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The Influence of Casein Protein Admixture on Pore Size Distribution and Mechanical Properties of Lime-Metakaolin Paste

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Abstract: Biopolymers based on proteins are applied in the building materials technology to modify and improve their selected properties. These polymers are designed as natural admixtures that improve the workability of materials. Casein is an example of a protein-based organic polymer. It is a protein obtained from cow's milk. The paper aimed at investigating the prospects of enhancing the strength properties of a binder prepared on a basis of metakaolin and hydrated lime. The mix was modified with powdered technical casein at 0.5%, 1%, 3%, and 5% as a partial replacement for the binder mix by mass. The study involved investigating the effect of the applied natural admixture on the flexural and compressive strengths, as well as pore size distribution. The average pore diameter decreased in the recipes with casein in the amount of 0.5% and 1%, while it increased when the amount of casein equaled 3% and 5%. Only the 0.5% casein admixture caused a decrease in the total porosity. The results show a clear dependence of the strength parameters on porosity. The admixture of casein significantly increased the flexural strength of the pastes, and decreased the compressive strength. The highest increase in flexural strength (by 205.7%) was caused by the admixture of 0.5% casein, while the greatest decrease in compressive strength (by 28%) was caused by the 3% casein admixture. The flexural strength was enhanced, i.a., due to the improved adhesion and mutual bonding of lime particles, resulting from the application of a sticky admixture. No notable difference was indicated during carbonation by the phenolphthalein test. The lime binder is characterized by a slow setting process and low mechanical strength. The results of the research showed the possibility of improving the flexural strength using small amounts of natural admixture, which may broaden the scope of application of this binder.

Keywords: casein; protein; lime; metakaolin; flexural and compressive strengths; porosity

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1. Introduction

Organic admixtures and additives have been used since antiquity for modifying the properties of building mortars. In ancient Rome, young fig wine was added to lime mortars, which, released carbon dioxide during fermentation and, thus, improved the efficiency of the carbonation process in the mortar structure [1]. Bovine blood was also used, mainly as an admixture to improve air entrainment in the mortar [1,2]. In turn, pozzolans were primarily used in order to improve the strength and durability of lime mortars. In ancient Egypt, egg white, keratin, and casein were used in construction [3]. Many of these practices are still being performed today. Research is also conducted to scientifically confirm the beneficial effect of the admixtures used in ancient times on the properties of mortars and concretes. Many studies confirm that the modification of lime, clay, and cement mortars with biopolymers has a positive effect on their various properties [4–10].

Jasiczak [11] investigated the effect of adding powdered protein derived from pig and cow blood on the properties of cement mortars. He applied an additive of 0.05%, 1%,

and 2% in relation to the cement volume. The effect was a significant increase in mortar resistance to the destructive impact of frost. The protein caused the air bubbles to enter the mixture. The effect was a decrease in the mechanical strength and a significant increase in mortar resistance to the destructive impact of frost.

In turn, Mydin [12,13], modified the lime mortars with a solution of chicken egg white at the concentration of 2%, 4%, 6%, 8%, 10%. The addition of white in the amount of 2% to 6% improved the workability and strength parameters of the mortars. In contrast, the amount of white over 6% resulted in deterioration of the mortar properties. On the basis of the results, it was found that after mixing the whites create a mutual bond, which hardens after drying, improving the strength of the mortar.

In the old mortars, the proteins contained in animal glues were also used [2]. Salavessa et al. [14] used the glue obtained by boiling the bones, skin and cartilages of a rabbit as a component of gypsum plaster. The purpose of the glue was to retard the setting process, improve the bonding and to assist the smoothing process of the plaster surface. The glue water decreases the compressive strength but increases the flexural strength. Animal glue improves the impermeability of the inner plaster surface by minimizing the number and size of pores. Ventola et al. [4] used animal glue as an additive to the lime mortar. The addition of this adhesive improved the compressive strength of the mortar twice and reduced the porosity.

Vegetable proteins are also used to modify mortars and concretes. Chandra et al. [15] used a cactus extract with a viscous consistency as an additive to cement mortar and as an impregnating agent of concrete surfaces. The extract contained proteins and polysaccharides. The film formed by the hydrophobic protein particles increased the resistance to water penetration of the concrete impregnated with the cactus extract. The cactus extract mix improved plasticity of the fresh mortar, substantially reduced the water absorption and enhanced the freeze-salt resistance of the cement mortar. Thirumalini et al. [16] applied the modification of lime mortars with biopolymers obtained from herbs (kadukkai, jaggery, kulamavu) which are currently used in the restoration of ancient structures in India. The addition of a biopolymer reduced the pore size and had a positive effect on the bond strength between the lime particles, which, in turn, improved the mechanical strength of the mortars.

