

Research Article

High Molecular Weight Cellulose Ethers Influence on the Rheological Properties of Fresh Mortars

Phan Van Tien¹, Nguyen Huu Cuong¹, Phan Dinh Quoc¹, Le Ngoc Hung²

¹Faculty of Construction - Vinh University, 182 Le Duan Str., Vinh, Nghe An, Vietnam

²Bordeaux University, I2M, Bordeaux, France

***Corresponding author**

Phan Van Tien

Email: vantien.phan1010@gmail.com

Abstract: This paper presents an experimental study on the effect of three types of water-soluble high molecular weight cellulose ethers on the rheological properties of cement mortars in fresh state. Vane-cylinder test was used to determine the rheological properties of fresh mortars. The flow curves, obtained in the tests, were exploited to determine the rheological parameters, including the yield stress, the consistency coefficient and the fluidity index. The results indicate a difference between the mixes corresponding to the different cellulose ethers at high shear rate, while at low shear rate, all the mortar mixes behaved as a shear thinning fluid. The investigation of the influence of molecular weight on the properties of fresh mortars has shown a similar observation to the reported research in literature. The yield stress of the mortar decreases with the increase of molecular weight. This decrease is not significant at low molecular weights, and becomes much more significant at high molecular weights. Inversely, the mortar consistency is found to increase with the increase of molecular weight.

Keywords: Rheological properties; Mortar; High molecular weight, Rheology test, Cellulose.

INTRODUCTION

The term "cellulose ether" refers to a wide range of commercial products and differs in term of substituent, substitution level, molecular weight (viscosity), and particle size. The most widespread cellulose ethers used in dry mortars as admixtures are methyl cellulose (MC), methyl-hydroxyethyl cellulose (MHEC) and methyl-hydroxypropyl cellulose (MHPC) [1].

According to their properties, cellulose ethers are used in various industrial fields, including food industry, pharmaceutical industry, in paints and adhesives, etc. They significantly modify the properties of materials even if they are introduced in small amounts (0.02-0.7 % [1]). They are used to control the viscosity of a medium, as thickeners or gelling agents. In mortar, cellulose can be added before or during the mixing as thickening and water retaining agents. However, the effect of cellulose ethers on the mortar in fresh state was not fully studied [2]. For example, there are few studies on the effect of methyl-hydroxyethyl cellulose (MHEC) on the rheological behavior of fresh mortar.

Cellulose ethers such as hydroxyethyl methyl cellulose (HEMC) is a common admixture in factory made mortars for various applications including cement

spray plasters, tile adhesives, etc. The influence of HEMCs have been published by many researchers in the case of various application fields, such as biological macromolecules [3,4,5], carbohydrate polymers [6,7,8], etc. However, there are few published studies concerning the influence of HEMCs on the fresh state properties of cementitious materials including cement grouts [9,10], cement-based mortars [11].

Patural et al. [9] had investigated the influence of cellulose ether on the properties of mortars in fresh state, in which the molecular weight of polymers is rather low (90-410 kDa). The effect of high molecular weight cellulose ether hasn't been studied. Thus, it is interesting to deal with high molecular weight cellulose ether in order to complement the effect of molecular weight of cellulose ether on the properties of fresh mortars.

The influence of high molecular weight cellulose ether on the adhesive properties of fresh mortars had been investigated, which indicated an important role of molecular weight of cellulose ether on controlling the adhesion force, the cohesion force and the interface adherence [2]. In this paper, the rheological properties of fresh mortar under the variation dosage of three type of HEMCs will be examined.

MATERIALS AND EXPERIMENTAL METHODS

Mix-design

The binder comprises a Portland cement (CEM I 52.5 N CE CP2 NF from Teil-France) and a hydraulic lime (NHL 3.5Z). In order to minimize phase

separation, the standard sand CEN EN 196-1 ISO 679 has been used. In this study, the effect of three types of high molecular weight cellulose ethers have been investigated. Typical characteristics of HEMCs are introduced in Table 1.

