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Use of ultrasonic degradation to study the molecular weight influence of polymeric admixtures for mortars

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ABSTRACT

The aim of this paper is to provide a methodology to study the influence of the molecular weight of polysaccharidic admixtures on mortar properties. A wide range of admixtures with different molecular weight and constant structure was prepared. This has been made possible by the use of ultrasonic treatment, a simple, effective, and without additive method. It appears that cellulose and guar gum derivatives, used as water retention agents, exhibit a significant molecular weight reduction according to the ultrasonic treatment duration. The water retention capacity of the mortars mixed with ultrasonically degraded admixture solutions increases with molecular weight for a same admixture. However, comparing water retention values obtained with similar molecular weight of a same family shows that effectiveness of polysaccharides as water retention agent is not linearly linked to their molecular weight.

KEYWORDS: polysaccharide, hydroxypropylguars, water retention, molecular weight, ultrasonic degradation

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HIGHLIGHTS

- Ultrasonic degradation is applicable to admixtures for building materials
- Admixtures with wide range of molar weight and constant structure were synthesized
- Ultrasonic degradation allows to establish structure-property relationships
- Effectiveness of WR agents are not only linked to their molecular weight

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1 Introduction

Polysaccharides are often added in modern factory-made mortars as water retention agent. Their function is to improve water retention capacity of the freshly-mixed paste. Water retention (WR) is a very sensitive mortar property. Indeed, mortars are often applied in thin layer or on highly absorbent substrate. In these hard conditions, WR agents allow limiting absorption of the mixing water by the substrate, which enhances cement hydration. Thus mortars exhibit better mechanical and adhesive properties [1,2]. As well, polysaccharides act as viscosity-enhancing admixtures to prevent segregation and thus improve the homogeneity and workability of the mortar [3–8].

The impact of polysaccharides in mortar formulation has mainly been studied in term of cement hydration kinetics [9–13]. Nevertheless, studies about working mechanism as water retention additives are scarce [14–18]. It still appears that the molecular weight would be the key molecular parameter driving the water retention ability of polysaccharides [19,20]. Authors reached this conclusion by working with panels of commercial admixtures of the same family and different molecular weights. Nevertheless, industrial molecules produced from a biological source such as cellulose ethers exhibit variability from one lot to another and therefore differ slightly in chemical composition [21]. Moreover, the molecular weight range of interest may not always match with what industrial suppliers can provide. In sum, there is no guarantee that different grades of commercially available polymers are suitable for establishing structure-property relationships. Therefore, the idea was to degrade one single native molecule to obtain identical sample with a range of molecular weights.

Different techniques allow to degrade polymers, such as chemical, thermal or mechanical methods. Knaus and Bauer-Heim [22] have studied the influence of molecular weights of

anionic cellulose ethers on the flowability of concrete thanks to acid-catalyzed and oxidative degradation. However, chemical degradation, as thermal [23] and enzymatic [24] methods, present important disadvantages. In particular, these random processes lead to unwanted mono- and oligomers and to modifications of the chemical microstructure of the side groups [25]. On the contrary, only ultrasonic degradation represents a suitable and established method for producing homologous series of lower molecular weights, according to many authors [25–28]. Moreover, these authors affirm that no side chain reaction takes place and that the structural and chemical structure of the polymer is maintained during the degradation process. This method presents also the advantage to be very simple, does not require the addition of reagents and therefore avoids purification process of the degraded samples.

The detailed principle of ultrasonic degradation is well described by Kulicke et al. [25]. It appears that the chain scission, due to elongational flow fields between collapsing cavitation bubbles, always occurs close to the center of gravity of the molecule. That is why no monomers are formed and no side reactions occur during ultrasonic degradation.

An exponential decrease of the molecular weights with time is observed, before to reach a constant minimum value. The rate of degradation was found to be dependant of many experimental factors, such as nature of the solvent, solution volumes, concentration of polymer and temperature [29]. Thus these factors should be constant to have comparable results.

In addition, Schittenhelm and Kulicke [26] have examined the impact of the chemical structure on the degradation process. They showed different comportments with starch and cellulose derivatives. The authors suggest that the ramification conformation of starch is responsible for the slower degradation rate, which is more important for linear cellulose

ethers. Nevertheless, for a same family, there is no impact of polymer molar degree of substitution on the degradation kinetics.

