Early Age Properties of Modern Rendering Systems Based on Mineral Binders Modified by Admixtures

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Abstract: This paper presents part of the results from a doctoral project studying the mechanism and chemistry of modern rendering systems. The study is focused on polymer modified renders, a type of material that possesses several superior properties to conventional renders, such as better workability, crack resistance, adhesion to substrate and flexural strength.

In this study the influences of different admixtures and additions on the early age properties, such as water retention, plastic shrinkage and dry shrinkage, are investigated. The flexural strength and the thermogravimetric analysis on hardened specimens were carried out in order to examine the mechanical property and to explain the early age behaviour of the modern rendering systems. The results show that the cellulose water retainer not only improve water retention, but also significantly introduce air content in both the cement and the cement-lime binder systems. Styrene-Butylacrylate based copolymer significantly increased the flexural strength as expected, but revealed a high dry shrinkage. Vinyl Acetate/Ethylene co-polymer tends to reduce the plastic shrinkage.

1. Introduction

Composite mineral–organic materials and in particular cement-organic materials are increasingly used in today's construction applications and civil engineering projects [1]. Polymer modified render is such type of material that possesses several superior properties to conventional renders, such as better crack resistance, adhesion to substrate and flexural strength. This improves the durability of the material. The importance of understanding the mechanisms behind the materials behaviour is crucial when designing new and advanced products for the industry [2]. There are many factors influencing the behaviour of a material and it is necessary to build up a fundamental knowledge on the chemistry and mechanisms affecting it. To improve the knowledge and understanding of modern rendering systems, a doctoral project was initiated at Chalmers University of Technology under the financial support of maxit Group. The main part of the doctoral project consists of studies on the interactions between composition, hardening process, microstructure and transport properties. The influence of different admixtures, especially organic polymers and air entraining agents, was studied. In the plastic state the consistency and plastic shrinkage as well as water retention are studied. Among the decisive properties of the hardened mortars the focus is kept on vapour transport, moisture transport properties and drying shrinkage [3]. The influence of the decisive property profile on durability of the hardened render during exposure to environment parameters is investigated. In this paper the experiments and findings of the early age properties are presented.

2. Experimental study

2.1. Experimental program

In this study the experiments were separated into 2 main groups, based on type of binder used; cement and lime/cement. Both groups of compositions had constant ratio binder/aggregate content and the water content was adjusted to maintain constant consistency. A reference composition, without any admixtures, was created for each group, thus forming the 2 reference mortars. These reference compositions are defined as “C” and “LC”, as shown in Tables 1 and 2, and were used for studying the effect of different admixtures. The two reference compositions were then developed further. An air-entraining agent was introduced as well as a water retainer, referred to in the text as Admixture 1 and Admixture 2 respectively:

- Admixture 1
  Air entraining agent
  C_{14}/C_{16}-alpha olefin sulphonate
  This is an anionic surfactant used for air entraining and modification of consistency. This is a good foaming powder and the foam quality is fine, with high stability. It is compatible with anionic and non-ionic surfactants and resistant to acids and alkalines.

- Admixture 2
  Water retainer
  Methyl-hydroxyethyl cellulose (MHEC)
  Non-ionic cellulose derivative. It provides a creamy consistency and easy workability to the fresh mortar, but more importantly, it has high water retention. Soluble in pH-neutral cold water (specifications).

The series then expanded further as the two final admixtures were introduced in varying amounts, Admixture 3 and Admixture 4:

- Admixture 3
  Vinyl Acetate/Ethylene Copolymer (Et/VAc)
  Thermoplastic latex of anionic type with good resistance to

saponification. Enhances adhesion, flexural strength, plasticity and workability of modified compounds.

- Admixture 4
  Styrene-Butylacrylate Copolymer (SBA)
  Synthetic rubber latex. Redispersible polymer powder of anionic character. Improves strength, adhesion and impermeability.

In Tables 1 and 2 all compositions are listed and grouped according to binder, amount of admixture and admixture type.

