

EFFECT OF CELLULOSE ETHER AS A THICKENING AGENT ON THE ADHESIVE AND RHEOLOGICAL PROPERTIES OF MORTARS

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ABSTRACT

This paper presents an experimental study of adhesive and rheological properties of cement mortars proportioned with various contents of a water-soluble polymer admixture. To determine the adhesive properties the probe tack test was used. The results have been exploited to identify the adhesion strength, the cohesion strength and the support' adherence force. It is found that the cohesion component displays a minimum when varying the polymer content. The behavior of the adherence force is more complex. The evolution of the adhesive force versus polymer content displays optima depending upon the tack test velocity. The rheological behavior of the mortars was also considered.

Keywords: adhesive properties, Rheological properties, mortar, cellulose ether, tack test.

1. INTRODUCTION

A number of studies have been reported in the literature concerning the influence of water-soluble polymers on the rheological behaviour of cement pastes [1, 2], mortars [3, 4] or concretes [5, 6]. Most of these studies reported a monotonic increase of the yield stress and plastic viscosity of the material when the admixture content was increased. However, in the particular case of mortars, it has been reported that the two rheological parameters displayed a minimum when the polymer content was increased [3]. This has been attributed to the competition between the thickening effects of the polymer, which is expected to lead to an increase of the yield stress and plastic viscosity, and air-entrainment increase due to the presence of this polymer, which would lead to the decrease of those two rheological parameters.

In contrast to the rheological behaviour, adhesive properties of cementitious materials in fresh state have been much less considered [7].

Adhesive properties of fresh mortars are decisive from different points of view:

(i) Placement process (pumping, casting, smoothing, etc.): the mortar paste must display sufficient tackiness to stay on its support, but the adherence must also be limited in order to avoid excessive sticking to the working tool or the ducts of the pumping circuit.

(ii) Long term behavior: the quality of adhesion between fresh mortar pastes and the support will condition the long term performance of the solidified product for rendering walls, as well as the efficiency of bonding for adhesive mortars.

The adhesive properties of fresh mortar have been characterized using probe tack tests. This kind of tests has been largely employed to characterize polymer-based adhesives [8, 9] and more recently to investigate the tackiness and various failure modes of smectite muds [10]. Kaci *et al.* [7] have been among the first to use the probe tack test to characterize the adhesive properties of cementitious materials. It has been shown that tack measurements allow dissociating several aspects of practical interest, related to adhesive properties [7]:

-*Interface adherence*, which expresses the product's ability to stand on its support.

-*Cohesion*: this property is related to the yield stress, and characterizes the material's resistance to flow initiation under extension.

-*Adhesion strength*: this quantity encompasses both cohesion strength and viscous dissipation, and can be employed to characterize adhesion properties under flow conditions.

Kaci [7] has investigated the influence of water-soluble polymers on the adhesive properties of fresh mortar joints. For those materials used in practice as thin joints to bind construction blocks together, the aim was to characterize the adhesive properties that guarantee an adhesion to the surface but not to the tool. In the present investigation we perform an extension of the aforementioned work.

Finally, in order to complete the characterization of placement properties of mortars, the rheological properties are determined at different thickening agent contents and compared to the adhesive properties.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Mix-design

The weight proportion of each constituent of the mortar is given in table 1.

Table 1. Mix proportioning of constituents of the mortar.

Constituent	Portland cement	Hydraulic lime	Siliceous sand	Air entraining agent	Cellulose Ether	Water
% (by weight)	15	5	80	0,01	0,05 - 0,25	16

The binder comprises Portland cement (CEM I 52.5 N CE CP2 NF from Teil - France) and natural hydraulic lime (NHL 3.5Z). The other constituents consist of silica-based sand and an air-entraining admixture (NANSA LSS 495/H). The mortar composition corresponds actually to a basic version of commercially-available render mortars [4].

In order to minimize phase separation, the sand size distribution has been obtained by combining two contrasted granulometries: a fine sand of mean diameter equal to 0.41 mm, and a coarse sand of mean diameter 1.13 mm. An optimal compacity is obtained by employing 30 % of fine sand and 70 % of coarse sand. The air entraining agent guarantees moderate rheological properties, within the resolution range of our rheometer. The water dosage rate is fixed to 16 %

by weight for all the investigated samples. The only variable parameter is the amount of polymer additives. In the present study, the high molecular weight water-soluble polymer is a commercial cellulose ether-based polymer (METHOCEL™ 306), available in powder form and usually employed to formulate industrial mortars. The polymer content is varied according to the following proportions: $C_e = [0.05; 0.1; 0.15; 0.2; 0.25]$ % by weight. Cellulose ethers are systematically present in industrial mortars in order to prevent bleeding as it thickens the aqueous phase by fixing water [11].