Casein is another natural protein-based biopolymer used in the modification of various building materials. It is a biopolymer belonging to the group of phosphoproteins. It makes up about 80% of the total amount of protein in cow's milk. Casein is used in the food industry, in the production of hard and processed cheese, bread coating agent, sausages, as well as for technical applications–adhesives, self-levelling compounds, and paints. For technical applications, acid casein is used, which is precipitated from milk by acidification with, e.g., hydrogen chloride, as well as centrifugation and filtration. Casein is poorly soluble in water, while it dissolves well in an alkaline solution. When mixed with an alkaline solution, casein is characterized by high viscosity and binding ability [17,18]. Chang et al. [19] modified a soil and sand mixture with casein in the amount of 2–6.7% of the mixture mass. The hydrophobic properties of casein improved the compressive strength of the soil in the wet state. In the dry state, the strength also increased along with the casein content. The soil with the casein addition in the amount of 6.7% showed twice the strength of the soil with the addition of 2%. Park [17] studied cemented sand bonded with a casein-based binder. Casein, in the amount of 2%, 3%, and 4% was exchanged with a solution of calcium hydroxide and sodium hydroxide in the proportion of 31 g ($NaOH + Ca(OH)_2$) per 100 g of casein. The compressive strength of cemented sand increased along with the content of casein binder. In the microstructure images, they showed that the casein bonded the sand particles effectively without voids on the contact surface. In turn, Chandra [20] investigated the effect of proteins obtained, among others, from milk and flour on the properties of cement mortars. The amount of admixtures used is 0.075% and 0.1% of the cement mass. The admixtures increased the air content in the mixture, improved the flexural strength by 28.6% and 15.7%, respectively (improve adhesion of the binder to

aggregate), as well as reduced the compressive strength (by 1.2% and 9.3%, respectively) and water absorption. Authors stated that the hydrophobic property of the mortars with protein addition increases with time. For comparison, the admixture of another protein (gluten) in the amount of 0.5% increased the flexural strength by 4.3–18.6%, and decreased the compressive strength by 7–12.8%, in comparison with the reference cement mortar. Ventola et al. [4] compared the compressive strength of protein-modified lime mortars. One mortar was modified with 5% casein and the other with 5% animal glue. Casein improved the compressive strength of the mortar by 92%, while the animal glue—by 68%. Casein dissolved in a lime solution was also used as a modifier for heat-retaining clay mortars, in the amounts of 0.5%, 1%, 1.5% by the weight of clay [21]. The resistance of the mortars to washing in water increased along with the casein content. It has also been proven that casein does not significantly reduce the vapor permeability of clay plaster [22]. In the technology of building materials, proteins are used for aerating and foaming concrete [23,24]. When casein is dissolved, air bubbles form as the mixture is mixed. The effectiveness of the reaction depends on casein concentration in an alkaline solution [19], temperature and pH [24]. Casein is also used as a plasticizing admixture in self-leveling concretes [25].

Very little work has been completed on the effect of casein incorporation in the lime mortar. Therefore, the aim of the article was to demonstrate the effect of casein admixture on the strength parameters and pore size distribution of the lime-metakaolin binder. Ultimately, it is planned to use the tested binder as a component of the hemp-lime composite [26,27], thus improving its strength and durability.

2. Materials and Methods

2.1. Materials Used in Investigation

The binder mix in the reference formulation consists of 90% of CL-90s hydrated lime and 10% of metakaolin. A pozzolanic additive was used, because, as mentioned in the introduction, it is planned to use this binder in hemp-lime composites. Nowadays, the binders in these composites are often modified with metakaolin [28–30]. The second reason was that pure lime binder had negligible strength, as well as exhibited a tendency to shrink and crack when drying, so imprecise results were expected.

Commercial acid casein without any treatment and purification, with 60 mesh granulation was used. It was obtained in the process of casein coagulation from skimmed cow's milk under the influence of acid. The protein content in dry matter is min. 90%, pH in the range 4.5 to 5.8, while the moisture content does not exceed 10%. The form of the casein used is a white/cream colored powder with a typical milky smell. Casein is a phosphoprotein, i.e., in its elemental composition, apart from carbon (53%), hydrogen (7%), oxygen (22%), nitrogen (15.65%), and sulfur (0.76%), it also contains phosphorus (0.85%).

The casein admixture was used in the amounts of 0.5%, 1%, 3%, and 5% by weight of the lime-metakaolin mix as a partial substitute for this mix. Table 1 shows the paste mix recipes. The recipe symbols contain the information about ingredients: LM—lime-metakaolin, 0; 0.5; 1; 3; 5—the percentage of casein in the mixture, C–casein. Table 1 presents the components of the tested pastes.

Table 1. Components of the tested pastes.

Recipe Symbol	Components		
	Binder	Casein/Binder Ratio	Water/Binder Ratio
LM-0C	Hydrated lime 90% Metakaolin 10%	0	0.68
LM-0.5C		0.005	
LM-1C		0.01	
LM-3C		0.03	
LM-5C		0.05	

The chemical composition of the mixtures was examined by means of X-ray fluorescence (XRF). The determined amounts of the individual components are presented

in Table 2. Casein was used as a partial substitute for the calcium-pozzolanic mixture; therefore, the amounts of individual oxides decrease proportionally with the increase in the content of casein. Only the sulfur oxide content increases along with the casein content, because casein contains about 0.8% sulfur in its composition. In the modified mixtures, in contrast to the reference blend, the presence of potassium oxide was also noted.

Table 2. Chemical composition of tested paste mixtures.

