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New Generation of Binders for 2K Fast Curing Waterproofing Membranes

ABSTRACT

Waterproofing membranes are typically used underneath tiles in bathrooms, terraces, swimming pools and water tanks. The fast curing of a membrane is an important attribute for the market of waterproofing because it offers the applicator the possibility to apply a second waterproofing layer and tiles within the same working day. A drymix formulated with fast cement and combined with standard latex results in a very short pot life mortar and a membrane that lacks flexibility and very often has cracks and hence is not waterproof. A new generation of latexes developed by Dow Construction Chemicals combined with a fast drymix provides superior waterproofing performance, very high flexibility and crack bridging, as well as elongation retention after water swelling. The new latexes provide long enough pot life to allow good workability and still enabling the application of a new layer on top of the first layer within 0.5-2h.This new technology will provide the waterproofing market an environmentally advanced option for both interior and exterior applications.

INTRODUCTION

Waterproofing membranes find use as the support and sealer layer underneath tiles in bathrooms, terraces, swimming pools and water tanks. In ordinary Portland cement (OPC) or standard two-component cementitious waterproofing membrane compositions, 2 mortar layers have to be applied to achieve sufficient thickness and waterproofing quality. When using OPC in a dry mix, the time to apply the second layer is after at least 24 hours.

Faster curing waterproofing membranes can be achieved by using fast setting cement like calcium alumina cement (CAC). However, there are multiple challenges when using emulsion polymers in fast setting cement compositions. As the wet mortar thickens very fast, the applicability and workability becomes very difficult; pot life is unacceptably short and the resulting waterproofing membrane is too rigid, and thereby lacks flexibility and often cracks so that it is not waterproof. Further, in fast setting waterproofing membrane compositions, the emulsion polymer does not provide enough flexibility to give sufficient crack bridging in dry/wet conditions. One very expensive way to solve the problem of the rigidity of the resulting waterproofing membrane would be to reduce the glass transition temperature (Tg) of the emulsion polymer, making it softer and more flexible, and to increase significantly the polymer to cement ratio.

An effective fast curing waterproofing membrane would enable the applicator to apply a first and a second waterproofing membrane layer and then a tile layer on the resulting waterproofing membrane within the same working day.

The present study has sought to solve the problem of providing a two-component composition of a fast curing dry mix and an emulsion polymer additive that makes a wet mortar composition suitable for use as a fast curing waterproofing membrane without significantly reducing the Tg of the polymer or increase of the polymer to cement ratio in the composition, while enabling both acceptable mortar pot life and flexibility in the final cured waterproofing membrane so that it does not crack as it cures.

MATERIALS AND TEST METHODS

Materials

The latex samples of the present study have been tested in the drymix formulation described in Table 1.

Table 1. Formulation of dry component in the 2K system

DRYMIX	%
OPC CEM I 42,5R	25.30
CAC	12.00
CaSO$_4$	2.70
Quartz sand FH32	36.40
Quartz sand FH36	23.45
HEMC	0.15

The main properties of the latex binders tested are summarized in Table 2.

TEST METHODS

Preparation of the Membrane Mixture

The liquid components are weighed into a beaker and mixed for 30 seconds at 200 rpm. The well mixed dry components are added carefully under stirring within 45 seconds. When all solid components are added, the slurry is stirred at 700 rpm for 2min15sec.

Pot-Life / Viscosity Increase

The freshly prepared membrane mixture is immediately transferred into a steel beaker. The steel beaker was jolted five times by hand and then the surface is smoothed with a scraper. By weighing the steel backer the density is determined.

30 seconds after the beaker is filled the viscosity is measured the first time. This measurement will be done also after 5, 15, 30, 45, 60, 90 and 120 minutes.

The viscosity is measured with a Brookfield RVT DV-II viscometer at 5 rpm with a T spindle on a Helipath stand at 23°C /50% RH.

Table 2. Main parameters of DCC and competitors latex used in commercial products

Latex Reference	Polymer Chemistry	Tg (°C)	Solid%	Process
Sample A	Styrene- Butylacrylate	-8	56	Y
Sample A '	Styrene- Butylacrylate	-8	56	X
Sample B	Styrene- Butylacrylate	-30	56	Y
Commercial Products				
System F	Styrene- EHA	-14	50	
System R	Styrene- EHA	-14	50	

Cement Setting with Ultra Sonic Tester

The freshly prepared membrane mixture is put into the testing chamber. An ultrasonic pulse will be sent from the transmitter to the receiver and the speed will be recorded. As the membrane becomes harder, the sound travel faster. The setting will be measured over 7 days.