Typical properties of cellulose ether is given in table 2.

Table 2. Typical properties of cellulose ether (METHOCEL™ 306).

Form	Powder
Solubility	Water soluble
Viscosity (1 % solution in water, Brookfield RV, 20 rpm, 20 °C)	5300 mPa.s
Viscosity (2 % solution in water, Brookfield RV, 20 rpm, 20 °C)	30000 mPa.s
Moisture content	< 6 %
Sodium Chloride	< 2 %
Particle size (< 70 U.S. Standard Sieve, 212 μm)	> 98 %

2.2. Test methods

2.2.1. Probe tack tests

The probe tack tests have been performed on a rheometer ARG2 of TA Instruments. The lower component of the measuring system is fixed, while the upper component is attached to a shaft. The force transducer is located on the fixed plate, and measurements can be made at torques as low as 0.01 $\mu\text{N.m}$ up to 200 mN.m , with a torque resolution of 0.1 nN.m and a displacement resolution of 25 mrad . The axial force range is from 0.005 to 50 N.

As the mode of preparation has a great influence on the final state of the suspension and therefore on its rheological behavior, we adopt the same experimental procedure for all the investigated formulations. A fine layer (about 3 mm in width, of diameter 40 mm, of fixed weight equal to 0.27 N) is inserted between two parallel plates of high roughness, which allows minimizing wall slippage. The material is left to rest for 2 minutes after casting, in order to avoid possible memory effects. The plates are then separated under a constant velocity, which is chosen among the following values: [10, 50, 100, 300 and 500] $\mu\text{m/s}$. Under each imposed velocity, the normal stretching force is measured concurrently with the instantaneous distance between both plates. Knowing the initial weight of the mortar, the measurement of the final weight enables us to determine the amount of material remaining on the mobile plate at the end of the test.

Three relevant properties can be directly identified from tack test, including adhesion strength, cohesion strength and cohesion, which will be presented in section 3.1.

2.2.2. Rheological measurements

The rheological properties are determined with the same rheometer, equipped with the vane geometry. The latter configuration is particularly well-suited for cement pastes (for granular suspensions in general), as it allows to minimize wall-slippage effects [12]. The gap, or distance between the periphery of the vane tool and the outer cylinder, is equal to 8.3 mm, which is more than seven times higher than the maximum grain size. Accordingly, we may assume that the rheological measurements are not affected by the discrete nature of the mortar. On the other hand, the shear rate and shear stress may vary along the gap since it is quite large as compared to the vane diameter. Therefore, the rheological properties cannot directly be inferred from the measured torque and the rotational velocity of the vane tool. A specific exploitation procedure is required, which is detailed in Bousmina *et al.*[13]. The flow curves were determined under controlled stress conditions, using the same procedure with all the studied samples.

3. EXPERIMENTAL RESULTS

3.1. Tack tests results with varying polymer content

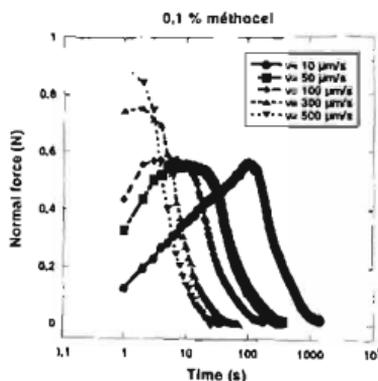


Figure 1. Evolution of normal force with time, for varying velocities, and for 0.1 % of cellulose ether.

Figure 1 illustrates typical time evolutions of the normal stretching force, under varying velocities and for the formulation with 0.1 % cellulose ether. A semi-logarithmic scale has been retained to bring out the behavior around the peak. The force curves are all qualitatively similar. The initial force increase can be related with elastic and visco-elastic deformations, under mixed conditions of shear and extensional flows. After reaching a peak which gets more pronounced as velocity increases, the normal force decreases abruptly during the paste progressive rupture, and we observe an inward flow towards the plates' center under tension. After completion of the rupture process, a residual force level is reached.

Three relevant properties can be directly identified from tack test curves of figure 1:

- The peak value F_{\max} is employed to determine the *adhesion strength* of the material, originating both from flow resistance (owing to viscous effects) and the material's intrinsic cohesion at rest.