Table-1: Typical physical characteristic of three types of HEMCs

Properties	Type A	Type B	Type C
Form	Powder	Powder	Powder
Solubility	Water soluble	Water soluble	Water soluble
Viscosity(1), mPA.s	20000	30000	70000
pH (2% solution)	Neutral	Neutral	Neutral
Molecular weight	600.000	680.000	1.000.000

(1).Solution in water, Haake Rotovisko RV 100, shear rate $2.55 S^{-1}$, $20^{\circ}C$

A certain dosage rate of a commercial air-entraining agent, NANSALSS, is used to guarantee

moderate rheological properties within the resolution range of the rheometer.

The weight proportion of each constituent of the mortar is represented in Table 2.

Table-2: Mortar formulation

Constituent	Cement	Lime	Sand	Air entraining	HEMC	Water
% wt. of dry mixture	15	5	80	0.01	0.19-0.31	19

The polymer content in the mortar formulation is varied according to the following proportions: Ce = [0.19; 0.21; 0.23; 0.25; 0.27; 0.29; 0.31] % by weight. The water dosage rate is fixed to 19% by weight for all the investigated samples. The mortar composition corresponds actually to a basic version of commercially-available render mortar [2].

TEST METHODS

For characterizing the rheological properties of the fresh mortars, the rheometer AR2000ex is equipped with 4-blade vane geometry. Vane geometry is appropriate for high yield stress fluids such as dense granular suspensions, including mortars [11], as slippage can be avoided and the material can be sheared in volume.

The yield stress is measured with the vane-cylinder geometry in stress controlled mode in which a "ramp" of steps of increasing stress levels is applied to the vane immersed in the material, and the shear rate is measured as a function of applied stress. The yield stress is determined from the critical stress at which the material starts to flow.

Depending on each specific experiment, test will be performed at least three times to determine the best possible experimental procedure. In the first run, the interval between two successive steps must be chosen large enough to reduce the duration of the test. The yield stress is determined, but with a low precision. For latter runs, the measuring points must be increased

around the determined yield point. That would help to determine a high accuracy yield stress of the materials.

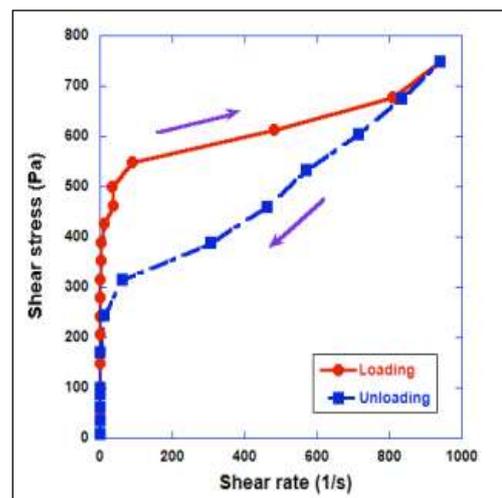


Fig-1: Typical flow curves of mortar with the addition of 0.29% of polymer

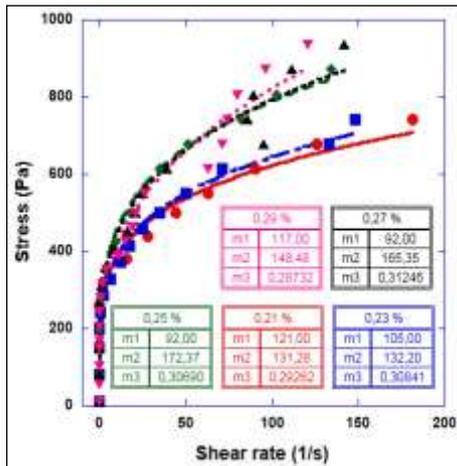


Fig-2: Perform the best fit of flow curves to Herschel-Bulkley models

A typical curve obtained in the rheology test is presented in Figure 1. The yield stress is determined by the critical stress at which we observe the transition from solid state to liquid state of the material. However, in actual experiments, almost all cases, the transition from solid to liquid state is occurred gradually and is hard to detect. Therefore, it is difficult to determine the exact value of the yield stress. So, different models have been developed in order to determine the value of the yield stress as well as other rheological parameters by fitting the flow curves' data with the model's equation. In this study, the most general models for concentrated suspensions, Herschel-Bulkley's, which is characterized by the following equation, has been used:

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n$$

The consistency coefficient K , the fluidity index n , and the yield stress τ_0 are three parameters characterize Herschel-Bulkley fluids. The consistency K is a simple constant of proportionality, while the flow index n measures the degree to which the fluid is shear-thinning or shear-thickening.