Water Impermeability according to EN 12390-8

Prepare a limestone brick with a drilled hole on the obverse side of the testing surface. The freshly made membrane mixture is applied at 1.3 mm thickness in one layer on the limestone brick. After 4h a second 1.3 mm layer of a freshly made membrane mixture is applied on the first layer. Let it dry for 7 days at 23°C and 50% RH. Put a water indication paper into the drilled hole. The membrane with the limestone is put into the water impermeability tester and a hydrostatic pressure of 1,5 bars is applied on the membrane for 4 days. If the water absorption is less than 25ml raise up the pressure to 5 bars. If the absorption is higher than 25 ml, hold the pressure an additional 3 days at 1.5 bar. After 7 days the water indication paper will be checked. The test is passed if no humidity is seen underneath the membrane. In parallel the water loss over time is read from the calibrated cylinder of the water impermeability tester.

Elongation and Tensile Strength measured according to DIN ISO EN 527-1 and DIN ISO EN 527-2.

Two different curing conditions are applied. The first one is curing of the membrane at 23°C/50% RH for 7 days and the second one curing for 7 days at 23°C/50% RH and additional 7 days under water (23°C). Curing time was shorter than usual (28d or 7d+21d under water) because the comparison data were needed as soon as possible. In a known formulation the data after 7d curing are good enough for comparison purposes.

Optionally the elongation and tensile strength can be measured at -5°C & -20°C.

The freshly prepared membrane mixture is applied at 2.6 mm thickness in one layer onto a Teflon film. The membrane is cured for 7 days at 23°C / 50% RH. After curing 14 specimens are cut out from each membrane. Half of the specimens are immersed into water for 7 additional days (23°C), the other half are measured immediately. The specimens for the water immersion test would be tested wet.

Elongation and tensile tests are run in a texture analyzer at a speed of 20 mm/min.

Crack Bridging according to EN 14891.

For this test concrete specimens (160 x 50 x 12 mm) are homemade according to EN 14891 from fresh mortar .The freshly prepared membrane mixture is applied with a metal frame of 3 mm thickness on one of the 160 x 50 mm sides of the concrete specimen and let it dry for 4h. Then new freshly prepared membrane mixture is applied on the other side of the specimen using the same frame.

The membrane is cured for 7 or 28 days.

After curing time the concrete specimen is broken carefully. The broken concrete specimen with the intact membrane is elongated with the texture analyzer at 0.15 mm / min. The surface of the membrane is monitored visually. The distance is reported when (1) at maximum force (2) the first cracks appear. Additionally the maximum force is reported.

For measures at low temperature, specimens would be stored over night at the -5°C or -20°C.

Adhesion strength according to EN 1542

The freshly prepared membrane mixture is applied at a thickness of 2.6 mm onto a hydrophobic concrete slab. Adhesion is measured after

(1) 7 days and 28 days storage at 23°C/50% RH,

(2) 7 days storage at 23°C/50% rel. humidity and 21 days in water,

(3) 14 days at 23°C/50% RH and 14 days at 70°C (air circulation) additional 1 day at 23°C/50% RH

RESULTS AND DISCUSSION

A general challenge of flexible and fast cementitious waterproofing membranes is given by the fact that the optimum pot life and fast drying and high deformability are typically in contradiction. Only a very good control and understanding of the different cement hydration phases would enable the desired outcome.

The evolution of a cement paste from a soft material to a hard solid occurs in several stages. Our aim is to control by designing the right latex, the correlation between cement hydration and cohesion evolution of final composite- flexible membrane - in that case.

When cement is mixed with waterborn latex, each cement phase dissolves at least partially, leading to the establishment of a supersaturated solution with respect to the different hydrates, which can precipitate (Taylor, 1997). But in order to obtain a rapid hardening and a rapid drying a hydraulic binder mix containing Calcium Aluminate Cement (CAC) in combination with Portland Cement (OPC) and/ or Calcium Sulphate (CS) is required.

It has been found that the early hydration reactions are always dominated by the ettringite formation – aluminum, sulphate and calcium ions in solution (Amathieu, 2001).