- The *cohesion strength* will therefore be identified by considering the adhesion force for pulling velocities tending to zero, i.e. when no viscous effects are present under quasi-static conditions.

- Finally, the residual force at the end of the pulling test corresponds to the weight of the material still remaining on the mobile plate, and allows characterizing the *adherence* at the plate-mortar interface.

3.1.1. Adhesion force

Figure 2 shows the variations of the maximum stretching force, or adhesion force, with pulling velocity for varying cellulose ether contents. For polymer contents between 0.15 % and 0.25 %, a strong dependency of adhesion force on velocity is noticed, while for low polymer contents (0.05 - 0.1 %) the force increase is much less significant. The more marked dependency of adhesion force on velocity, observed for high polymer contents, can be attributed to an increase of the paste viscosity with polymer content, which can overshadows the air-entraining and hydrodynamic lubrication effects of the polymer [14].

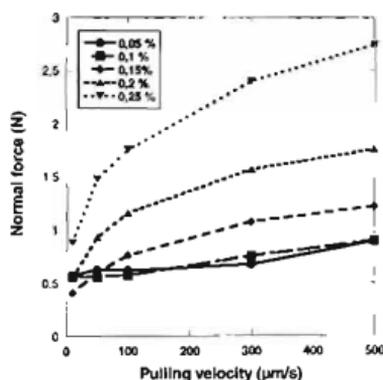


Figure 2. Evolution of the adhesion force versus pulling velocity for varying cellulose ether contents

From a practical point of view, the latter results enhance the essential difference of behavior between render mortars (which are formulated with $C_e < 0.1$ %), and adhesives mortars characterized by C_e values higher than 0.2 %, which can sustain higher normal stress levels.

3.1.2. Cohesion force

The cohesion force can be identified as the adhesion force corresponding to the lowest value of pulling velocity that can be attained with our rheometer (10 µm/s). As illustrated in Figure 3, the cohesion force evolution with varying polymer content is non-monotonic. For high percentages in cellulose ether, the observed cohesion increase could either be attributed to viscous effects originating from the finite value of velocity employed, or to cohesive effects related with the formation of a polymer gel. If the first assumption is valid, the cohesion should

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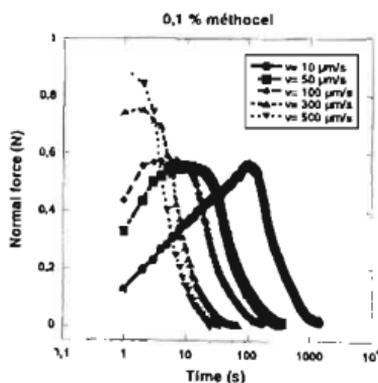


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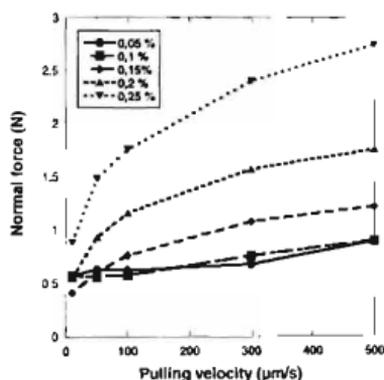


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decrease with the pulling velocity employed for its identification. From figure 2, we notice that the adhesion force displays an important decrease at low velocities and for high cellulose ether contents. By extrapolating the results to lower values of velocity, we can conclude that the cohesion effort identified at a velocity of $10 \mu\text{m/s}$ is likely to be over-estimated, and there is no firm evidence that the polymer will increase the *true* cohesion. At low pulling velocities, we also observe a local minimum in cohesion around 0.15 %. Cohesion variations will be discussed further in section 4 in relation with the yield shear stress identified from rheological tests.

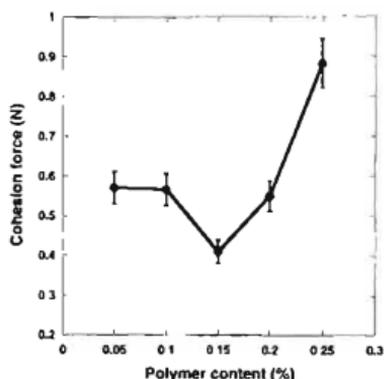


Figure 3. Evolution of the cohesion force with polymer content.

