# Rheological properties of cellulose ethers and their application in cementitious tile adhesives formulation

Fabio Curto, Matteo Monaco, and Stefano Carrà

Mapei S.p.A., Milan, Italy

## ABSTRACT

Cellulose ethers (CE) are very important components of cementitious mortar formulations, in particular of cement-based tile adhesives, since they determine and control their wet properties such as workability, open time and sag resistance. Cellulose ethers are either used "pure" in formulations, or modified, i.e. mixed with "rheology modifiers", such as starch ethers, polyacrylamide, inorganic modifiers (bentonites, sepiolites) that essentially have the role of controlling the low shear viscosity of the product.

Actually, all wet properties depend on the rheological characteristics of the product's wet mix. The main feature of cellulose ethers themselves for what concerns cementitious mortar formulation is a rheological attribute, i.e. the viscosity of a 2% solution in water, that depends on the molecular weight of the cellulose ether.

In this paper several rheological characterizations will be discussed, varying parameters like the cellulose ether viscosity and its modification with starch ether and polyacrylamide through a simple experimental design. The correlation among rheological properties of cellulose ethers and their behavior in a standard formulation of a cementitious tile adhesive will be then studied using multivariate analysis tools (Principal Component Analysis).

## INTRODUCTION

Tile adhesives are formulated cementitious mortars that have the duty of assuring good and durable adhesion between tiles, of whatever sort they might be, – wall tile, ceramic tile, porcelain tile, etc. – and various types of substrates, concrete plywood, water-proof membranes, etc.

Adhesion is a property of the mortar once – by effect of the cement hydration reaction – it has hardened. However in the tilers' evaluation of the product its "wet" properties are obviously even more important because – all together – they determine its ease of application.

Typical "wet" properties of a tile adhesive are workability, open time and sag resistance. They are all, generally speaking, rheological properties. The role of controlling them is delegated by the use in formulations of cellulose ethers. The most commonly types of celluloses ethers in tile adhesives formulations are hydroxy-ethyl and hydroxy-propyl. They are either used pure or "modified" by a mix of starch ether (SE), polyacrylamide (PAA), inorganic thickeners (bentonites, sepiolites, etc.) that have the role of increasing the low shear viscosity of the wet mix.

The main feature of pure cellulose ethers themselves is a rheological property, i.e. the viscosity of a 2% solution in water.

In this paper, initially, we studied the viscosity effect of Methyl Hydroxyethyl Celluloses (MHEC) in aqueous solutions[1].

Moreover, the rheological profiles detected on these systems has been compared to those measured in alkaline solutions prepared at pH ≃13 in order to simulate the typical environment of a cement paste.

After these preliminary tests, the effects of MHEC were investigated in cementitious tile adhesives formulations and, together with physical-mechanical properties like specific gravity, sag resistance and wetting capability, we measured their rheological properties via flow curves.

Finally, all the results obtained on different formulations of cement-based adhesive with rheological measurements and conventional mechanical tests have been used to find correlations using a multivariate analysis tool such as the "Principal Component Analysis"[2].

## MATERIALS AND METHODS

### Materials

Three different cellulose ethers, one starch ether and one polyacrylamide have been investigated, identifying them by their declared nominal viscosity in a 2% solution:

Table 1. Rheology modifiers

| Water retainer | Viscosity (mPa·s) |
|---|---|
| CE-A | 3000 |
| CE-B | 15000 |
| CE-C | 25000 |
| SE | 100 |
| PAA | 10000 |

These rheology modifiers agents have been hence employed in a standard cementitious tile adhesive formulation, prepared with pure clinker Type I cement, according to the following recipe:

Table 2. Tile adhesive formulation

| Component | Dosage (w/w) |
|---|---|
| CEM I 52.5R | 30.00 % |
| Silica sand | 67.95 % |
| Re-dispersible polymer | 1.00 % |
| Calcium formate | 0.60 % |
| Rheological modifiers | 0.45 % |

Silica sand used has a 0.1-0.4 mm granulometry, which is the most typical used in tile adhesives.