Constituents	LM-0C	LM-0.5C	LM-1C	LM-3C	LM-5C
	Composition (g per 100 g)				
MgO	0.34	0.32	0.34	0.34	0.32
Al_2O_3	3.00	3.08	3.08	2.99	2.63
SiO_2	5.42	5.64	5.66	5.12	4.64
SO_3	0.19	0.20	0.21	0.26	0.28
K_2O	-	0.07	0.06	0.07	0.11
CaO	90.33	89.43	88.89	87.47	86.30
TiO_2	0.21	0.23	0.24	0.23	0.22
MnO	0.02	0.02	0.02	0.02	0.02
Fe_2O_3	0.49	0.51	0.50	0.49	0.48
ZnO	0.01	0.01	0.01	0.01	0.01

2.2. Sample Preparation

The mixes were prepared as follows: first, lime and metakaolin were dry mixed. The resulting binder mixture was slowly poured into the water while mixing continuously. After obtaining a mixture of a homogeneous consistency, casein was gradually added, mixing continuously until it dissolved and the mixture was homogenized.

During the preparation of the binder mix, it was observed that the addition of casein (Figure 1a) provided that the fresh mix turned sticky (casein glue was formed). This phenomenon can be beneficial when using the binder in combination with the aggregate. In [20], it was confirmed that the adhesion between the binder and the aggregate improved after adding the protein. It was also noticed that when increasing the amount of casein admixture (3% and 5%), the binder mixture was liquefied during mixing after dissolving the casein. This phenomenon is due to the introduction of air bubbles into the mixture, as foam is formed when the casein is mixed with the alkaline solution (Figure 1b). With the casein content equal to 0.5% and 1%, despite its dissolution, the binder mixture did not liquefy but thickened instead.

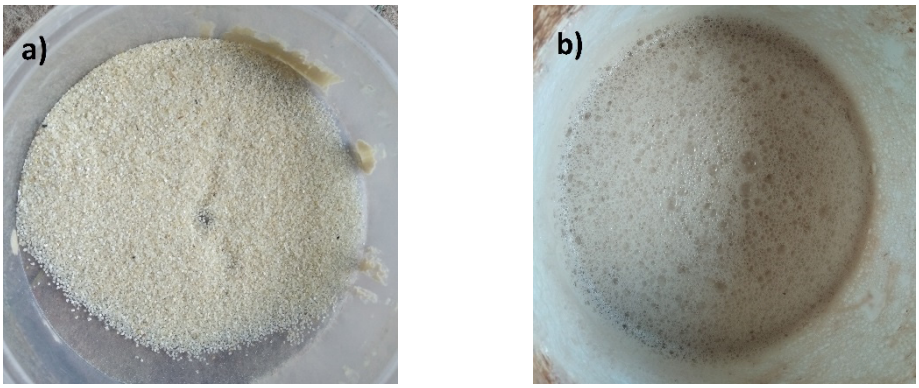

Figure 1. Casein used in the research: (**a**) casein powder, (**b**) casein dissolved in a calcium solution.

The mixture was placed in triple molds with dimensions of 40 mm × 40 mm × 160 mm and compacted for 15 s on a vibrating table. The samples were matured under the air-dry conditions (temperature: 21 °C ± 2 °C and relative humidity: 50% ± 5%) for 40 days. After this time, the investigation was carried out.

2.3. Pore Size Distribution

In the study of the pore characteristics of the porous medium by mercury porosimetry, the amount of mercury that is introduced under pressure into the pores of the tested material is determined, assuming that the increase in pressure will fill the pores of progressively smaller size. With this method, it is possible to identify the pores with a size from about 0.003 to 360 µm. The tests were performed using an Autopore IV 9510 mercury porosimeter (Micromeritics, Norcross, GA, USA). Before the measurement, the samples weighing about 0.6 g were dried at 105 °C to remove the physically absorbed water vapor and other gases from the pore surface.

The equivalent pore radius was determined from the Washburn Equation (1). Distribution of pore size and surface area was presented by means of cumulative and differential curves in the diameter range from 0.003 µm to 360 µm. The mean pore diameter (D) was obtained assuming that all pores are cylindrical; thus, when the total pore volume ($V = \pi r^2 L$) is divided by the total pore area ($S = 2\pi rL$) the value of the mean pore diameter equals 4V/S. The bulk density of the samples was determined according to Formula (2). In turn, the apparent density of the samples was determined in line with Formula (3).

$$R = \frac{2\sigma_m \times \cos\theta_m}{P_m} \tag{1}$$

where: R—is the pore radius, σ_m—is the mercury surface tension (0.485 J·m^{-2}), θ_m—is the mercury contact angle (assumed as 130°), P_m—is the external pressure (Pa).

$$d_n = d_{Hg} \times M/(M1 - M2 + M) \tag{2}$$

where: d_n—is the bulk density (g/cm^3), d_{Hg}—is the density of mercury at the measurement temperature (g/cm^3); M—is the sample mass (g), $M1$—is the mass of the mercury-filled dilatometer (g), $M2$—is the mass of the mercury-filled dilatometer and the sample (g).

$$d_p = 1/\left(\frac{1}{d_n} - V\right) \tag{3}$$

where: d_p—is the apparent density (g/cm^3), d_n—is the bulk density (g/cm^3), V—is the total pore volume (cm^3/g).

The total porosity of the samples was calculated according to the Formula (4):

$$P = V \times d_n \times 100\% \tag{4}$$

The analysis of the pore distribution was performed using a scanning electron microscope Quanta FEG 250 (FEI, Hillsboro, OR, USA) that enabled to present the material structure in greater details. The samples of the pastes with breakthrough surfaces intentionally sampled for strength tests were glued with carbon glue. Such prepared samples were covered with a carbon layer having a thickness of about 50 nm to achieve the conductivity on the their surface.