Explanation of codes used in Tables 1 and 2:
C = cement based
LC = lime/cement based
a = air entraining agent included
b = water retainer included
c = Admixture 3 (number indicating amount by binder in %)
d = Admixture 4 (number indicating amount by binder in %)

The groups are then identified as:
C-c = cement based, increasing amount of Admixture 3
LC-c = lime/cement based, increasing amount of Admixture 3
C-d = cement based, increasing amount of Admixture 4
LC-d = lime/cement based, increasing amount of Admixture 4

Table 1. Compositions based on constant consistency and grouped by binder. Increasing amount of Admixture 3.

	Constant consistency	
	Group: C-c Cement + aggregate	Group: LC-c Cement/lime + aggregate
Reference	C	LC
Ref. + Adm. 1	C-a	LC-a
Ref. + Adm. 2 (0,60%)	C-b	LC-b
Ref. + Adm. 1 & 2 (0.60%)	C-a-b	LC-a-b
Ref. + Adm. 1 & 2 (0,60%) + Adm. 3 (3%)	C-a-b-c3	LC-a-b-c3
Ref. + Adm. 1 & 2 (0,60%) + Adm. 3 (6%)	C-a-b-c6	LC-a-b-c6
Ref. + Adm. 1 & 2 (0,60%) + Adm. 3 (12%)	C-a-b-c12	LC-a-b-c12
Ref. + Adm. 1 & 2 (0,60%) + Adm. 3 (24%)	C-a-b-c24	LC-a-b-c24

Table 2. Compositions based on constant consistency and grouped by binder. Increasing amount of Admixture 4.

	Constant consistency	
	Group: C-d Cement + aggregate	Group: LC-d Cement/lime + aggregate
Reference	C	LC
Ref. + Adm. 1	C-a	LC-a
Ref. + Adm. 2 (0,60%)	C-b	LC-b
Ref. + Adm. 1 & 2 (0.60%)	C-a-b	LC-a-b
Ref. + Adm. 1 & 2 (0,60%) + Adm. 4 (3%)	C-a-b-d3	LC-a-b-d3
Ref. + Adm. 1 & 2 (0,60%) + Adm. 4 (6%)	C-a-b-d6	LC-a-b-d6
Ref. + Adm. 1 & 2 (0,60%) + Adm. 4 (12%)	C-a-b-d12	LC-a-b-d12
Ref. + Adm. 1 & 2 (0,60%) + Adm. 4 (24%)	C-a-b-d24	LC-a-b-d24

2.2. Constituents used in formulations

For all of the compositions the following formulation was used as a base: (percentage by weight)

Cement binder base:
CEM II/A-L 42,5 R: 16.67%
(“Byggcement/Slite”)

Lime/cement binder base:
CEM II/A-L 42,5 R: 8.33%
(“Byggcement/Slite”)
German Technical Lime, Scheaffer: 8.33%
(”Släckt Murkalk E”)

Aggregate:
Natural silica sand: 83.33%
The sieve curve of sand used in the study is shown in Table 3.

Table 3. Passing percentage for sand sieve curve.

Sieve curve	Passing percentage [%]
2 mm	100
1 mm	80
0.5 mm	50
0.25 mm	25
0.125 mm	4
0.075 mm	2

The four admixtures were weighed as a ratio to the binder, the polymer/binder ratio:

- C_{14}/C_{16}-alpha olefin sulphonate
  0.02 %
- A methyl-hydroxyethyl cellulose (MHEC)
  0.60 %
- Ethylene-Vinyl Acetate Copolymer (Et/Vac)
  3.0, 6.0, 12.0, 24.0 %
- Styrene-Butylacrylate Copolymer (SBA)
  3.0, 6.0, 12.0, 24.0 %

2.3. Water content in the compositions

For all compositions, the criteria constant consistency, or constant flow, was used. The amount of water used is shown in Tables 4 and 5.

Table 4. Water content for Groups C-c and LC-c, based on total dry weight.