The formation of ettringite results from nucleation and growth from solution. The chemical reactants – aluminum, calcium and sulphate ions in – come from the dissolved solid mineral constituents for which the equilibrium solubility constant is Kett = 4.9x10-44 .

The rate of nucleation and growth of crystals depends, amongst others things, on the supersaturation coefficient β which is related to the energy available for the formation of the nuclei that in the case of ettringite is (Matchei T, 2007) :

$$6Ca^{2+} + 2Al\,(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O \rightarrow 3CaOAl_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$
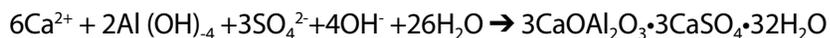
$$\beta = (a\,Ca^{2+})^6 * (a\,Al(OH)_4^-)^2 * (a\,SO_4^{2-})^3 * (a\,OH^-)^4 / K_{ett}$$

The "a" coefficients are the ion activity (which is the ion concentration multiplied by the activity coefficient γ)

For crystallization to occur β must be greater than one. Kinetics of nucleation depends strongly on the concentration of calcium ions in solution and fairly strongly on the hydroxyl ion concentration or pH of the media (Bertrand L, 2014).

We believe that with the right latex design we could control the different ion activity and hence growth conditions of ettringite formation which results in different crystal morphology and crystal quantity that will strongly influence the mortar properties.

The two latex samples A and A' (which composition is summarized in table 2) have identical backbone but they have been produced following different processes: Our hypothesis is that when mortar slurry is prepared using Sample A, β < 1 while with sample A' β > 1.
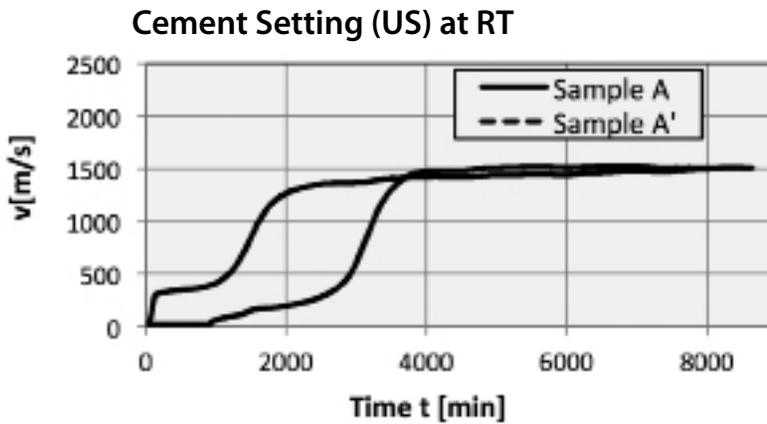
Cement Setting (US) at RT

Figure 1. Cement setting profile using Ultrasound equipment. The mortars measured are prepared with sample A and A' using the same fast drymix (table 1)
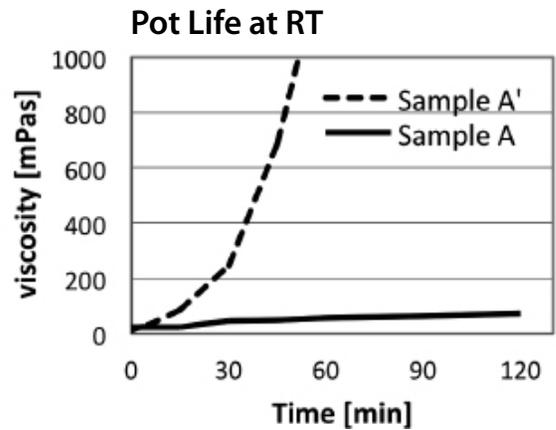
Pot Life at RT

Figure 2. Pot life of mortar prepared with samples A and A' in the same fast drymix (table1)

In Figure 1 and 2 could be observed the difference in wet mortar behaviour; speed of nucleation phase while measuring cement setting and pot life of membranes prepared respectively with sample A and A'

Both cement setting and pot life for sample A' are extremely fast and result in a very rigid, non cohesive membrane due eventually to a too fast /uncontrolled crystallization of ettringite during nucleation phase, while sample A for which pot life and also setting profile are much longer, provides a highly flexible membrane.

As indicated in Table 1, Tg and polymer backbone for sample A and sample A' are identical. This is therefore clear evidence that a low polymer's Tg is not enough to guarantee good flexibility.