Redispersible polymer powders are polymers emulsion that have been converted by spray-drying into powdered thermoplastic resin materials that, when mixed with water, can re-disperse back into emulsions with essentially identical properties to the original copolymer emulsions.

The most common polymer compositions used for tile adhesives are vinyl-acetate copolymers, with ethylene or vinyl-verstatate, with a $T_g$ typically between 0 and 30°C, depending on the copolymer composition. Redispersible polymers influence hardened properties such as adhesion and mortar deformability but they also decrease the viscosity (mainly at low shear) of the wet mix, but in this paper all the formulations contained the same quantity and type.

Consistently with several previous works carried out on cementitious tile adhesive systems[3,4], the composition of the rheology modifiers mixtures has been determined using the Experimental Design approach and choosing a "Central Composite Design"[5], for a total of 18 experiments, summarized in the Table 3. The use of an Experimental Design approach has been chosen because it allows the generation of an efficient modelling of the whole investigated system, using a chemometric software developed at Mapei laboratories and available with free license[6].

Table 3. Central Composite Design of retainers' mixtures

| | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** |
|---|---|---|---|---|---|---|---|---|---|
| **% PAA/Rh. Mod.** | 0 | 0 | 0 | 0 | 6.6 | 6.6 | 6.6 | 6.6 | 3.3 |
| **% SE/Rh. Mod.** | 0 | 0 | 33.3 | 33.3 | 0 | 0 | 33.3 | 33.3 | 16.6 |
| **CE Viscosity** | 3000 | 25000 | 3000 | 25000 | 3000 | 25000 | 3000 | 25000 | 15000 |
| | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** |
| **% PAA/retainers** | 3.3 | 3.3 | 0 | 3.3 | 3.3 | 3.3 | 3.3 | 0 | 6.6 |
| **% SE/retainers** | 16.6 | 16.6 | 0 | 16.6 | 16.6 | 0 | 33.3 | 16.6 | 16.6 |
| **CE Viscosity** | 15000 | 15000 | 15000 | 3000 | 25000 | 15000 | 15000 | 15000 | 15000 |

CE Solutions preparation

The CE aqueous solutions were prepared at 2, 1, 0.5 and 0.25% of cellulose by mass of water, dissolved with mechanical agitation for 3 min in a blender. Then, a slake time of 24h in laboratory conditions (23°C) has been imposed before any measurements, in order to obtain a homogeneous solution free of any entrained air bubbles. Furthermore, the solutions with a 2% concentration were also prepared using a saturated calcium hydroxide solution in order to study the influence of pH.

Adhesive mortars preparation

The cementitious tile adhesive formulations are prepared as a mechanical mixture of all their powdered ingredients, homogenized during a 20 minutes mixing. Hence, these powders have been mixed with the required amount of water according to EN 12004[6] procedures: the adhesive is mixed for 30 seconds in a planetary mixer and, after a manual cleaning of its bowl, it is re-mixed for another 60 seconds. The sample then observes a 10 minutes slake-time before its final 15 seconds remix.

Cementitious tile adhesives test methods

A Brookfied viscometer has been used in order to define the correct amount of water necessary to obtain the desired consistence of the mortar ($\simeq$ 500.000 mPa·s). After this initial check, the specific weight of the mixture has been obtained by filling a calibrated pycnometer, proceeding then with the EN 12004[8] testing of the cementitious tile adhesive.

The slip resistance of the tile adhesive has been evaluated applying two tiles of different size and weight (100 mm x 100 mm at 200 g and 150 mm x 150 mm at 650 g) over a thin layer of product spread on concrete slab with a 6 mm x 6 mm square notched trowel and then keeping the substrate in vertical position for 20 minutes. The so-called "adjustability time" has been evaluated too, by applying porous tiles over the cementitious tile adhesive and controlling the amount of time necessary to stick the tile in a non-reversible way.

Wetting capability was evaluated by applying the mortar on a concrete slab and putting on top of it standard porous tiles (defined once again by EN 12004) after 5, 20 and 30 minutes using 20 N weights for a standard time of 30 seconds and then overturning the correspondent tile and visually evaluating the percentage of adhesive transferred from the substrate to the tile itself.