Group: C-c	**Water content**	**Group: LC-c**	**Water content**
C	14.7%	LC	17.9%
C-a	13.3%	LC-a	15.7%
C-b	15.0%	LC-b	17.6%
C-a-b	13.6%	LC-a-b	17.0%
C-a-b-c3	14.0%	LC-a-b-c3	17.3%
C-a-b-c6	14.0%	LC-a-b-c6	16.6%
C-a-b-c12	13.3%	LC-a-b-c12	16.0%
C-a-b-c24	13.3%	LC-a-b-c24	16.3%

Table 5. Water content for Groups C-d and LC-d, based on total dry weight.

Group: C-d	**Water content**	**Group: LC-d**	**Water content**
C	14.7%	LC	17.9%
C-a	13.3%	LC-a	15.7%
C-b	15.0%	LC-b	17.6%
C-a-b	13.6%	LC-a-b	17.0%
C-a-b-c3	14.6%	LC-a-b-c3	16.7%
C-a-b-c6	14.0%	LC-a-b-c6	16.7%
C-a-b-c12	13.3%	LC-a-b-c12	18.0%
C-a-b-c24	12.7%	LC-a-b-c24	15.0%

2.4. Measurements of relevant properties – fresh mix

A number of properties were measured in the fresh state including rheology but in this paper the following properties are presented.

2.4.1. Density and air content

The air contents of the fresh mortars were measured using the pressure method, EN 1015-7. The density was measured using the same container used for measuring the air content of exactly 1 dm^3.

2.4.2. Consistency using the flow table

This procedure was performed in accordance with EN 1015-3. After the material had spread on the table, the average diameter was measured and round off to the nearest 5 mm.

2.4.3. Water retention

The water retention tests were performed in accordance with EN 1015-8. The principle is to measure the water retained in a sample of fresh mortar when subjected to suction.

2.4.4. Plastic shrinkage

In this test, the shrinkage of the render was measured at a very early age, that is, when the material was still in a plastic state. The first measurements started roughly 30 minutes after mixing and the shrinkage was then monitored for 48 hours. The equipment used for the measurements was the Delta-L developed by Cementa Research in Sweden (former Scancem Research). This equipment measures length change during a specified time period at intervals set by the user. The precision of the length measuring gauges used was 1/1000 mm length change. The form was custom made for this series of experiments. The inner size of the form was 150 mm in length and 100 mm width, see Figure 1. The depth of the cast specimen was 10 mm, making the experiments more realistic for thin coat renders.

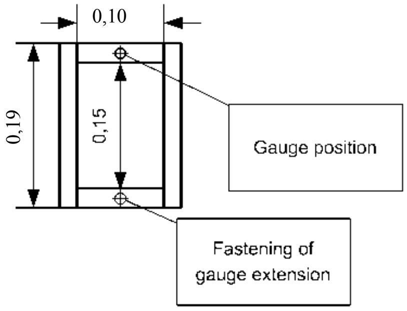

Figure 1. Simple sketch of the form used for measuring plastic shrinkage.

2.5. Measurements of relevant properties – early age to hardened state

Specimen was also cast to measure several properties in the early age to hardened state and two of the experiments measured are described below.

2.5.1. Drying shrinkage properties

Prisms were cast to measure the drying shrinkage of each composition, according to EN 1052-1. After curing, the specimens were placed in a climate room (RH=50% and T=20ºC) and measurements were made continuously to monitor the relative length change. The drying shrinkage at 28 days was noted.

2.5.2. Thermogravimetric analysis

The thermo balance used in this study is a LECO MAC-500. It can be programmed in five temperature steps in the range from room temperature up to 1000ºC [4]. It can analyse up to 19 samples simultaneously. In the thermogravimetric analysis performed, the specimens were fully saturated with water before the start of the analysis and then placed inside the furnace. Starting at room temperature, the heating rate was set for 10ºC/minute until the next temperature step was reached. Here the temperature remained until all the compositions had reached weight equilibria. Once they were all stable, the heating rate proceeded until the next level and so on. In Table 6 the temperature ranges and corresponding decomposing compounds are shown.

Table 6. Temperature ranges for the thermogravimetric analysis [4].

Temperature range	Decomposing compound
-105	Evaporable water
105-380	Most water in the CSH and CAH phases
380-450	Hydroxyl in Ca(OH)2
450-600	Some hydrates + carbonation products other than calcite
600-975	CaCO3 (calcite) + Other non-defined components

3. Main results and discussion

In this experimental study, the influence of different admixtures with the special focus on organic polymers and air entraining agents was investigated.

