sole effect of increased w/b, which is indicated in the literature (e.g., “the most complete contact of mortar with brick and joints with highest tensile strength are likely to be obtained if the mortar is as wet as may be used conveniently” [13]) [14,17] is not supported by the results. For example, ALGNA- and HPCH-modified mortars with 1% addition of biopolymer was shown to be inferior to mortars with higher WRV despite containing more water. As Ritchie and Davison [14] stated, modification of WRV leads to changes in the...
composition of mortar (in this case mainly w/b, viscosity, and air content), so that the isolated effect of WRV on the bond properties is difficult to establish. However, the results support the conclusion of most works regarding the mortar–brick bond characteristics that a higher WRV leads to improved bonding to a highly absorptive substrate [13–15, 68], even though some regarded as doubtful (H. F. Gonnerman in the discussion of [69]) and were in opposition to the conclusions presented by Högberg [17] (pp. 38–40). The highly modified HMPC and HPG mortars showed failure in the mortar, meaning that the adhesive strength is higher than the presented values. The change in failure mode may be caused by a different water gradient in the mortar during hydration [70] (pp. 59–80) or simply by preloading the mortar by stresses from shrinkage, which, however, did not develop noticeable cracks. Either way, in combination with relatively weak mortar (Figure 3b), it may lead to further weakening of the mortar, failing in tension [71]. The DG 1.0 mortar showed failure in both mortar and contact zone for each testing place. In this case, the failure behaviour is caused by the development of microcracks, as seen in Figures 5 and 8c.

Although no visible differences in the texture of the mortar were evident, the adhesive strength of the samples subjected to temperature cycling in a highly humid environment decreased. The trends regarding dosage dependency and admixture influence remained the same as for the respective non-cycled samples. The failure in mortar occurred more frequently, especially on dry bricks. There was a clear difference in the depth of in-mortar failure between HPMC 1.0 D and W mortars (Figure 7c,d), respectively. The mortar applied on wet brick showed shallow failure a few mm below the surface; however, the D mortar failed deeper in the mortar. The HPG and HPMC addition led to the best retainment of the adhesive properties of the non-cycled samples, this being probably thanks to hindered water transport and increased air content. The non-air-entrained DG samples performed significantly worse.

3.6. Microscopy

The microphotographs in Figure 8 show the contact zone between the modified mortar and the brick substrate. The mortars applied on pre-wetted bricks (Figure 8a,e) show a crack-free contact zone, indicating the good adhesion of the entire surface; the small isolated crack, which occurred in REF mortar (Figure 8a), is only local and at its size cannot influence the performance of the whole mortar. On the other hand, the mortars with no or less efficient admixture applied to dry brick showed detachment from the substrate, as seen in Figure 8b,f. The REF mortar detached from the substrate in large areas, being probably supported by local “bridges”, which are present probably somewhere deep in the crack. Unfortunately, no such connection was observable in the prepared specimens. The HPCH 1.0 mortar shows a significantly smaller crack of approximately 80 µm width interrupted by binder paste in several places. The connection of HPMC-modified mortar with either wet or dry brick is good, with no observable crack on the interface; however, the mortar itself is much more porous, containing large amounts of aerial pores thorough the whole thickness of the mortar. This structure of the mortar is most likely responsible for the in-mortar failures reported in the adhesive strength study; however, in the studied case, the interruption of the interfacial zone by the aerial pores (even though clearly visible) did not lead to the weakening of the adhesion as suggested in the literature [11, 15–17, 20], because the weakened mortar failed before the contact zone. The sizes of pores and their distribution in the mortar are similar to those observed by Högberg [17] (p. 55) and Lawrence and Cao [20]. The DG-modified mortars, represented here by the mortar applied to pre-wetted brick (Figure 8c), also showed good adhesion in both cases; however, the microcracks earlier mentioned (Figure 5, Section 3.5) appeared isolatedly thorough the thickness of the mortar, most likely resulting in the type of failure depicted in Figure 7b.

4. Conclusions

The study deals with the influence of biopolymeric viscosity-modifying admixtures with water-retentive function on the physico-mechanical properties of natural hydraulic
lime-based mortars and their adherence to the traditional fired-clay brick substrate. The incorporation of all admixtures led to increased water demand to achieve the same workability. The increased water content led to the growth of the main pore size, which promoted the capillary water transport in the mortars with the exception of higher doses of two admixtures (hydroxypropylmethyl cellulose (HPMC) and hydroxypropyl guar gum (HPG)), which showed air-entraining function. Changes in the microstructure led to a drop in the flexural and compressive strength, with the compressive strength being more affected.

While applied onto dry fired-clay brick substrate, the highly water-retentive mortars with high water content (modified by HPG, HPMC, and diutan gum) showed good resistance to initial cracking, which in the other cases occurred almost immediately after application due to rapid drying and subsequent shrinkage—a failure that was not present on the pre-wetted surface combined with any mortar.

The adhesive strength on the wet substrate was promoted by increased viscosity of mortars with the addition of sodium alginate (ALGNA) and hydroxypropyl chitosan (HPCH) and impaired by high air content and high water retention value combined with an excessive amount of kneading water in the case of HPMC and diutan gum. On the contrary, the excessive kneading water and high water retention value were two main properties preserving the strength of the bond on the dry substrate. Subduing the mortar-brick samples to temperature cycling in a humid environment led to a decrease in the bond strength, but with no additional damage observable prior to pull-off tests. During the pull-off test, the samples subdue to temperature cycling showed more frequent occurrence of in-mortar failures, with depth varying depending on the substrate type (wet or dry) during the application and the admixture present in the mortar (air-entraining HPG and HPMC being more prone to this failure).

The contact zone between the dry brick substrate and the mortar was interrupted by cracks and affected by delamination caused by initial shrinkage in the case of mortars modified by less effective admixtures (HPCH and ALGNA), resulting in mortar binding by local contact points and not the whole contact area. The aerial pores in highly air-entrained mortars occurred in the binder matrix through the thickness of the mortar, decreasing the contact surface area and, thus, also the adhesive strength.

By modifying the mortars with suitable admixtures, the mortar with the properties counteracting the inappropriate characteristics of the substrate can be prepared. However, the results indicate that the approach has to be cautious, and there cannot be made any generalising assumptions such as “the more water-retentive the mortar, the better”. From the admixtures studied, each proved to be useful in improving the adhesive properties of mortar in some of the defined conditions.

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