Finally, two different operators have been asked to express their judgement about the workability of each formulation, evaluated by troweling the products on concrete slabs, with a mark from 1 (worst) to 10 (best).

RHEOLOGY PROTOCOLS

Rheological measurements were carried out using a strain-controlled rheometer (Anton Paar Mod. 302) equipped with different tools, depending on the system texture which is being considered. The CE solutions were made by a cone-plate geometry (diam. 50 mm, truncation gap 0.1 mm); the tile adhesive cementitious based formulas were measured through the "ball measuring system" (ball diam. 15 mm) and plate-plate with both rough faces (diam. 50mm and 1,5mm gap). All these tools are dedicated to ensuring the border's conditions for a correct rheological characterization. At the beginning the measurements were focused on the "swelling" effect in water with the flow curves measurements at 23.0 ± 0.2°C in a shear rate range from 0,01 to 1000 s-1 in 120 s.

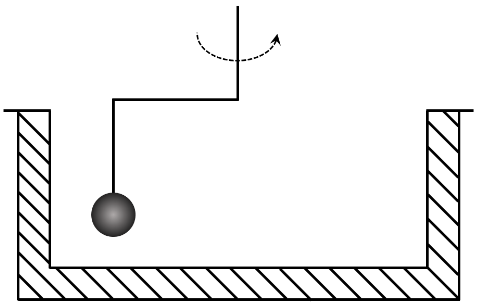

Figure 1. Ball system measurements

The device for the cement-based sample "ball system" consists of a large cup where the mortar has been placed and the tool with a ball in a non-coaxial position applies the shear needed to measure the flow curve (Fig. 1). This device has been designed to avoid problems that occur when composite materials are characterized, in particular, it guarantees the "non-slip" condition and avoids the problem related to a compressed material by ensuring a normal force close to zero during all measurements. Furthermore, a creep test was performed on adhesives applying a constant stress of 300 Pa for 3 minutes. This measurement protocol is correlated to the slip resistance test described in the previous paragraph as it simulates the ability of the mortar to keep a tile vertically still despite its weight[8].

RHEOLOGY RESULTS

At first, the flow curve tests were performed on solutions with 2% of MHEC by mass of water to verify the swelling capacity. Moreover, the solutions were also prepared with pH 12, using a calcium hydroxide saturated solution, in order to simulate the cellulose behavior in presence of the cement[9]. The superimposition of the curves means, the MHECs are not affected by the alkaline solution (Fig. 2).

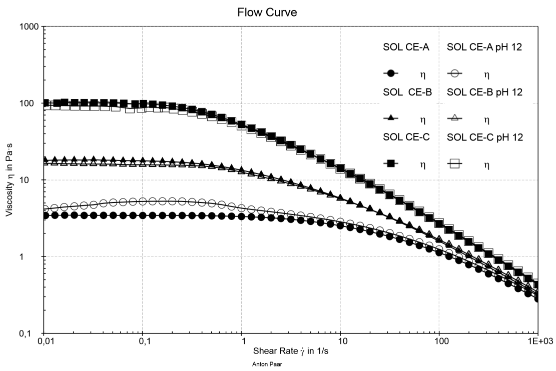


Figure 2. Solutions at pH 7 and 12

For all tile-adhesives, a basic-formulation of dry mix mortar was employed, where a mix of rheology modifiers was added. The mix was composed of polyacrylamide, starch and MHEC. The water demand of the mix was assessed with a preliminary test performed by a viscometer: the water amount is the one that allows the mortar to have a 'Brookfield' viscosity around 500 Pa·s, which corresponds to which tilers commonly apply these products.

Flow curves were performed on the sample 1, 2 and 12 (Fig. 3), and they are all very close to each other, due to the fact that the mixing water was changed in order to obtain the 500 Pa·s Brookfied viscosity: sample 1 made with the MHEC A, requested 21.5% of mixing water, sample 12 with cellulose B was mixed with 23% of water and sample 2 with cellulose C needed the 26%.