3.1.3 Interface adherence

The adherence force is taken to be equal to the weight of product remaining on the mobile plate at the end of the tack test, and corresponds to the residual value of the stretching force after completion of the rupture process. Although the adherence force is clearly not a material property, from a practical point of view, it will determine the tackiness for render mortars, and the effective bonding between masonry elements for adhesive mortars.

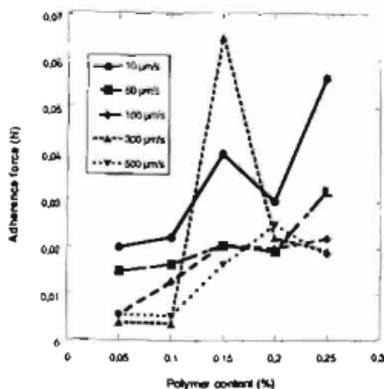


Figure 4 Evolution of the adherence force versus polymer content with varying tack velocities.

Figure 4 represents the variations of the adhesion force with pulling velocity, for varying polymer content, evidencing the increase of the interface adherence with polymer content. For low cellulose ether contents ($< 0.1\%$) and high values of pulling velocity, the adherence force is vanishingly small. On the other hand, for low values of pulling velocity ($10\ \mu\text{m/s}$), the significant increase in adherence observed still remains to be interpreted. On the whole, the quasi-monotonic decrease of adherence force with pulling velocity has also been observed by Kaci [7] for mortar joints with polymer additives. This has been interpreted in relation with the occurrence of various debonding modes. In particular, it has been shown that such mortar pastes display debonding patterns intermediate between a liquid and an elastomeric adhesive, depending on pulling velocity and polymer concentration. For a liquid, rupture occurs through an axisymmetric flow towards the center of the sample, while an elastomeric adhesive displays an adhesive rupture at the material-plate interface in which most of the material remains on the lower plate.

3.2. Rheological behaviour with varying polymer content

Flow curves in the stress-controlled mode, such as illustrated in figure 5, allow determining in particular the yield shear stress that characterizes the onset of fluid flow. With the employed vane geometry, the smallest measurable shear-rate value is about $0.01\ \text{s}^{-1}$, and will therefore serve as the lower bound for fluid flow. For 0.05% polymer content, the behavior is elastic-perfectly plastic: below the yield stress, the shear rates are vanishingly small, and above the yield stress the measured stress is independent of the applied shear rate.

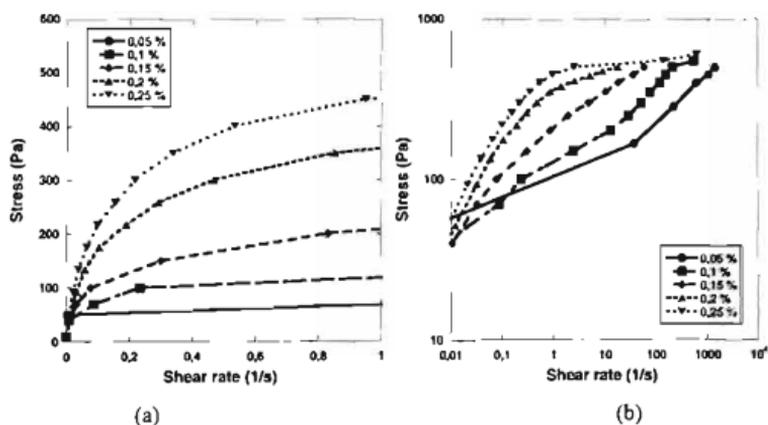


Figure 5. Flow curves obtained in the stress-controlled mode using different polymer contents. (a) Linear plot (for lower shear rate values). (b) Logarithmic representation (for higher shear rate values).

The yield stress is related with the cohesion of the material, and should therefore be correlated to the cohesion strength identified during tack tests. From figure 5, we observe a qualitative change of the rheological behavior with increasing polymer contents. At low shearing rates (figure 5 a), we observe a gradual transition from a visco-plastic behavior to a shear-thinning behavior. At high shearing rates (figure 5b), the material is shear-thinning at low cellulose ether contents, but remains shear-thinning for high cellulose ether contents.

4. COMPARISON BETWEEN TACK TESTS AND RHEOLOGICAL MEASUREMENTS

4.1. Overall behavior

Strain rates involved during a typical tack test are rather low. For the highest value of pulling velocities considered (500 $\mu\text{m/s}$), the maximum strain rate can be estimated as the ratio between the velocity and the gap thickness, which gives: 0.17 s^{-1} . Consequently, any comparison between tack tests and rheological measurements must be made at low shear rates, such as illustrated in figure 5a. From figure 5a, we see that the corresponding rheograms are qualitatively similar to the force curves measured during the tack test displayed in figure 2. From figure 2, the computed nominal stresses vary between 700 and 2100 Pa for a strain rate around 0.17 s^{-1} , for the latter value of strain rate we therefore observe that the stress levels are about one order of magnitude higher during tack tests as compared to the flow curves in figure 5a. The contribution of the extensional stress to the tack force may then be deemed significant compared to the shear component.