In some cases the use of Herschel-Bulkley model leads to non-physical values of the yield stress (negative), this parameter is then determined by the

applied stress at which we obtained a finite shear rate (0.01 s^{-1}). Figure 3 shows the best fits of flow curves to Herschel-Bulkley models in the variation content of A, in which $m1$ =yield stress, $m2$ = consistency coefficient, $m3$ =fluidity index.

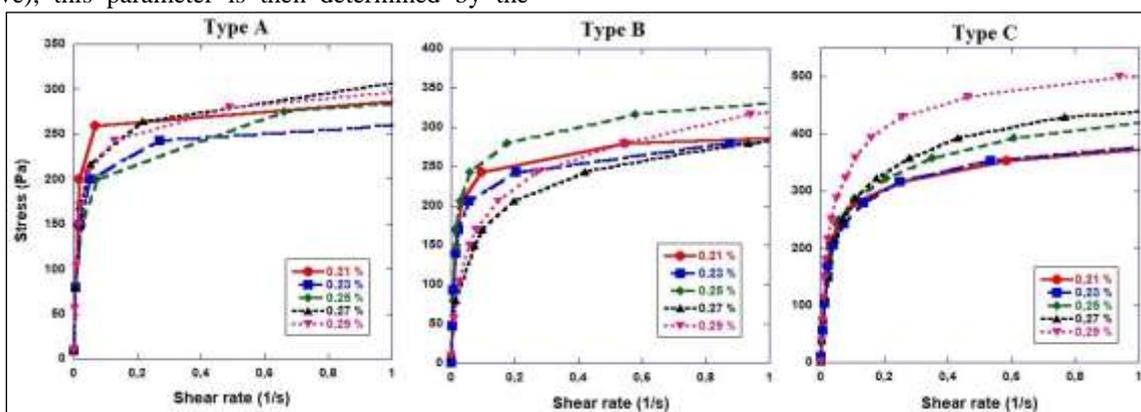
EXPERIMENTAL RESULTS

Evolution of the shear rate versus applied stress

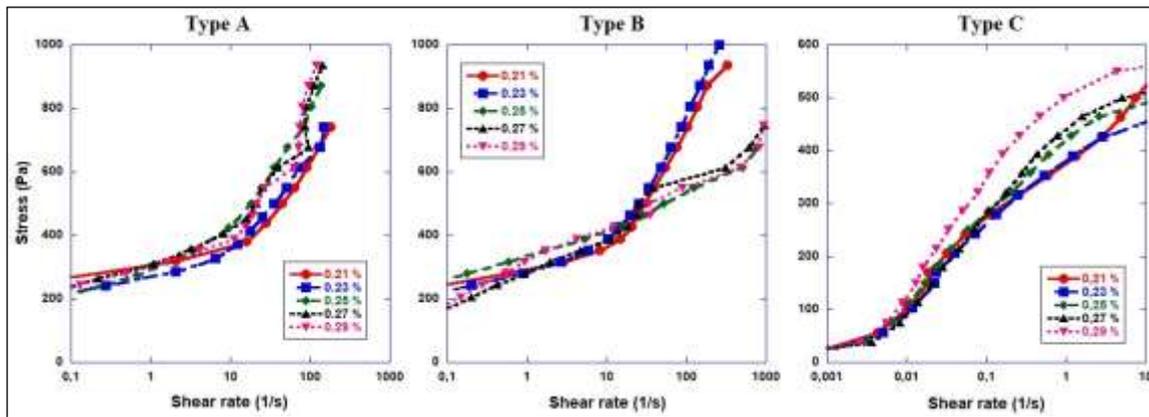
A comparison of the loading curves corresponding to different polymer contents is presented in Figure 1, both in linear and in logarithmic scale. A qualitative similarity of the rheological behaviour with the increasing of polymer content has been observed. The flow curves indicate that the mortar pastes behave as a shear thinning fluid with a yield stress.