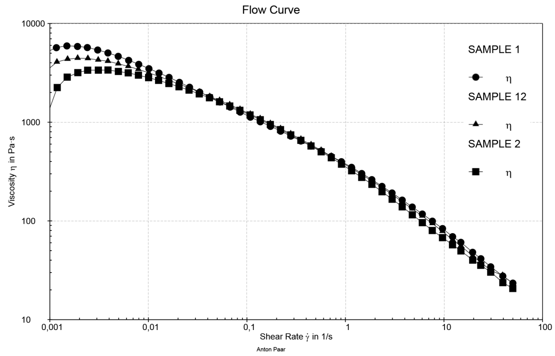


Figure 3. Mortars with pure CE

All show a pseudoplastic profile which is typical of cement-based systems: a solid up to a critical value called yield, corresponding to low shear viscosity[10], afterwards as the shear increases the material is subjected to an internal structural rearrangement and the flow occurs. Viscosity profiles in general, are very comparable in the medium high shear-rate range; at 1 $s^{-1}$ the viscosity is found between 400 and 650 Pa·s.
This shear corresponds to the shear at which Brookfield measures viscosity: flow curve viscosities fall very close to each other at this range, because we varied mixing water in order to target the same Brookfield viscosity. However, rheological tests through a stress-controlled rheometer allows to have a more detailed description of the rheological behavior of the mix.

The real difference between samples 1, 3 5 and 7 is represented by the low shear viscosity. This value can be tuned by changing the composition of the rheology modifiers: samples 3 and 5, increased it since the 6.6% of polyacrylamide and the 33.3% of starch was added respectively. The adhesive sample 7, formulated with 6.6% of polyacrylamide and contemporarily 33.3% of starch shows the higher low shear viscosity value: $35 \cdot 10^4$ Pa·s.

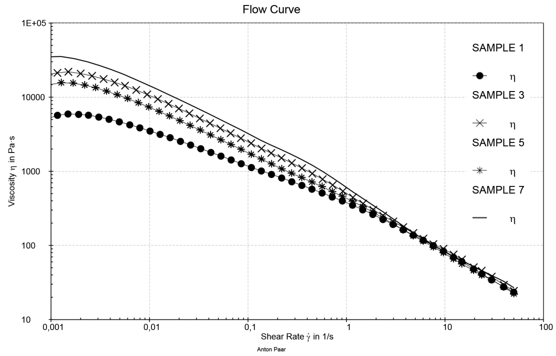


Figure 4. Mortars with blended CE

The creep test was performed on the same formulations (1, 3 5 and 7) by applying a constant stress in order to verify that the deformation measured is related to the yield. By doing this it was found that there are proportional inverses between the deformation and the yield so sample 7 has a creep value around 10% and sample 1 is 1000%.

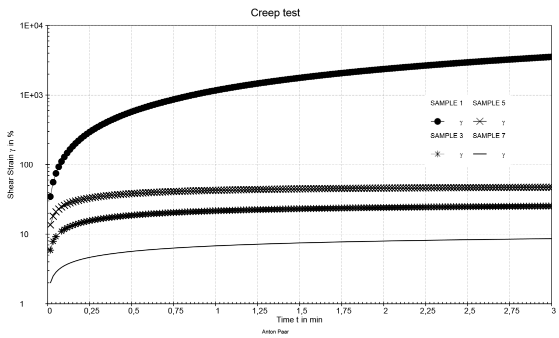


Figure 5. Creep: mortars with blended CE

All composition samples which are showed in Tab. 1 were also characterized by rheometer: the behavior found was comparable to samples 1, 3, 5 and 7 and the results are summarized in Tab. 4.