The previous statement applies at room temperature but as shown in Figure 3, to obtain deformation at low temperature (-20°C) , a very low Tg is necessary. Only sample B, with Tg -30°C, provides deformation at -20°C. Both sample A and B have been produced following the same production technology especially adapted to fast drymix systems.

As mentioned in the beginning of this report the aim of this project was to develop a binder that combined with a fast drymix would enable applicators to work long enough with wet slurry, resulting in sufficient pot life and at the same time to develop strength fast enough to be waterproof as soon as possible. Figure 4 shows pot life data of the two binders developed with the new technology compared to commercially available fast systems.
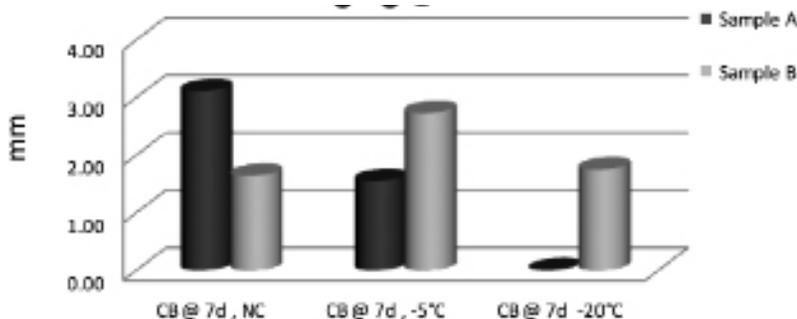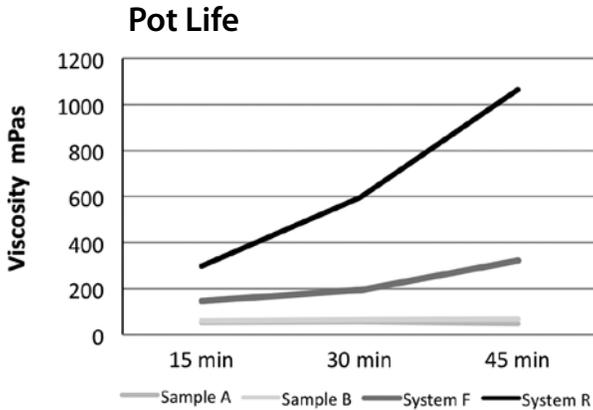
Crack Bridging @ Max Force

Figure 3. Crack bridging results according to EN-14891 of membranes prepared with sample A (Tg -8°C) and sample B (Tg -30°C) and measured at different temperatures. All membranes were cured during seven days.

Pot Life

Figure 4. Viscosity build up of wet mortar membrane prepared with a fast drymix systems

Table 3. Water proofing results of membranes cured 24h and 3 days at 5°C

Water proofing EN 12390-8	Sample A	Sample B	System F	System R
Curing 1 day @5°C / ml water after 7d @ 1.5 bar	5	0	90	420
block under WPM wet ?	no	no	yes	yes
Curing 3 days @5°C / ml water after 3d @ 1.5 bar	0	0	1000	1000
block under WPM wet ?	no	no	yes	yes