2.4. Flexural and Compressive Strengths

The flexural strength was tested according to the PN-EN 1015-11 standard on four samples with dimensions of 40 mm × 40 mm × 160 mm from each recipe. The compressive strength was also tested on the basis of the above-mentioned standard, on the breakthroughs of the samples obtained from the bending test. The strength tests were carried out on the MTS 809 hydraulic press. It was assumed that the head press displacement would be 0.2 mm/min in the bending test and 3 mm/min in the compression test. In other studies on lime-pozzolanic binders [31], the displacement of the head was stressed by the force increment: 50 N/s for the bending test and 200 N/s for compression.

In the case of lime binders, the strength is also influenced by the advancement of the carbonation process. A control test with phenolphthalein was performed. The fractures of the samples were wetted with a 1% phenolphthalein solution, and then the color changes were observed. The pink color obtained at the sample surface indicated the areas where calcium hydroxide has not yet transformed into calcium carbonate. The absence of a pink color indicates an area where the calcium carbon from carbonation is present. In this way, the depth of carbonation can be measured.

3. Results

3.1. Pore Size Distribution

Table 3 shows the average results of the paste tests performed by means of mercury porosimetry.

Table 3. The average results of the paste tests performed by means of mercury porosimetry.

Parameter	Unit	LM-0C	LM-0.5C	LM-1C	LM-3C	LM-5C
Total pore surface	m^2/g	13.70	20.13	18.78	17.16	15.81
Average pore diameter	nm	120.90	95.67	107.88	123.15	137.27
Total pore volume	ml/g	0.41	0.48	0.51	0.53	0.54
Total porosity	[%]	49.50	48.62	52.23	53.36	53.94
Density	g/ml	2.37	2.19	2.18	2.16	2.16
Bulk density	g/ml	1.20	1.01	1.03	1.01	0.99

The microstructure of the pastes was visualized by SEM analysis (Figure 2). The photos were taken at different magnifications on the breakthroughs of the samples.

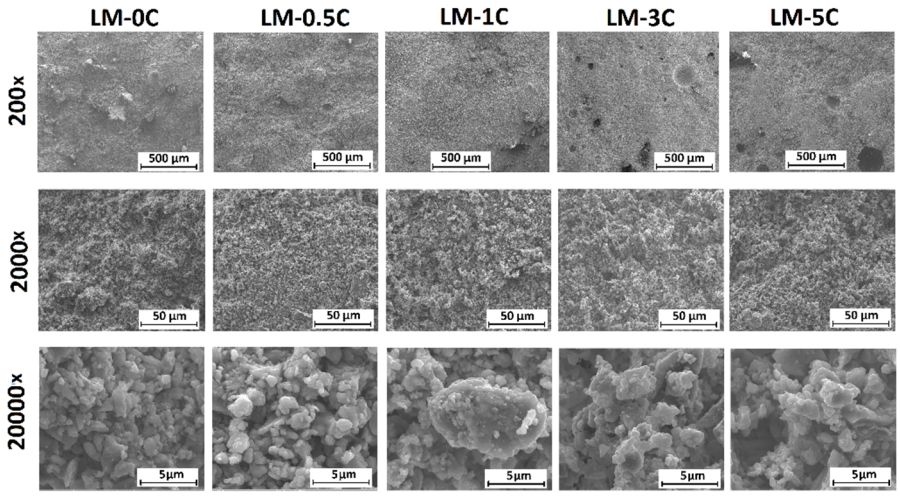

Figure 2. SEM images of paste samples.

The cumulative intrusion versus pore diameter curves and differential curves is shown in Figures 3 and 4, respectively. The total pore surface versus pore diameter curves is shown in Figure 5.

3.2. Flexural and Compressive Strengths

The relationships between the bending force and the displacement of the press head of all samples within an individual recipe are shown in Figure 6.

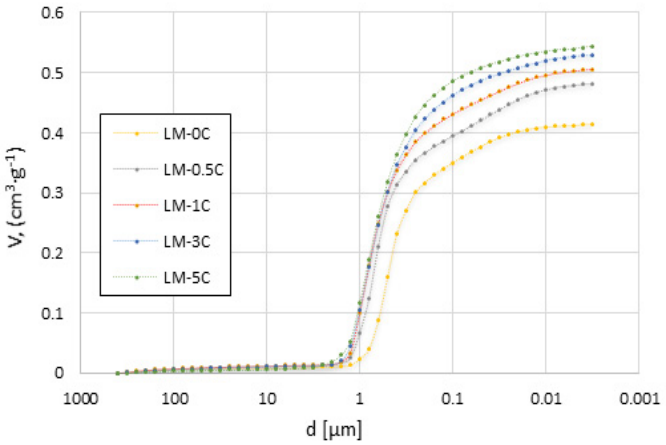

Figure 3. Cumulative volume of intruded mercury versus pore diameter for tested lime-metakaolin pastes.