Table 4. Experimental results

| Test | Mix water | Spec. weight | Adj. | EN Tile Slip | Heavy Tile Slip | Op. 1 Eval. | Op. 2 Eval. | Wett. 20' | Wett. 30' | Def. | LSV | Plat. | Visc $1s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| - | % | g/cm³ | min | mm | mm | - | - | % | % | % | (Pa·s) | (Pa·s) | (Pa·s) |
| 1 | 21.5 | 1.42 | 60 | 5 | 10 | 6 | 8 | 50 | 30 | 3580 | 5936 | 3.8 | 3.64 |
| 2 | 26.0 | 1.4 | 70 | 5 | 10 | 10 | 9 | 65 | 50 | 4200 | 3855 | 108.1 | 54.90 |
| 3 | 22.0 | 1.56 | 18 | 0.3 | 0.6 | 6 | 7 | 60 | 20 | 22.3 | 22010 | 2.5 | 1.82 |
| 4 | 24.0 | 1.45 | 25 | 0.6 | 1.8 | 9 | 8 | 70 | 35 | 57.5 | 13160 | 37.1 | 12.74 |
| 5 | 26.5 | 1.46 | 12 | 0.3 | 0.6 | 5 | 7 | 80 | 50 | 43.6 | 15740 | 9.6 | 7.06 |
| 6 | 28.5 | 1.36 | 40 | 0.8 | 4.5 | 10 | 9 | 90 | 50 | 91 | 17740 | 118.3 | 48.97 |
| 7 | 26.5 | 1.56 | 8 | 0.3 | 0.6 | 6 | 6 | 70 | 30 | 10 | 35390 | 7.6 | 4.38 |
| 8 | 26.5 | 1.45 | 15 | 0.3 | 0.4 | 10 | 10 | 85 | 30 | 29.6 | 20730 | 47.8 | 17.08 |
| 9 | 27 | 1.4 | 30 | 0.9 | 2.5 | 8 | 8 | 90 | 80 | 260.6 | 14210 | 18.8 | 10.57 |
| 10 | 26.5 | 1.42 | 30 | 0.7 | 1.5 | 9 | 9 | 90 | 75 | 31.6 | 14110 | 18.8 | 11.18 |
| 11 | 27 | 1.41 | 30 | 0.6 | 1.9 | 8 | 8 | 90 | 75 | 64.2 | 11730 | 19.2 | 11.70 |
| 12 | 23 | 1.39 | 60 | 5 | 10 | 6 | 7 | 75 | 60 | 3810 | 4455 | 22.6 | 16.31 |
| 13 | 26 | 1.49 | 18 | 0.3 | 0.7 | 6 | 7 | 75 | 40 | 49.25 | 16710 | 4.7 | 3.58 |
| 14 | 28.5 | 1.43 | 25 | 1.1 | 2.5 | 10 | 10 | 95 | 80 | 77 | 11760 | 79.1 | 34.40 |
| 15 | 26.5 | 1.4 | 50 | 1.9 | 9.6 | 9 | 9 | 70 | 40 | 1230 | 12300 | 20.6 | 13.92 |
| 16 | 25.5 | 1.46 | 18 | 0.6 | 1.8 | 7 | 7 | 85 | 75 | 31.5 | 16360 | 14.4 | 6.88 |
| 17 | 23 | 1.45 | 45 | 1.5 | 4.1 | 9 | 8 | 80 | 40 | 63.6 | 12410 | 13.0 | 8.87 |
| 18 | 28.5 | 1.43 | 18 | 0.5 | 1 | 9 | 8 | 95 | 90 | 43 | 14860 | 25.6 | 13.31 |

## PRINCIPAL COMPONENT ANALYSIS AND DATA MODELLING

Principal Component Analysis[2] is the most used multivariate data analysis technique and the software[11] can be resumed by two charts, the so-called "Loadings plot" and the so-called "Score plot", the first showing the correlations among the different tests taken in account and the second one showing the relative positioning of each single experiment in this multivariate space. The comparison between "Loadings plot" and "Score plot" is the key to determinate the influence of each parameter on the investigated responses.

Generally, directly correlated responses are close in the "Loadings plot" while inversely correlated tests are diametrically opposed. On the other hand, uncorrelated results are orthogonal among themselves in this plot and showing totally independent behaviors.