a) Early Strength Development @ RT

b) Early Strength Development @ 5°C
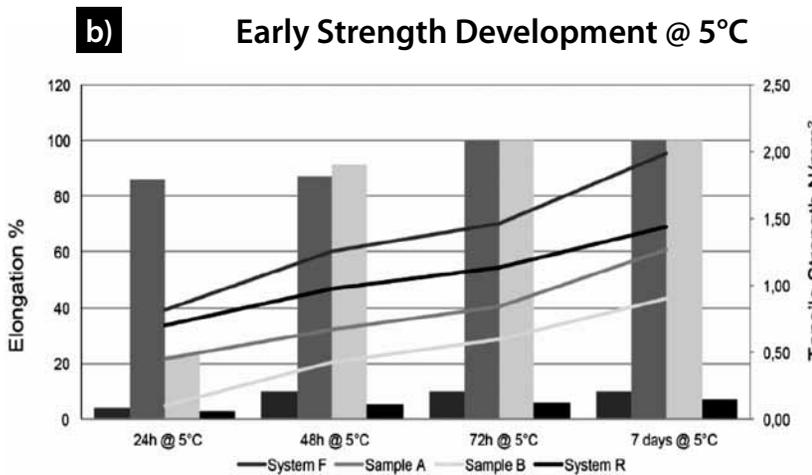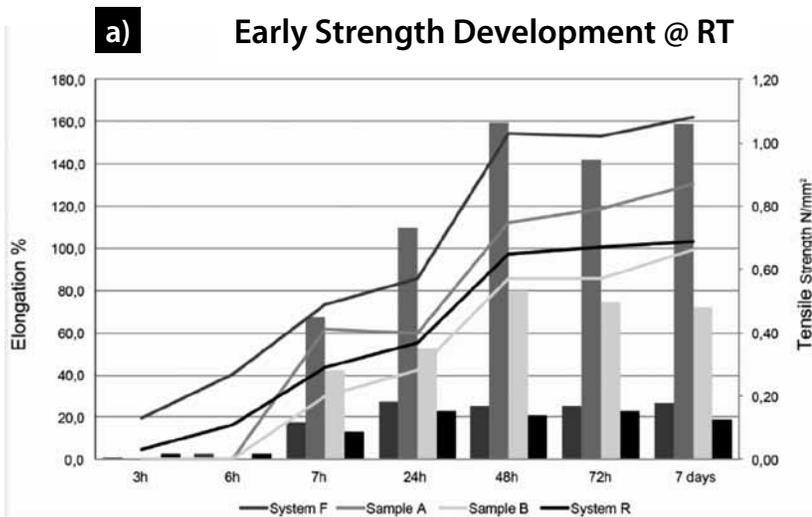
Our system is building up viscosity slower than the commercially available one. However , when we look at the early strength development both as water impermeability results as shown in Table 3 , and also in terms of elongation /tensile at low temperature over time, as presented in Figure 5, we could confirm that the new technology provides superior performance in absolute terms of timing and mechanical strength compared to commercially available systems.

Results are self explanatory and we could state that after 24 hours both at room temperature and at 5°C the membranes prepared with the new binders have developed more than 80% of the total mechanical strength and the absolute value is so high, that membranes are already water proof even under the highest pressure conditions.

Figure 5. (a,b) Early Strength development in terms of Elongation and Tensile at room temperature and at -5°C

a) CB @ RT
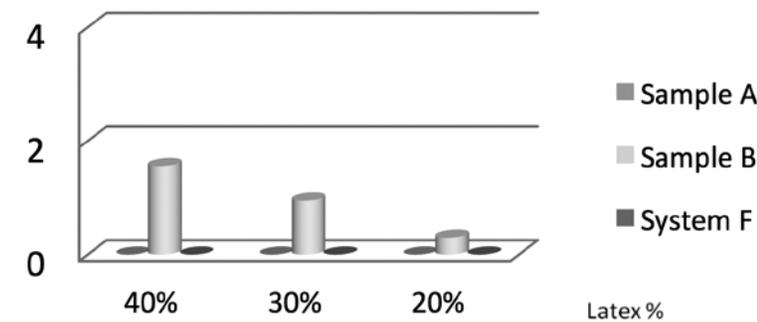
mm

b) CB @ -5°C

mm
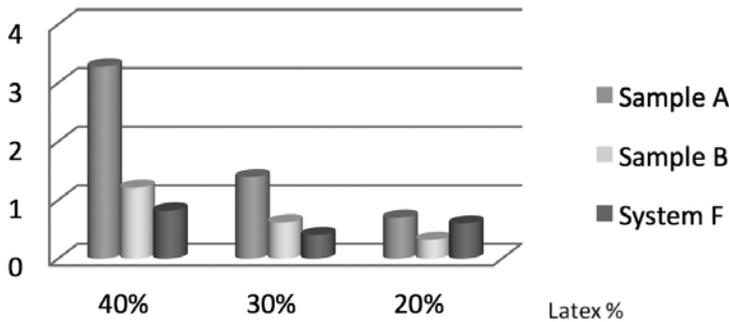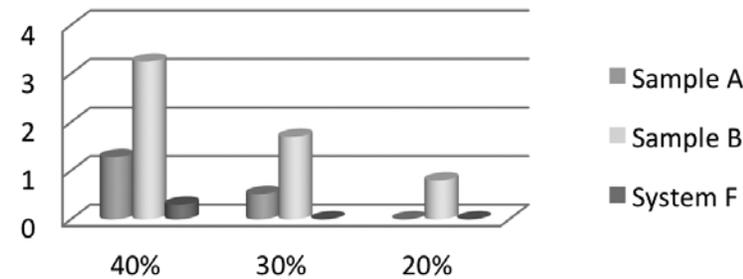
c) CB @ -20°C