The current work presents the use of ultrasonic degradation in order to carry out investigations into the specific effect of molecular weight on the water retention capacity of mortars. Thus results obtained and conclusions reached should be more accurate scientifically than if a lot of different commercial admixtures were tested or chemical degradation used.

Two polysaccharidic admixtures families were chosen to be investigated: on the one hand cellulose ethers, which are the most widely used admixtures as water retention agents in dry-mix mortars. Moreover, the efficiency of ultrasonic degradation on these molecules has been already established in the literature [25,26,28,29]. On the other hand, hydropropylguar were tested. In 2004, these guar gum derivatives were presented by Plank as promising new class of water-retaining agent [30] because of high water retention capacity [31–33] and a low pollution process of manufacturing [34]. HPG use is now well-established in industrial construction chemistry.

In the first time, efficiency and repeatability of ultrasonic treatment on these two kinds of additives were checked by viscosity measurements and size-exclusion chromatography. Then, the water-retention capacity of mortars admixed with the degraded polysaccharide solutions was investigated. Finally, a systematic investigation of the influence of the molecular weight of cellulose and guar derivatives on the water retention of mortars will be presented.

2 Materials and methods

2.1 Mineral and organic compounds

2.1.1 Mineral products

The investigated ordinary Portland cement (OPC) was a CEM I 52.5 R CE CP2 NF type cement according to the EN 197-1 and NF P 15-318 standards. Oxide composition was determined by X-ray fluorescence spectroscopy (SRS3400, Bruker-AXS). Phase composition was quantified after XRD analysis (D5000, Siemens) by means of Rietveld refinement method (Siroquant V2.5 software). Chemical and phase compositions of the cement used are given in Table 1.

Siliceous sand (DU 0.1/0.35, Sibelco) and limestone filler (BL 200, Omya) were also used. The average particle diameter by mass (D_{50}%) are 250 µm and 7.5 µm respectively, provided by the manufacturers.

Table 1: Chemical and phase compositions of the investigated cement.

Chemical composition (% wt)				**Phase composition (% wt)**			
Oxides	XRF	Oxides	XRF	Phases	XRD (Rietveld)	Phases	XRD (Rietveld)
CaO	66.1 ± 1.2	TiO_2	0.24 ± 0.01	C_3S	73.0 ± 0.53	Gypsum	1.7 ± 0.15
SiO_2	20.2 ± 0.4	P_2O_5	0.05 ± 0.01	C_2S	12.7 ± 0.50	Anhydrite	2.3 ± 0.28
Al_2O_3	4.8 ± 0.1	MnO	0.04 ± 0.00	C_3A	4.2 ± 0.18	Hemi-hydrate	0.8 ± 0.30
SO_3	3.5 ± 0.2	K_2O	0.01 ± 0.01	C_4AF	6.1 ± 0.22	Free CaO	0.5 ± 0.13
Fe_2O_3	2.9 ± 0.1	LOI	2.2 ± 0.2				
MgO	1.11 ± 0.02						

2.1.2 Organic admixtures

Five commercial polysaccharidic water retention admixtures were selected for this study: two hydroxypropyl methyl cellulose (HPMC1 and HMPC 2) and three hydroxypropyl guar (HPG 1, HPG 2 and HPG 3).

Cellulose is a polysaccharide composed of individual anhydroglucose units linked through β(1-4) glycosidic bonds. It consists of amorphous and mostly crystalline domains of parallel oriented polymer molecules because of strong intermolecular hydrogen bridging bonds. Thus cellulose is not soluble in water. Thereby, cellulose ethers are obtained by pretreating cellulose with base (alkali cellulose) in order to break hydrogen bonds and to make the active groups accessible for etherifying agents. In the case of HPMC, the substitution of the hydroxyl groups takes place by reacting alkali cellulose with the combination of two etherifying agent: propylene oxide and methylchloride.

Guar gum is a galactomannan consisting of a β(1-4)-linked D-mannopyranose backbone, with random branchpoints of galactose via an α(1-6) linkage [35]. The ratio of mannose to galactose is about 1.8. This polysaccharide is extracted from the seed endosperm of Cyamopsis tetragonolobus, a native plant from India. HPG is obtained from the native guar gum via an irreversible nucleophilic substitution, using propylene oxide in the presence of an alkaline catalyst. The chemical modification of the native guar gum does not require hard reaction conditions of temperature and pressure, does not generate large quantity of by-products and needs weak purification procedure [34]. Indeed, this polysaccharide exhibits a high chemical reactivity and is soluble in cold water.