3.1. Air content, consistency and workability

Adding air entraining agents and cellulose ethers to the reference compositions dramatically increases the air content in the mortar. However, for the compositions based on a lime/cement binder, the effect is somewhat reduced. This can probably be attributed to the hard ions in calcium-enriched samples, which depress the foam. When introducing Styrene/Butylacrylate copolymers (SBA) the air content is further reduced for the lime-enriched samples, i.e. Group LC-c, see Figure 2.

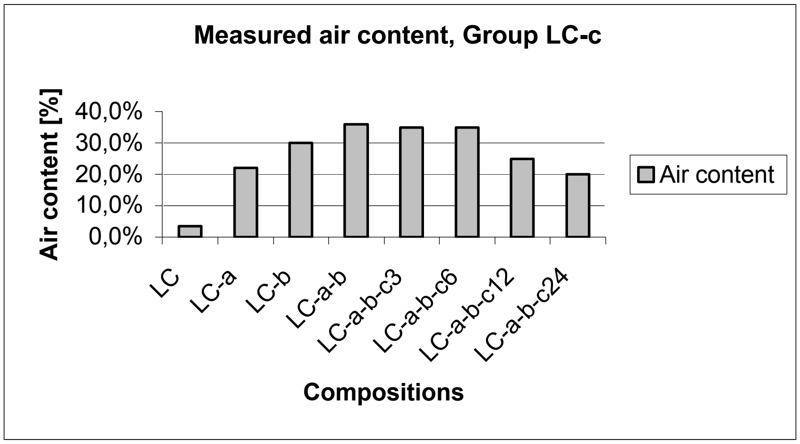

Figure 2. Measured air content in the fresh mix for Group LC-c, lime/cement compositions, increasing amount of Styrene/Butylacrylate copolymers (SBA).

The water demand is lower for polymer-modified renders. Most of the effect comes from the surfactants introducing air into the system. The increase in workability is often ascribed to some sort of “ball bearing” action of the air bubbles. The highly numerous air bubbles are compressible compared to the other constituents of the mortar and allow for easier deformation when the mortar is worked, resulting in an improvement in workability.

3.2. Water retention

It is expected that water absorption of methylcellulose-modified systems should increase with rising polymer/cement ratio. Methylcellulose causes a considerable swelling due to water absorption, and seals capillary cavities in the modified systems. This decreases bleeding and keep the water inside the material hence retain water. On the introduction of cellulose ethers the water retention for all compositions was well above 95% but an interesting find was the contribution of the copolymers, Admixtures 3 and 4. For the SBA, this could probably be explained by the hydrophilic colloidal properties and the inhibited water evaporation due to the filling and sealing effects of impermeable polymer films. To separate the effect of these admixtures a new investigation was carried out where these admixtures where introduced to the reference compositions separately. The results are shown in Figure 3 and clearly indicate the copolymers contribution to water retention.

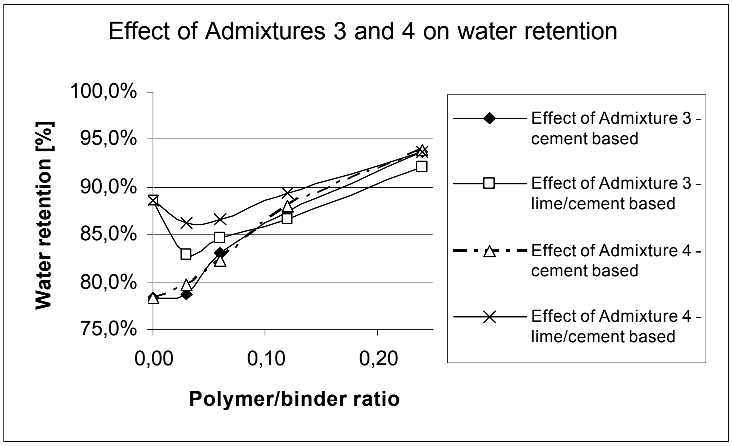

Figure 3. Effect of Admixtures 3 and 4 on water retention.