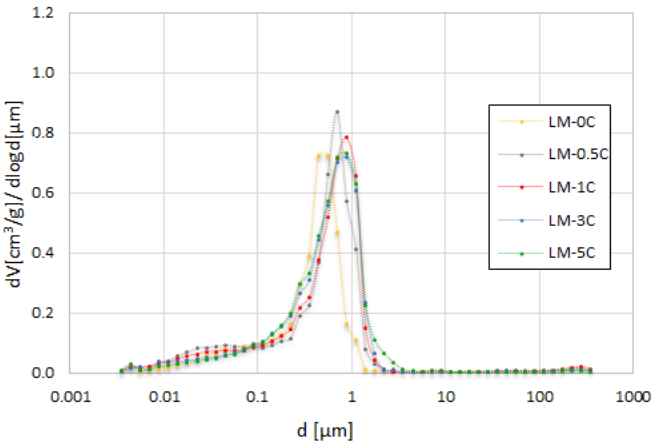

Figure 4. Differential volume of intruded mercury versus pore diameter for tested lime-metakaolin pastes.

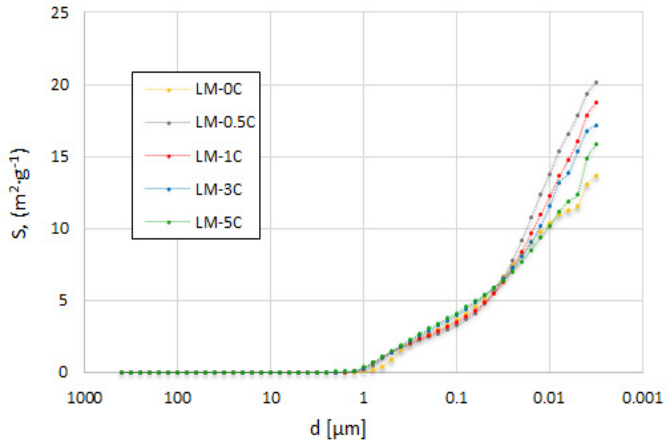

Figure 5. Total pore surface versus pore diameter for tested lime-metakaolin pastes.

The relationships between the stress and the strain of all samples within an individual recipe are shown in Figure 7.

The results of the flexural and compressive strength tests are shown in Figure 8. Error bars depict standard deviation.

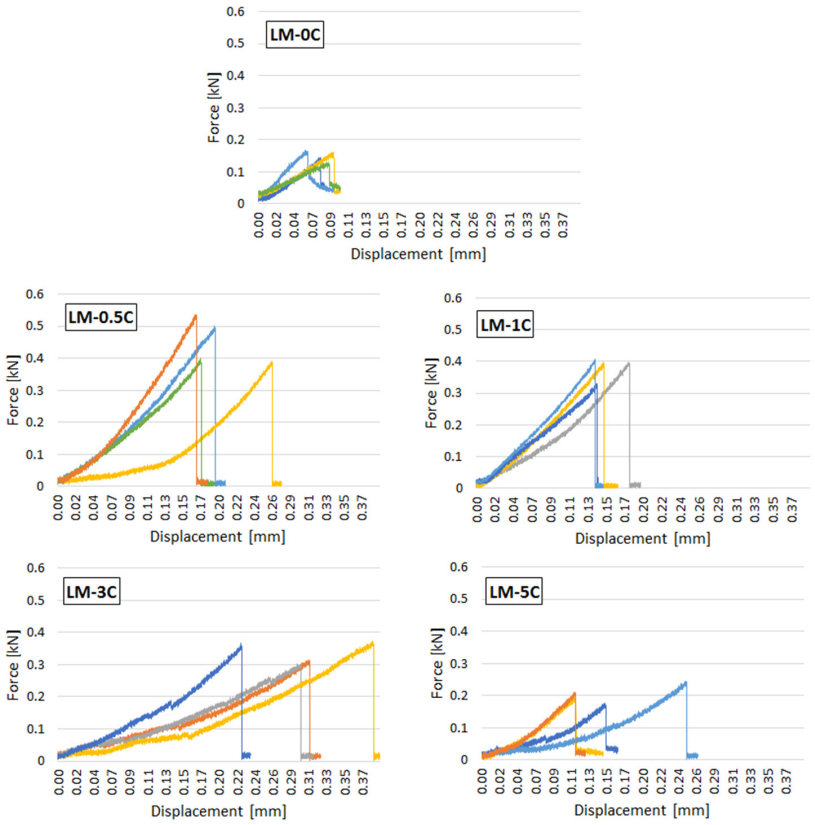

Figure 6. The dependence of the bending force on the press head displacement.