Figure 6. (a,b,c) Crack bridging according to
EN-14891 at room temperature, -5°C and -20°C at
different binder dosage

Another important attribute that 2K water proofing market expects from a binder is efficiency. If one takes a very low Tg pure acrylic binder and loads high dosage of polymer, it is possible to get the desired outcome but at a very high price. The outstanding mechanical strength values in terms of elongation and tensile at room temperature with sample A and at very low temperature with sample B enables a very efficient system.

As shown in Figure 6 and Figure 7, the EN- 14891 crack bridging and adhesion standard can be reached at lower latex dosage compared to commercially available system.

CONCLUSIONS

– Control of β – initial nucleation phase - by new latex technology - during cement hydration in a ternary binder system - enables superior mechanical performance of final membrane

– Tg and polymer backbone are not sufficient parameters to predict performance of a cementitious membrane

– A very low Tg (< - 20 °C) and right polymer backbone are critical to develop crack bridging at −20°C

– DCC new latex echnology provide simultaneously long pot life and early strength development at low temperatures

– DCC new latex technology enables waterproof after 24 hours at 5°C

– DCC new latex technology proves higher latex efficiency.

N/mm² **Adhesion @ RT 28 days**

a)
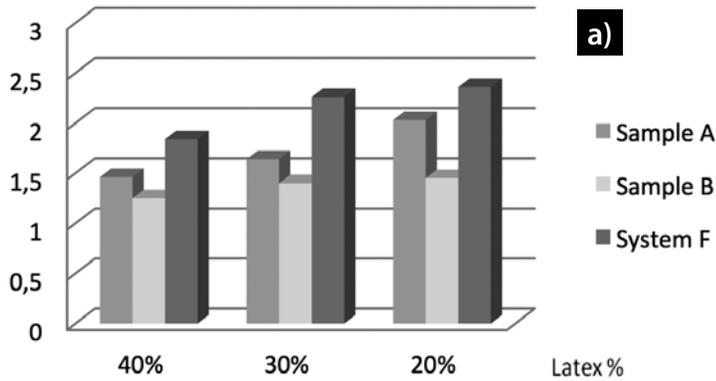
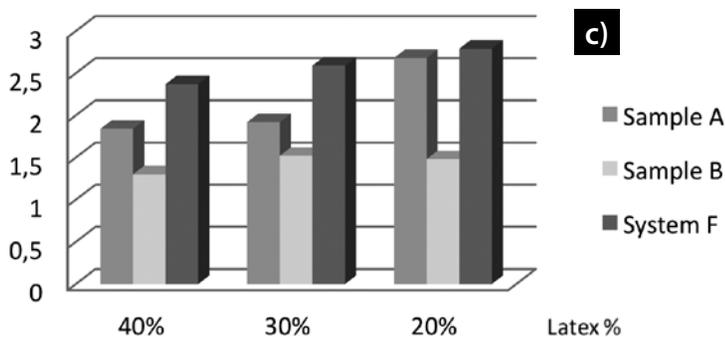N/mm² **Adhesion after Water Immersion**

b)
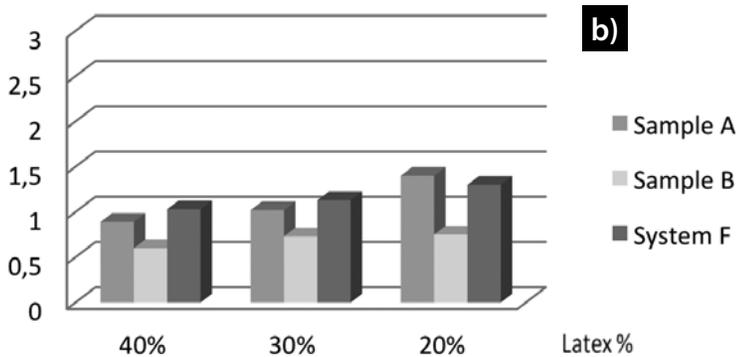
N/mm² **Adhesion after Heat**

c)

Figure 7. (a, b, c) Adhesion Strength values of membrane using different latex dosages measured according to EN-1542

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