The schematic structure of these molecules is shown in Fig. 1 (substituent positions are arbitrary). It appears that HPMC are linear polymers whereas HPG exhibit branched-chain structure. Table 2 presents the weight-average molecular mass (determined by size-exclusion chromatography, see Section 2.2.3), the qualitative substitution degrees (provided by the

manufacturer) and the zero-shear rate viscosity (see Section 3.1.1) of these admixtures. The weight-average molecular mass is noted Mw and the zero-shear rate viscosity is noted η_0. The molar substitution ratio (MS_{HP}) is defined as the number of moles of hydroxypropyl groups per mole of anhydroglucose units and is less than 3 for our molecules. The degree of substitution, noted DS_M, represents the amount of substituent methoxyl groups on the anhydroglucose units of cellulose and is about 1.8 for HPMC 1 and HPMC 2 according to the manufacturer.

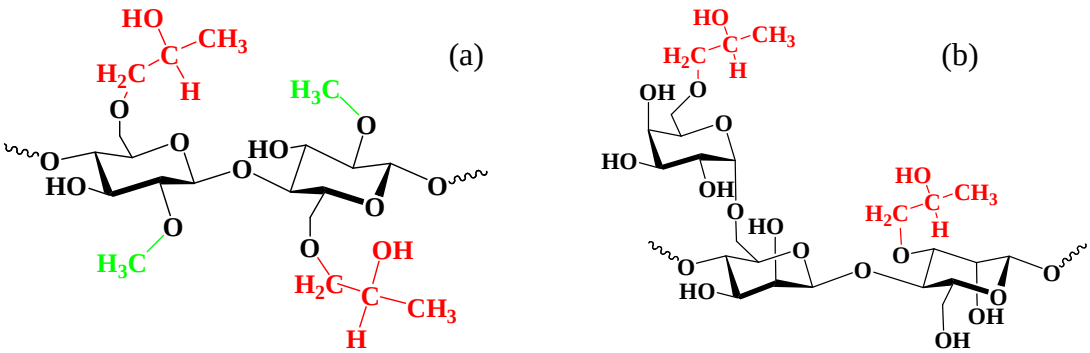

Fig. 1 : Molecular structure of HPMC (a) and HPG (b).

Table 2: Description of the admixtures used.

Admixtures	M_w (10^3 g.mol^{-1})	MS_{HP}	DS_M	η_0 (Pa.s)
HPMC 1	240 ± 50	Very low	Very high	0.04
HPMC 2	950 ± 50	Very low	Very high	17.34
HPG 1	1700 ± 80	Low	/	3.29
HPG 2	2100 ± 30	Medium	/	1.66
HPG 3	1800 ± 50	High	/	1.66

2.2 Experimental methods of investigation

2.2.1 Ultrasonic degradation of polymer solutions

Polymer solutions were exposed to ultrasonic treatment. The solutions were obtained after dispersion of 10 g of polymer powder in 1 L of deionized water, under mechanic stirring for 8 h, in a sealed reactor thermostated at 25 °C. HPMC or HPG powder was introduced through a sieve in order to have a good dispersion of the sample into the vortex created by the mechanic stirrer and thus a homogeneous polymer solution. After 8 h, solutions were stored in a refrigerator at 4 °C for at least 12 h prior to use.

Then, 250 mL of the solution were introduced in a glass beaker which was placed in a thermostatic bath. The temperature of the bath was fixed at 3°C. The thermostatic bath allows to avoid heating of the solution and thus thermal degradation and solvent evaporation during the ultrasonic treatment. The temperature of the polymer solution was not routinely monitored but it has been checked that the temperature of the liquid media did not exceed 7 °C during the ultrasonic treatment. Sonication was performed using a probe sonicator (Vibracell 72401, Bioblock) operating at 50% of its maximum output (300 W) at 20 kHz. The tip of the probe was positioned approximately at 5 cm from the bottom of the beaker. Different durations of ultrasonic treatment (t_{US}) were tested for each polymer solution (Table 3). For a given t_{US}, ultrasonic degradation is carried out in triplicate. These experimental settings were previously adjusted in order to obtain a wide range of M_w with an acceptable duration (about 2 h).