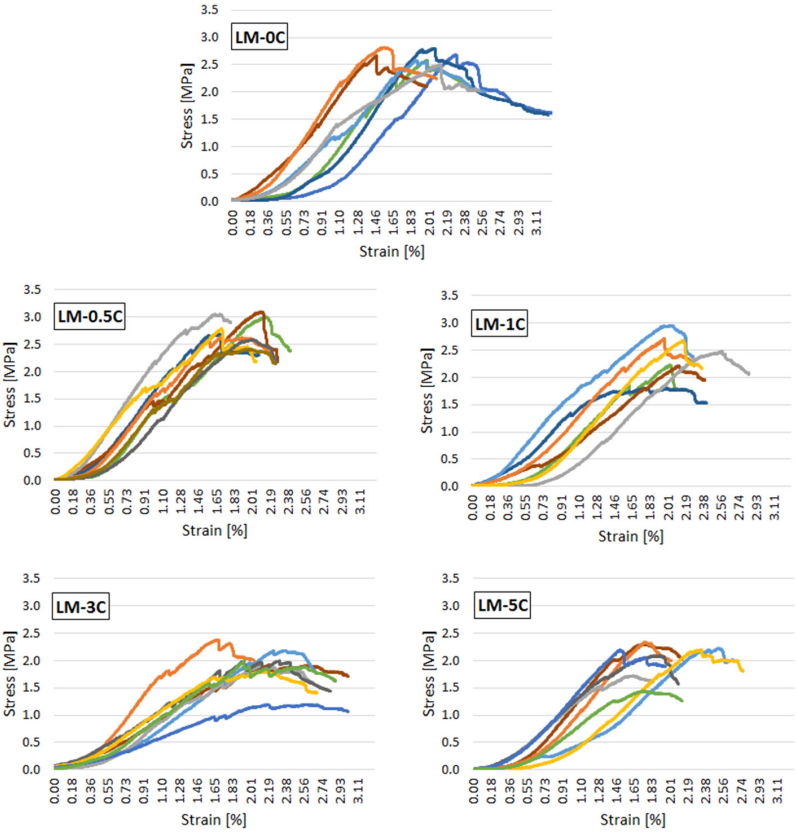

Figure 7. Stress–strain relationship for the tested pastes.

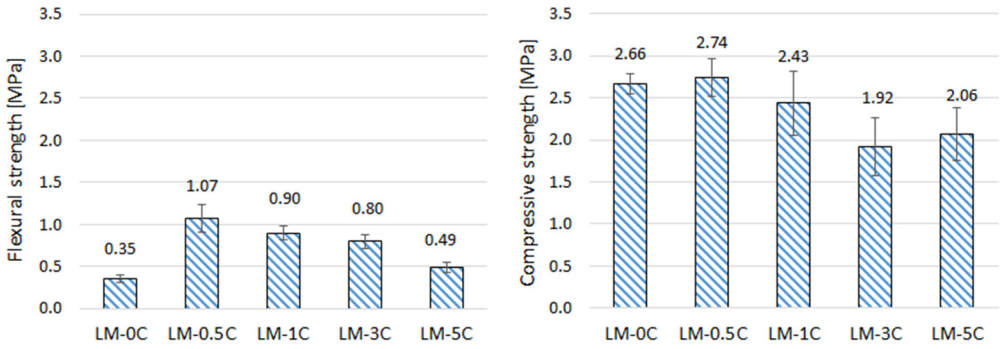

Figure 8. Average values of flexural strength (**left**) and compressive strength (**right**) of the tested samples (error bars mean standard deviation).

Figure 9 shows the effect of carbonation progress on sample breakthroughs after the phenolphthalein test.

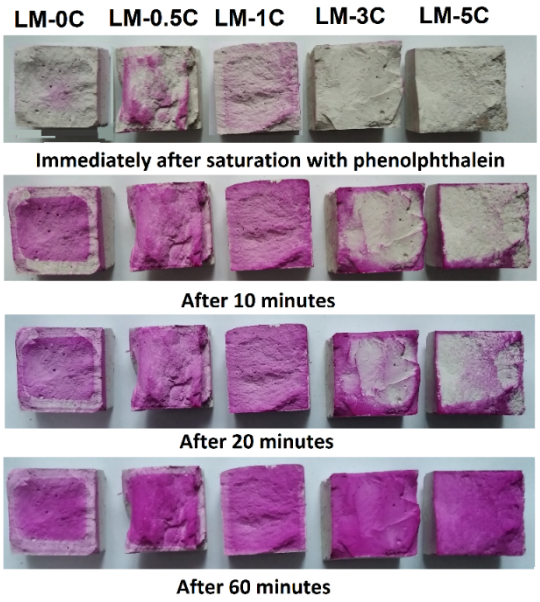

Figure 9. Progress of carbonation of the tested pastes.

4. Discussion

4.1. Pore Size Distribution

The 0.5% and 1% casein admixture led to a reduction in the pore diameter, as well as a significant increase in the total pore area (Table 3). In turn, an admixture of 3% and 5% liquefying the blend led to an increase in the mean pore diameter. The total pore volume increased along with the casein content. The 5% admixture increased the pore volume by nearly 32%. In turn, Ventola et al. [4] observed a reduction in the volume and average pore diameter in lime mortars after adding casein. In general, the overall porosity of the pastes increased along with the casein content. The increase in porosity is due to the introduced air bubbles during the mixing of the ingredients. The increased air content in mortars after adding casein was also observed in [20]. The air bubbles are created by the degradation of proteins. Small hydrophobic molecules are formed as a result of breaking the peptide bonds of large protein molecules [24]. The exception is the lowest content of 0.5%, which caused a decrease in the total porosity. The LM-0.5C mix was sticky and poorly workable during mixing, which could prevent the formation of air bubbles. The admixture of casein, by increasing the pore volume, led to a significant reduction in the bulk density of the pastes.