3.3. Plastic shrinkage

Compared to the reference compositions, plastic shrinkage was generally reduced for the lime/cement-based compositions modified by admixtures, whereas an increase was found in the cement-based. Also interesting is the effect of Admixture 3 on the dormant period in the cement-based groups, see Figure 4. The shell formation of cement grains seems to be prevented by the polymers, resulting in an unclear dormant period which is eliminated with higher amounts, probably due to continued access to mixing water. This effect is not seen for the lime-enriched samples where the shell formation in cement grains is not clear, see Figure 5.

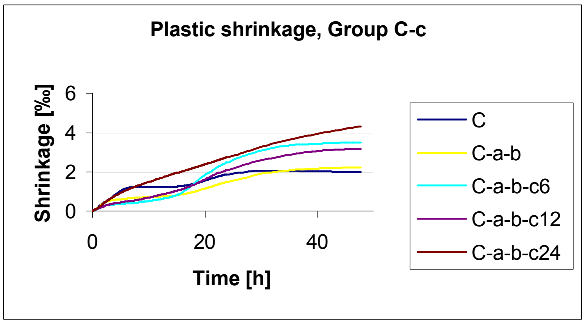

Figure 4. Effect of Admixture 3 on plastic shrinkage, Group C-c, cement based renders with constant consistency.

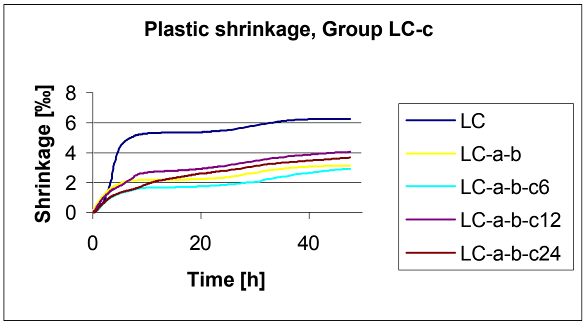

Figure 5. Effect of Admixture 3 on plastic shrinkage, Group C-d, cement based renders with constant consistency.

3.4. Drying shrinkage

From the results obtained it is clear that the drying shrinkage increases on the introduction of air entrainers and cellulose ethers and combinations of these. This was seen for both cement and lime/cement based compositions, see Figures 6 and 7. The effect of Vinyl Acetate/Ethylene Copolymer (Et/VAc), Admixture 3, was negligible compared to the air entrained reference compositions, see Figure 6. This was seen for both cement and lime/cement based mortars.

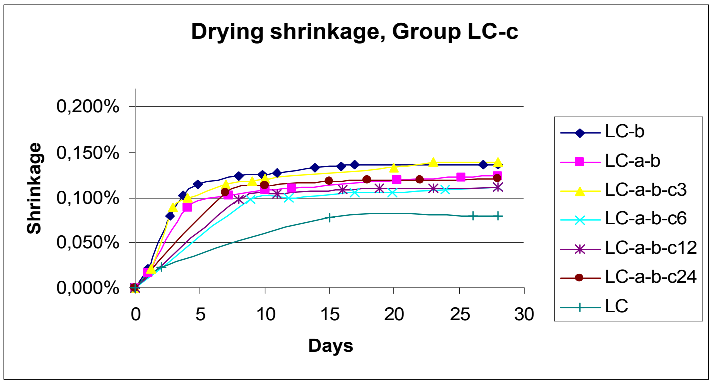

Figure 6. Drying shrinkage for Group LC-c, lime/cement based compositions with increasing amounts of Admixture 3, Vinyl Acetate/Ethylene Copolymer (Et/VAc).

Admixture 4, Styrene-Butylacrylate Copolymer (SBA) however, shows an increase in drying shrinkage with increasing polymer binder ratio, see Figure 7, both for cement and lime/cement based mortars.