4.2. Yield stress and cohesion

The yield stress is identified as the applied shear stress corresponding to a finite shear rate value equal to 0.01 s^{-1} . The yield stress evolution with polymer content is represented in figure 6. Similarly to the cohesion force identified from tack tests (figure 3) the yield stress displays a minimum value at $C_e = 0.15 \%$. From figure 3, we obtain that the cohesion stress varies between 450 and 700 Pa, and as in section 4.1, the observed stress levels derived from tack tests are about 10 times higher than the stresses recorded during rheological tests under shearing conditions. The occurrence of a local minimum has also been reported in the literature concerning other types of mortars [3, 4] and has been attributed in particular to the competition between air-entraining enhancement due the presence of the cellulosic ether polymer and its thickening effect. At low polymer contents, the air-entraining effect would dominate which leads to the decrease of the yield stress. Increasing further the polymer content may lead to the formation of a gel which will result in an increase of the apparent yield stress. Actually the increase of the yield stress at high polymer contents may rather correspond to an increase of the stress at low shear-rates than the true yield stress. This needs to be investigated further.

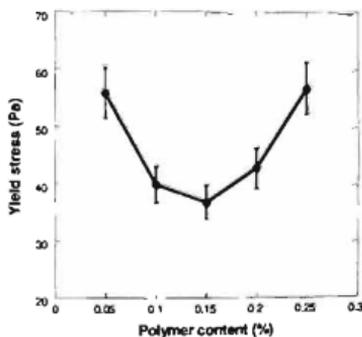


Figure 6. Evolution of the yield stress with polymer content.

5. CONCLUSIONS

In the present paper, the effect of cellulose ether on the adhesive and rheological properties of mortars in fresh state has been investigated using tack tests and rheological experiments. A marked dependency on pulling velocity, and a non-monotonous variation with polymer content during tack tests and yield stress measurements have been observed. A local minimum has been observed in the evolution of the cohesion force and the yield stress at around 0.15%. This has been attributed to the competition between air-entraining enhancement due to the presence of the cellulose ether polymer and its thickening effects.

Several mechanisms have been proposed to interpret the observed results; in particular the role of the viscosity of the fluid phase should be investigated further by performing viscosity measurements for the suspending fluid alone.

The comparison between tack tests and rheological measurements, represented in figure 3 and 6, has shown that the cohesion force can be related to the yield stress identified on flow curves, while the viscosity correlates well with the interface adherence.

Finally, water-soluble polymer can be used to adjust viscosity and adherence properties of cement mortar.

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TÓM TẮT

TÁC DỤNG CỦA VIỆC SỬ DỤNG XENLULO ÊTE NHƯ MỘT CHẤT CÔ ĐẶC TỚI TÍNH ĐÍNH VÀ TÍNH LƯU BIẾN CỦA VỮA

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Bài báo trình bày nghiên cứu thực nghiệm về ảnh hưởng của một loại phụ gia xenlulo dạng bột tan trong nước tới tính dính bám và tính lưu biến của vữa xi-măng tươi. Tính dính bám của vữa được xác định bằng thí nghiệm dính bám, từ thí nghiệm này cường độ dính bám, lực cô kết và sức bám của vật liệu được xác định. Tính lưu biến của vữa cũng được xem xét bằng thí nghiệm đo lưu biến. Kết quả thí nghiệm cho thấy lực cô kết luôn đạt cực tiểu tại một hàm lượng phụ gia nhất định. Sự biến thiên của sức bám phức tạp hơn và không có quy luật cụ thể, trong khi đó lực dính kết của vật liệu được cải thiện với hàm lượng phụ gia. Ứng xử lưu biến của vữa cũng được nghiên cứu qua sự biến thiên của ứng suất tới hạn khi thay đổi hàm lượng phụ gia. Kết quả cho thấy phụ gia xenlulo tan trong nước có thể dùng để tăng độ nhớt và sức bám của vữa xi-măng.

Từ khóa. tính dính bám, tính lưu biến, vữa, xenlulo, thí nghiệm dính bám.