On the basis of SEM images (Figure 2), from the photos with magnification of 20,000 taken as an example, it can be seen that casein did not visibly affect the size, arrangement, and shape of the calcium hydroxide crystals. It can only be seen that as the casein content increases, the crystals are more dispersed, which is in line with the MIP results, according to which the casein admixture increases the porosity. The casein was dissolved in the calcium hydroxide solution to form a film coating the lime and metakaolin particles as the ingredients were mixed. Similar observations were described in [19], examining the soil modified with casein binder. In contrast, the photos at a magnification of 200 show that in the samples with an admixture of casein in the amount of 3% and 5%, there are air bubbles that were introduced during mixing.

In all pastes, pores with a diameter of 0.1–1 μm constitute the vast majority of the total pore volume. This is a common pore diameter range in lime pastes [32]. The cumulative pore volume of this diameter increases along with the admixture content (Figure 3). The cumulative volume of pores larger than 1 μm increases with the casein content. In the case of the reference mortar it is about 0.02 cm^3/g, while in the case of pastes with an admixture of casein it ranges from 0.07 to 0.12 cm^3/g. This may be related to the mixing process, during which the air bubbles were formed, especially in the LM-3C and LM-5C mixtures. The literature [33] confirms that through the mixing process and introducing air into the mixture, the number of pores with a diameter of more than 1 μm may be increased. Another reason may be that the mixtures with an admixture of casein in the amount of 3% and 5% were liquefied and mechanical compaction in the molds was not necessary. In this way, more pores larger than 1 μm could remain in the mix. When analyzing the distribution of pores with a diameter of less than 0.1 μm, it can be seen that the cumulative volume of these pores decreases with the increasing casein content (about 0.09 cm^3/g for LM-0.5C and about 0.06 cm^3/g for LM-5C).

Figure 4 shows clear differences in the pore distribution between the reference recipe and the casein-containing samples. The most visible difference is in the range of pores with a diameter of 0.9 to 1.1 μm. This shows that the casein caused the formation of significant amounts of larger pores in the paste. The reference sample has definitely fewer large pores than the modified pastes. The maximum pore diameters recorded in the reference sample are 1.4 mm; in the samples with the casein content it is 1.8–2.2 μm, while in the sample with the highest casein content it is 3.5 μm. The content of pores with larger diameters increases along with the content of casein. The 0.5% admixture caused a significant increase in the number of pores in the diameter of about 0.7 μm compared to the samples with the higher admixture content, which showed a similar content of pores of such diameter. In the case of pores with a diameter of about 0.9 μm, the opposite situation occurred—the LM-0.5C sample contains much fewer large pores than the rest of the modified pastes. In the case of LM-0C and LM-0.5C samples, there is a clear shift of the graph peaks to the left of the samples with higher casein contents. This proves that the pores with smaller diameters (<0.9 μm) prevail in the reference sample and the sample with the lowest casein content than in the samples with a higher casein content.

The diagram (Figure 5) shows that in the pore range from 0.5 to 1.5 μm, the greatest total pore area is found in the paste with an admixture of protein in the amount of 5%. The greatest differences in the values of the total pore area, as well as their dynamic growth, are visible in the case of the pores with diameters lesser than 0.5 μm. It can be noticed then that the lower the casein content, the greater the total pore area, while the lowest is in the case of the reference paste.

4.2. Flexural and Compressive Strengths

The samples with an admixture of casein in the amount of 3% behaved most flexibly under the load, i.e., the damage occurred at the largest deflection of the samples (about 0.23–0.38 mm). In the case of the samples from other recipes, as a rule, the deflections did not exceed 0.2 mm (apart from exceptions, significantly deviating from the average). In the samples with the highest amount of casein (3% and 5%), the behavior of the samples

under load was the most varied (destruction, despite the similar destructive force, occurred at different deflection), while in the case of the samples with smaller amounts of casein, a greater predictability of the material behavior under load (especially LM-1C) can be seen. These observations prove a greater homogeneity of the structure of the mixtures containing 0.5% and 1% casein. The samples from LM-1C showed the greatest stiffness because the destruction force equal to about 0.4 kN occurred with the smallest deformation (axial displacement in the range of 0.14 to 0.18 mm). On the basis of the behavior of the LM-3C sample, it could be concluded that the more casein in the blend, the greater the flexibility of the binder, but the behavior of the LM-5C samples contradicted this.

When analyzing the stress-strain diagrams, one can see the same dependencies as in the case of the behavior of the samples in the bending test. The most similar and reproducible behavior of samples within the same recipe was observed in the case of LM-0.5C and LM-1C recipes. The destruction of the samples from the LM-0.5C recipe took place with a deformation of about 1.5–2.1%, while the samples from the LM-1C recipe had a deformation of about 1.9–2.5%. The samples containing 3% casein showed the greatest elasticity, because the maximum stress (20–30% lower than for LM-0.5C and LM-1C) occurred at a strain above 2% (except for one sample).