The lower-left side of the graphs shows the area with pure CE in the formulations (experiments 1, 2, 12) and this is clearly highlighted by the presence of adjustability and slip tests that show their higher values in presence of non-modified CE. The presence in this area of the creep test results (Deform.) indicates the excellent correlation among this test and the mechanical behavior in EN standardized tests.

On the right side of the graphs, in opposition to the tests described in the previous paragraph, Low Shear Viscosity can be found, in correspondence of the retainer mixtures with the highest modification and with the lowest base viscosity, showing an opposite behavior to those of the unmodified CE.

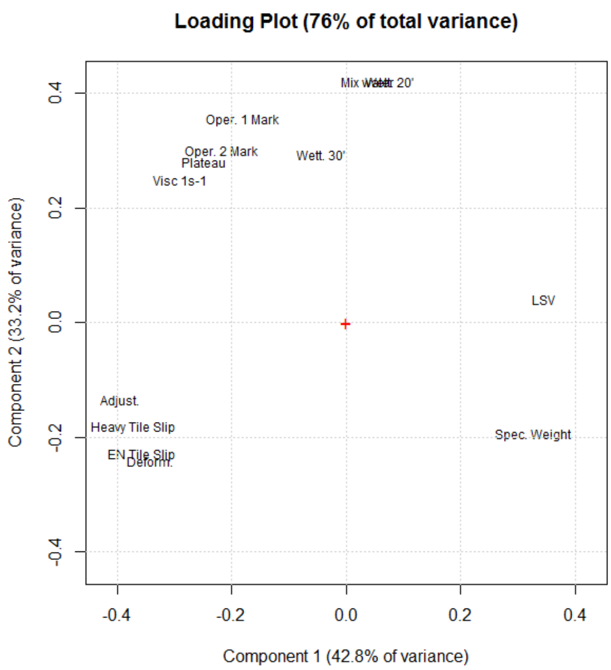


Figure 7. Loadings plot

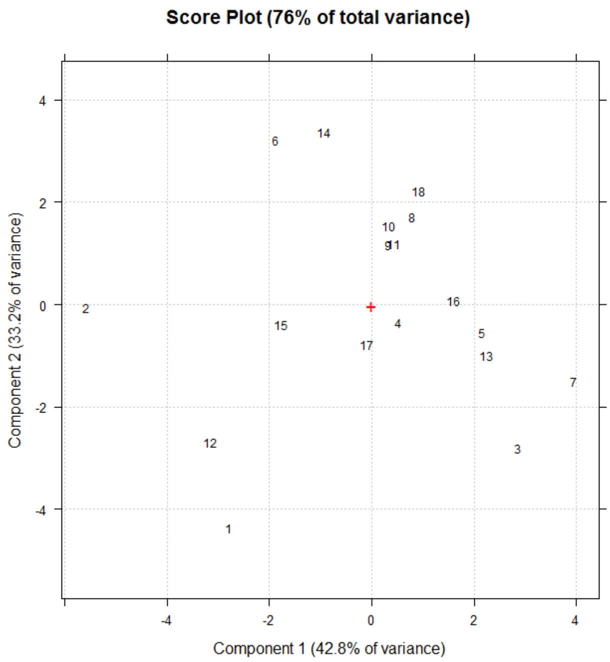


Figure 8. Scores plot

Orthogonal to these two groups a third cluster of experiments (wetting capabilities, workability according to the operators, water mix ratio and CE solution plateau) can be found. The corresponding experiments are the ones with a high base viscosity and with high amounts of polyacrylamide, indicating that a higher amount of water in the formulation improves the workability properties of the mortar and its capability to keep a good wetting capability during time. All these properties are contemporarily opposite to the specific weight of the paste, confirming, as already known, that a low water mix ratio with a low air mounting in the product could be the responsible of its unpleasant appearance and workability.

All these results are confirmed by the model responses obtained from the mathematical elaboration of the whole Design of Experiment. In particular, the behavior of slip and creep test is clearly equivalent and opposite to that of the adhesive's low shear viscosity.