Considering the evolution of the applied stresses as a function of recorded shear rate at some given stresses and for different polymer contents of B, we can see that: At certain stress, for instance 600 Pa, the recorded shear rates are about 60 s^{-1} for 0.21%, and 500 s^{-1} for 0.25% and 0.29%. This indicates that for certain given applied stresses, the recorded shear rates increases with the increase of polymer content. This observation is inverse to that in case for mortars with polymer A. The crossover of the flow curves indicates that the evolution of the apparent viscosity (stress divided by shear rate) versus polymer content is dependent of the shear-rate interval considered. This may be attributed to the different antagonistic effects of the polymer.

In case of C, the mortar rheological behavior is close to that of a Bingham fluid. The mortars are shear thinning at lower polymer content. However if we zoom in the flow curves around low shear rates (see figure 3b) we can observe that the mortar behave rather as Herschel-Bulkley shear-thinning fluids for all the dosages rates. This change in the rheological behavior of mortar pastes at low and high shear rates is represented by the evolution of the rheological parameters, including yield stress, consistency and fluidity index, which will be discussed in the following.



a) Linear plot



b) Logarithm plot

Fig-3: Flow curves comparisons with the variation of polymer contents

Evolution of the rheological parameters

The rheological parameters are determined by performing the best fits of the loading curves with the Herschel-Bulkley model. Figure 4-6 represents the evolutions of the rheological parameters, including the yield stress, the consistency coefficient and the fluidity index as a function of polymer content, in case of different polymer type.

It can be seen that an optimum is observed in the evolution of the yield stress with the variation of polymer content. The yield stress reaches a minimum for a content of 0.25%. The observation of such a minimum has already reported by several authors concerning other types of mortars [9, 10]. This has been attributed to the air-entraining effects of cellulosic ether polymers [10]. In fresh state, the air bubbles in the mortar may lead to an increase of the resistance to flow initiation due to capillary forces. However, these bubbles along with the lubrication effects of the polymer would decrease the resistance to flow initiation due to decrease of granular contacts. These effects have opposing impacts. The interplay between them would lead to the appearance of minimum value in the resistance to flow initiation.

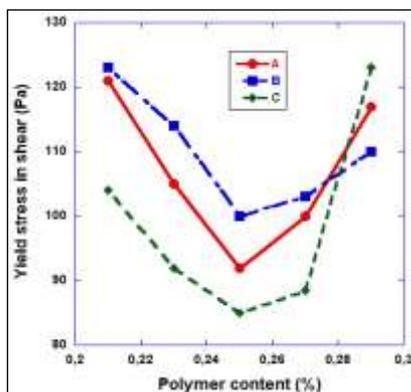


Fig-4: Evolutions of the yield stress as a function of polymer content, in case of different polymer types

In case of A, the consistency reaches a maximum for a concentration of 0.25%. In contrast of the yield stress, the consistency increases slightly, reaching a maximum at 0.25%, followed by a decrease of the consistency when increasing the polymer content. As discussed above, the interplay between increasing of pore solution viscosity, lubricating and air-entraining effects would lead to the decreasing of the viscous effects. The presence of a maximum in the evolution of the consistency can be attributed to the competition of the three effects, which lead to the increase or decrease of the viscous effects.

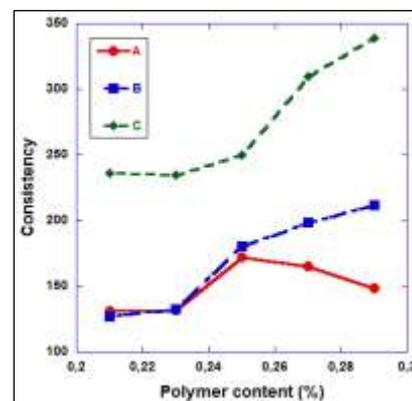


Fig-5: Evolutions of the consistency coefficient as a function of polymer content, in case of different polymer types

In two other cases of B and C, which have higher molecular weight, we observe a monotonous increase of the consistency when increasing the polymer concentration, reflecting the increase of the viscous drag effects with polymer content. A similar observation concern the effect of another type of cellulose ether polymer on mortar joints has been reported [9]. B has much higher effect on consistency than A. This is rather expected since the molecular weight of B is higher, so its effect on the viscosity of

the pore solution is higher due more entanglement. A huge increase of the consistency can be observed when the polymer content is above 0.23 %. They may correspond to a transition from dilute/semi-dilute to concentrated regimes in the polymer pore solution.