The flexural strength of the tested pastes ranged between 0.35 and 1.07 MPa (Figure 8). The examined admixture (casein) improved the flexural strength. The produced casein glue (casein dissolved in a lime solution) could have contributed to the improvement of the adhesion of lime particles, as a result of which the bending strength was increased. The admixture in the amount of 0.5% turned out to be the most effective, and with the increase in the casein content, the flexural strength decreased. The additive of 0.5%, 1%, and 3% increased the average strength of the pastes by 205.7%, 157.1%, and 128.6%, respectively, compared with the LM-0C formula. With the 5% admixture, there was a marked decrease in performance compared to the lower amounts of casein, but still the flexural strength was improved by 40% with respect to LM-0C. In turn, Mydin [12], by modifying the lime mortar with another protein (from egg white), noticed an increase in the flexural strength with the protein content, but only up to 6%. The amount of additive above 6% resulted in a decrease in strength. The reason for the decrease in strength along with the increase in casein content may be the use of the same water-to-binder ratio. The pastes with a casein amount of 3% and 5% had a liquid consistency. The admixture acted as a superplasticizer. Therefore, the excess of water, in the amount which was necessary to obtain the appropriate consistency and workability in LM-0.5C and LM-1C, could weaken the matrix of the paste in the LM-3C and LM-5C blends.

The compressive strength of the tested pastes ranged between 1.92 and 2.74 MPa (Figure 8). Almost each of the analyzed contents of the admixture deteriorated the compressive strength of the lime-metakaolin paste. The exception is an admixture in the amount of 0.5%, which improved the average strength by 3%, but within this recipe there was a greater scatter of results than in the case of the receptive binder. The greatest decrease in strength was recorded in the LM-3C formulation, i.e., by nearly 28% in relation to the reference paste. However, this result and the flexural test results confirm the need for further testing of these binders with less than 0.5% casein. Each amount of casein increased the discrepancy of the results (higher standard deviation than the reference samples), which proves that the homogeneity of the paste structure is weakened. Similar dependencies were observed in the compressive strength test. A decrease in the compressive strength with an increase in the protein content (but derived from bovine blood) was observed by Jasiczak [11]. However, in this case, the addition of 0.5% of the cement volume caused a drastic decrease in strength, by about 50% in relation to the reference cement mortar.

There is a noticeable influence of the total porosity size on the compressive strength. Usually, the porosity of building materials increases, as their compressive strength decreases [34,35]. Here, this relationship is true, because LM-0.5C is characterized by the lowest porosity and the highest strength, while porosity increases with the casein content, but the compressive and flexural strengths decrease. The number of pores with larger

diameters increases with the amount of admixture, which is also disadvantageous due to the strength parameters.

In the own research, the proportions of the binder components were the variables. Along with the increase in the casein content, the amount of metakaolin decreased, which could also reduce the strength. The casein binding capacity depends on the pH of the solution in which the protein is dissolved [36], as well as on the weight or volume ratio of the alkali to casein [17]. In this study, casein was dissolved in a ready-made mixture of water, lime, and metakaolin (amounts according to recipes), in the ratio (lime-metakaolin: casein) 99.5:0.5; 99:1; 97:3, and 95:5. Other papers report different ratios, namely 1:3.2 (alkaline: casein by weight). In subsequent studies, it would be advisable to check whether pre-dissolving the casein in a solution of a different concentration and then adding this solution to the lime-pozzolanic mixture causes changes in strength.

On the basis of the phenolphthalein test (Figure 9), it can be concluded that the greatest depths at which calcium hydroxide was converted to calcium carbonate were 6 mm in the reference sample and 4 mm in the sample containing 0.5% casein. In the case of the sample with an admixture of 1%, the maximum depth is smaller and amounts to 2 mm. An interesting observation is that the admixture of 3% and 5% slowed down the reaction of phenolphthalein with lime particles. The admixtures in these amounts liquefied the mixture, thoroughly coating the lime and metakaolin particles with a film that limited the absorption of phenolphthalein. In turn, after 60 min of testing, these samples were completely covered with a pink color, which may indicate that the presence of casein led to a decrease in the pH value of the paste.

5. Conclusions

This article presents the research on the pore size distribution and mechanical properties of the lime-metakaolin paste differing in the amount of casein admixture. A thorough analysis of the results made is possible to formulate the following conclusions:

- Casein addition affects the pore size distribution and total porosity within the lime-metakaolin paste. The casein addition in the amount of 0.5% and 1% reduced the pore diameter while substantially increasing the total pore area. In turn, the 3% and 5% addition increased the mean pore diameter compared to the paste used as reference. The porosity increased as a result of air bubbles being introduced in the course of ingredient mixing;
- The admixture of casein significantly increased the flexural strength of the pastes. The admixture in the amount of 0.5% turned out to be the most effective, and with the increase in the casein content, the flexural strength decreased;
- Only the 0.5% casein admixture improved the compressive strength of the lime-metakaolin paste. In general, the strength decreased with the increasing casein content, with the samples containing 3% casein having the lowest strength;
- The results show a clear dependence of the strength parameters on porosity. Total porosity of the pastes increases along with the casein content, whereas the compressive and flexural strengths decrease. The increase in pore diameter with casein content may also cause a decrease in strength;
- The phenolphthalein test showed no significant differences in the progress of the carbonation process of the pastes. In addition, the SEM observations did not show any significant differences in the structure of the pastes with a variable amount of casein.

In further research, it is planned to check the parameters of binders with an admixture of casein in an amount lesser than 0.5%, because this study has shown that the lower the casein content, the better the strength parameters. Another prospective research is to use these binders in the composites based on hemp shives. Perhaps, other effects are to be expected in this case, e.g., the stickiness of the dissolved casein may improve the adhesion of the binder to the shives resulting in an increased strength.

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