After ultrasonic treatment, the solution was kept at 23 °C under magnetic stirring. An aliquot of approximately 5 mL was taken from the solution to be characterized by means of viscosity and size-exclusion chromatography as described below. The major part of the admixture solution was used to mix with dry mortar in order to perform a water retention test.

Table 3: Duration of ultrasonic treatments according to the polymer used

Admixtures	Duration of ultrasonic treatments (t_{US}) (min)
HPMC 1	0 – 15 – 30 – 45 – 60 – 75
HPMC 2	0 – 30 – 60 – 120 – 210
HPG 1	0 – 15 – 30 – 45 – 60 – 75 – 90 – 120
HPG 2	0 – 5 – 10 – 15 – 30 – 45 – 60 – 120
HPG 3	0 – 15 – 30 – 45 – 60

2.2.2 Steady-shear flow measurements

All rheological measurements were conducted with the help of Anton-Paar Rheometer MCR 302 equipped with cone and plate CP50/2 geometry (2° cone angle, 50 mm diameter), thermostated at 20 °C. Aqueous dissolved admixture solutions, before and after sonication, have been investigated under steady shear conditions, using decreasing logarithmic ramps in the 10^2-10^{-2} s^{-1} range.

2.2.3 Size-exclusion chromatography

Size-exclusion chromatography (SEC) was performed on un-degraded and ultrasonically degraded polysaccharides samples. This technique allows obtaining the weight average molecular mass (noted M_w) and the number average molecular mass (noted M_n). It gives also an indication of the polydispersity (noted I_P) of the sample.

SEC analyses were carried out on a Waters apparatus equipped with a pump Waters 916. The eluent was a 0.5 mol.L^{-1} sodium chloride solution, filtered and on-line degassed. The flow rate was set to 0.5 mL.min^{-1}. The column used and kept at 35 °C in an oven was the Tosohaas TSK Gel GMPWXL for HPMC samples, and the OHpak SB-806 M HQ for HPG samples. Detection was achieved thanks to a refractometer-type detector Waters 2410.

Ultrasonic treatment can take a long time and any bits of titanium could be shed by the probe [28]. Thus prior to SEC analysis, the degraded polymer samples were first centrifuged

(Eppendorf MiniSpin Plus) for 5 min at 14,500 rpm to remove these particles. Then, the supernatant was collected, homogenized by vortex-stirred and diluted twenty times in the eluent. The solution obtained was homogenized again and injected in the SEC apparatus thanks to a needle.

SEC is not an absolute method and is based on the hydrodynamic radii. The average molecular mass and the molecular mass distribution need to be calculated from a calibration curve constructed using polymer standards and according to international standard ISO 16014-1:2003 [36]. The SEC system was calibrated by the use of nine pullulan calibrants of known molecular mass ($6 \times 10^3 < M_p < 2350 \times 10^3$ g.mol^{-1}, where M_p is the molecular mass at peak maximum). The retention time of each standard, depending of its molecular weight, was determined. The calibration curve is obtained by plotting elution times versus log(M_p). Polynomials of degree three were used to describe calibration curves. The calculation was done by calculating the molecular mass M_i and signal intensity H_i at each elution time using the calibration curve and the chromatogram of each polymer sample. M_n, M_w and I_P were calculated from the values of M_i and H_i using following equations:

$$M_n = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} (H_i / M_i)}$$

$$M_w = \frac{\sum_{i=1}^{n} (H_i \times M_i)}{\sum_{i=1}^{n} H_i}$$

$$I_p = M_w / M_n$$

2.2.4 Water retention measurements

Different tests allow measuring the water retention capacity of freshly-mixed mortar. They are based on a measurement of the removed water after suction or depression [20]. These tests are

subject to debate in order to determine if one represents realistically the water adsorption condition between the mortar and a porous substrate. Thus, without consensus, WR tests should be taken as purely comparative tests. ASTM C1506-09 standard [37] describes one of these tests. ASTM measurements were performed 15 min after mixing in order to measure the water loss of mortar under depression. The standardized apparatus was submitted to a vacuum of 50 mm of mercury for 15 min. Then, water retention capacity, noted WR, was calculated using the following equation:

$$WR\ (\%) = \frac{W_0 - W_1}{W_0} \times 100$$

W_0 represents the initial mass of mixing water; W_1 is the loss of water mass after aspiration.