The evolution of the fluidity index is less significant. We observe a slightly increase of the fluidity index when increasing the content of A. This is followed by an approximate plateau and for a dosage rate of 0.27%, the fluidity index decreases. This evolution of the fluidity index is similar to the observation of A.Kaci *et al.* [10] in case of mortar joints with the variation of another type of cellulose ether polymer. The evolution of fluidity index in case of B indicates that the fluidity of the mortar is high at low content, and significantly decreases to a small value at high polymer contents. We can recognize two areas of

the fluidity index of mortar as circled in Figure 6. At low polymer contents, including 0.21 and 0.23 %, the mean value of the fluidity index of is around 0.34, while it is around 0.21 at high polymer contents. It means that the mortar becomes more shear-thinning with increasing polymer content. The transition from high to low fluidity indexes coincides with that of low to high consistency.

The presence of a minimum value of fluidity index in case of C may result from the competition between the shear-thinning character of the addition polymer and the shear-thickening contribution of the granular phase in the suspension. In addition some associative polymers are known to present shear-thickening at low shear-rates, and this is probably the case here.

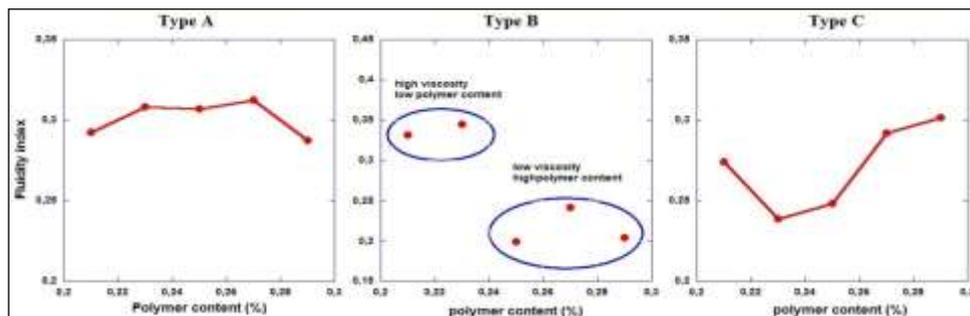


Fig-6: Evolutions of the fluidity index as a function of polymer content, in case of different polymer types

Influence of the molecular weight Mw

Influence of Mw on the yield stress

The effect of molecular weight on the yield stress of the mortar is highlighted in Figure 7. It can be seen that we observe an evolution with an optimum for a concentration of 0.25 % independently of the molecular weight. As discussed in the previous sections, several authors have reported the presence of such a minimum and this has often been attributed to the air-entraining effects of cellulose ether polymers. There is no direct correlation between the depth of the minimum and the molecular weight.

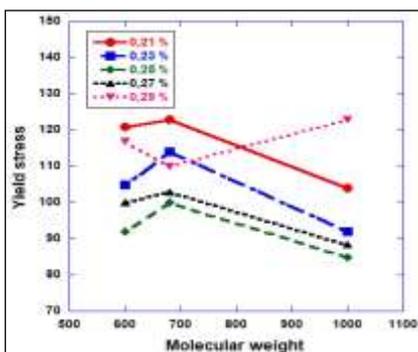


Fig-7: Evolution of yield stress in shear for the variation of molecular weight

Figure 7 shows the dependency of the yield stress on the molecular weight. Increasing the molecular weight first leads to a slightly increase of the yield stress to reach a maximum value, followed by decrease of the yield stress. These trends are observed for all the polymer concentrations expect the highest one (0.29%). For this dosage, the maximum transforms into a minimum.

Influence of Mw on the consistency of the mortar

The evolution of the consistency of the mortar pastes as a function of molecular weight is represented in figure 8. We can observe a significant increase of the consistency of mortar pastes when the molecular weight increases. This dependence of the consistency of mortar on the molecular weight is also in agreement with the results reported by L.Patural (2011) [9] on the effect of other types of cellulose ethers on cement-based mortars. The increase of consistency with molecular weight is not surprising since the viscosity of polymer solution make up by the cellulose ether dissolved in the pore solution should increase with molecular weight.