## CONCLUSIONS

In this work the effects of MHEC was investigated on the workability and

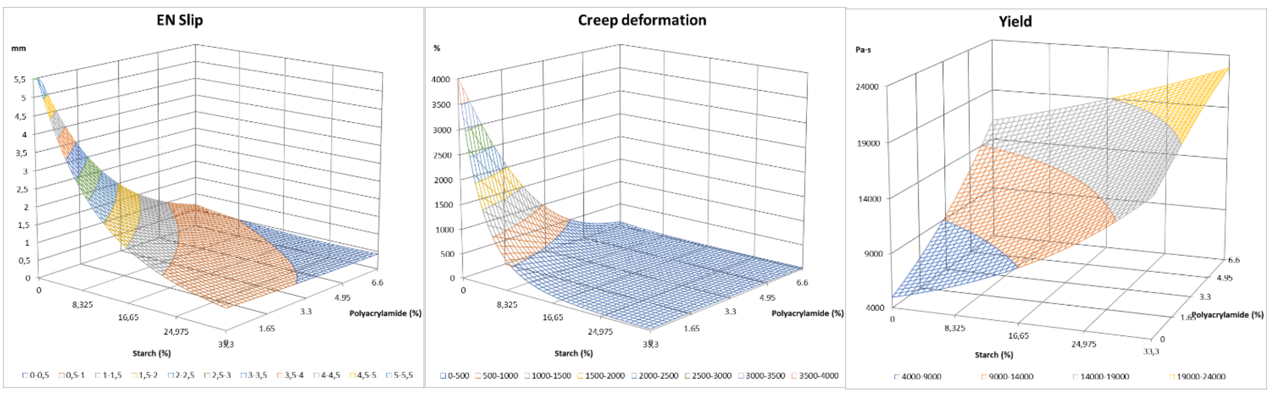


Figure 6: Slip, creep deformation and yield in function of SE and PAA % with a CE viscosity of 15000

performances of cementitious tile adhesives. The choice of an Experimental Design that considered the dosage of MHEC and their viscosity as input variables, allowed us to reach optimal sag resistant formulations avoiding a high number of empirical tests and, consequently, time and money.

Tests focused on the viscosity enhancing effect in aqueous solution showed that, within the investigated range, their behavior is not affected by the pH typically found in a cement paste

Moreover, physical phenomena that influence rheological behavior of a cementitious adhesive has been studied and a clear inverse correlation between zero-shear viscosity and creep-deformation has been found as well as a direct correlation between creep-deformation and tile slip resistance.

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REFERENCES

1. D. Bülichen, J. Kainz, J. Plank, Working mechanism of hydroxyethyl cellulose (MHEC) as water retention agent, Cement and Concrete Research 42(2012) 953-959, Elsevier
2. R. Leardi, 2000, Methods of Treatments of Data, Handbook of water analysis – Third Edition, CRC Press, 47-76
3. M. Monaco, S. Carrà, 2018, Chemometrics application in cementitious tile adhesives formulation, Drymix Mortar Yearbook 2018, drymix.info 42-60
4. M. Monaco, S. Carrà, 2019, Cement quality influence in cementitious tile adhesives formulation, Drymix Mortar Yearbook 2019, drymix.info 4-17
5. R. Leardi, 2009, Experimental design in chemistry: A tutorial, Analytica Chimica Acta 652 161–172
6. M. Monaco, R. Leardi, 2019, BasiCAT, freely downloadable from website http://gruppochemiometria.it/index.php/software
7. EN 12004-2:2017, Adhesives for ceramic tiles - Part 2: Test methods, CEN norm
8. T. G. Mezger, The rheology handbook, 3rd Revised Edition, Vincentz
9. C. Brumaud, H. Bessaies-Bey at all, Cellulose ethers and water retention, Cement and Concrete Research 53 (2013) 176-184, Elsevier
10. C. Brumaud, R. Baumann at all, Cellulose ethers and yield stress of cement pastes, Cement and Concrete Research 55 (2014) 14-21, Elsevier
11. R. Leardi, C. Melzi, G. Polotti, CAT (Chemometric Agile Tool), freely downloadable from website http://gruppochemiometria.it/index.php/software