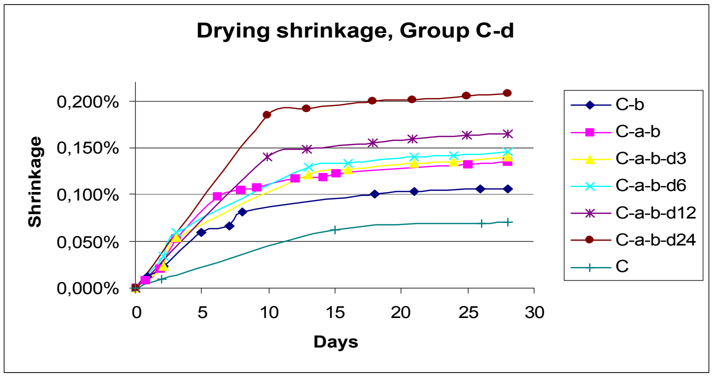

Figure 7. Drying shrinkage for Group C-d, cement based compositions with increasing amounts of Admixture 4, Styrene-Butylacrylate Copolymer (SBA).

3.5. Flexural strength

In Figure 8 the effect of Admixtures 3 and 4 on flexural strength is shown. Styrene-Butylacrylate based copolymer significantly increased the flexural strength but Vinyl Acetate/Ethylene copolymers also give a higher flexural strength, especially for lime/cement based compositions.

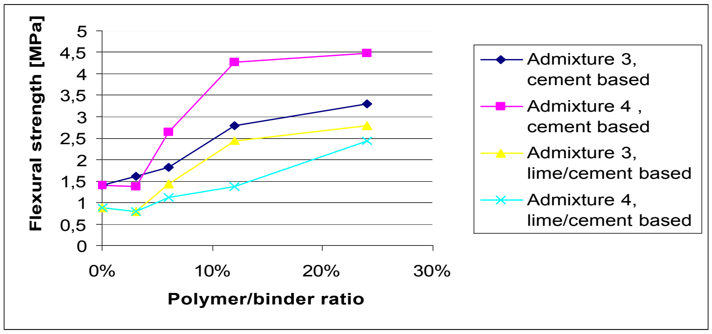

Figure 8. Effect of Admixtures 3 and 4 on flexural strength.

3.6. Thermogravimetric analysis

The chemically bound water can be measured as a weight decrease in the interval 105-380ºC during the thermogravimetric analysis. The results of the analysis showed a clear trend with an almost linearly increasing amount of decomposing compounds in the specimen with increasing amount of Admixtures 3 and 4 for all groups, see Figure 9. However, separate tests showed a major weight loss of the copolymers in the same temperature ratio, and the total weight loss is therefore a combination of chemically bound water and decomposing copolymers.

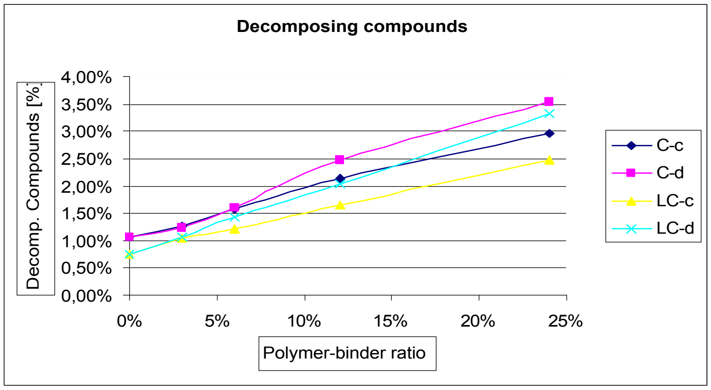

Figure 9. Effect of Admixtures 3 and 4 on decomposing compounds (105-380ºC) in hardened mortars.

4. Concluding remarks

- The results show that the cellulose water retainer not only improve water retention, but also significantly introduce air content in both the cement and the cement-lime binder systems.
- Styrene-Butylacrylate based copolymer significantly increased the flexural strength as expected, but revealed a high dry shrinkage.
- Vinyl Acetate/Ethylene co-polymer tends to reduce the plastic shrinkage of lime/cement based materials whereas an increase was found for cement-based compositions.
- SBA, Styrene/Butylacrylate copolymers increase the flexural strength for both cement and lime/cement base mortars.

References:

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