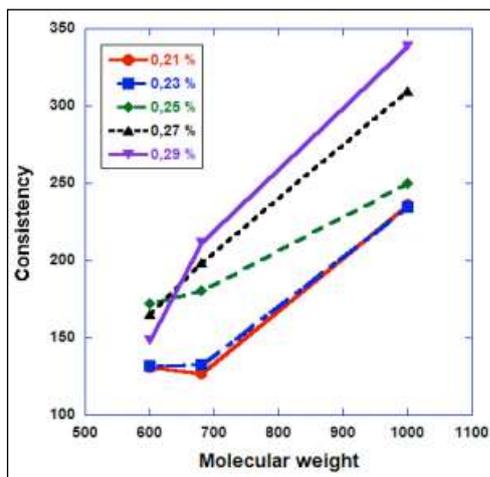


Fig-8: Evolution of the consistency of mortar pastes as a function of molecular weight

CONCLUSIONS

The rheological properties of mortars in the fresh state have been investigated by varying the content of three types of hydroxyethyl methyl cellulose denominated A, B and C. These polymers differ from each other mainly in their molecular weights.

At low shear rates, all the mortar mixes behaved as a shear-thinning fluid. However at high shear rates, we observed a difference between the mixes corresponding to the different cellulose ethers. In case of A, the mortar pastes behave as shear-thinning fluids for all investigated concentrations. In case of B, the rheological behavior of mortar is shear thinning at low concentrations, while it behaves as Bingham fluids at high contents. In case of C, the mortars behaved much like Bingham fluids through the entire shear-rate interval investigated.

The investigation of the influence of molecular weight on the properties of fresh mortars has shown a similar observation to the reported research in literature. The yield stress of the mortar decreases with the increase of molecular weight. This decrease is not significant at low molecular weights, and becomes much more significant at high molecular weights. Inversely, the mortar consistency is found to increase with the increase of molecular weight.

REFERENCES

1. Bayer R, Lutz H; Dry mortar - Ullmann's Encyclopedia of Industrial Chemistry, Sixth Edition 2003 Electronic Release, Wiley - VCH Weinheim, 2003.
2. Le TH, Phan VT; High molecular weight cellulose ether influence on the adhesive properties of fresh mortars - Journal of Science and Technology, 2014; 52(6): 787-793.
3. Jiang YC, Wang X, Cheng PS; Synthetic and solution behavior of poly-caprolactone grafted hydroxyethyl cellulose copolymers, International Journal of Biological Macromolecules, 2011; 48(1): 210-214.
4. Angadi SC, Manieshwar LS, Aminabhavi TM; Interpenetrating polymer network blend microspheres of chitosan and hydroxyethyl cellulose for controlled release of isoniazid, International Journal of Biological Macromolecules, 2010; 47(2): 171-179.
5. Said GS, Kader FHA, Naggar MME, Anees BA; Differential scanning calorimetry and dielectric properties of methyl-2-hydroxyethyl cellulose doped with erbium nitrate salt, Carbohydrate Polymers, 2006; 65(2): 253-262.
6. Stefan, Erkselius, Ola JK; Free radical degradation of hydroxyethyl cellulose, Carbohydrate Polymers, 2005; 62(4): 344-356.
7. Sigh NK, Mishra PC, Singh VK, Narang KK; Effect of hydroxyethyl cellulose and oxalic acid on the properties of cement, Cement and Concrete Research, 2003; 33(9): 1319-1329.
8. Pourchez J, Peschard A, Grousseau P, Guyonned R, Guilhot B, Vallée F; HPMC and HEMC influence on cement hydration, Cement and Concrete Research, 2006; 36(2): 288-294.
9. Patural L, Marchal P, Govin A, Grousseau P, Ruot B, Devès O; Cellulose ethers influence on water retention and consistency in cement-based mortars, Cement and Concrete Research, 2011; 41(1): 46-55.
10. Kaci A, Bouras R, Chaouche M, Andréani PA, Bouras H; Adhesive and rheological properties of mortar joints, Appl. Rheol, 2009; 19: 51-71.
11. Kaci A, Bouras R, Phan VT, Andreani PA, Chaouche M, Bouras H; Adhesive and rheological properties of fibre-reinforced mortar, Cement and Concrete Composites, 2011; 33(2): 218-224.