Mortars were prepared according to the following mixture proportions: 30 wt.% of cement, 65 wt.% of siliceous sand and 5 wt.% of limestone filler. Dry mixture (*i.e.* cement, sand and filler) was homogenized in a shaker (Turbula, Wab) with low shear forces for 15 min. Admixture solution (ultrasonically degraded or not) was then added in order to obtain a water to cement ratio W/C = 1. The admixture amount corresponds to 0.3 wt.% in addition to the total dry mixture. Dry mixture and admixture solution were mixed (MIx40, CAD Instruments) in accordance with EN 196-1 [38] (60 s at low speed, 30 s at high speed, 90 s at rest and 60 s at high speed; low and high speeds correspond to 140 and 280 rpm respectively). All tests were carried out at controlled temperature of 23 °C because water retention is temperature-dependent. A control test was performed with a mortar without admixture.

The mortars formulation with high W/C was adapted from the CEReM (European consortium for study and research on mortars) mixture design [19,20]. In these conditions, a high admixture dosage of 0.3 wt.%, considering the values normally used by the industry, was chosen. This allows obtaining high WR for mortars admixed with un-degraded polymer solution. Therefore it is possible to obtain a wide range of WR by increasing the duration of ultrasonic treatment (Section 3.1.3).

3 Results and discussions

3.1 Suitability of ultrasonic degradation

3.1.1 Evidence of the degradation

The aliquots taken from the ultrasonically degraded solutions of polymer were characterized by means of viscosity measurements and size-exclusion chromatography.

Fig. 2 shows example of flow curves obtained for HPG 3 after 0, 15, 30, 45 and 60 min of ultrasonic treatment. It appears that flow curves exhibited typical shear thinning behavior with a Newtonian region in the low shear rate range. Experimental data were well correlated with the Cross model. Among Cross parameters, the zero-shear rate viscosity, noted η_0, represents the constant viscosity in the Newtonian plateau region at low shear rate.

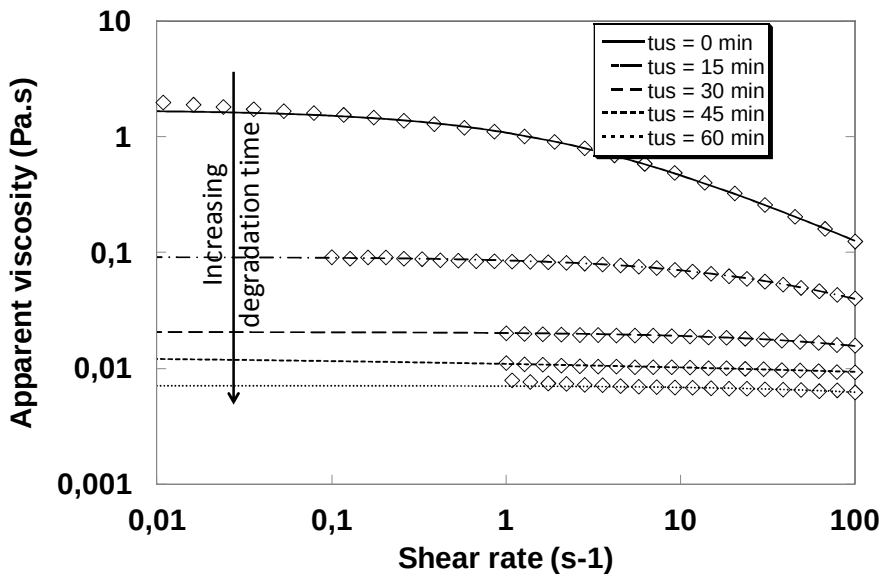

Fig. 2: Flow curves of HPG 3 solutions according to ultrasonic degradation time (diamonds represent experimental data and lines represent the calculated values according to the Cross equation)

The degradation is highlighted by plotting the zero shear viscosity of the solution against degradation time (see Fig. 3). Whatever the polymer, the zero shear viscosity is significantly reduced as a result of ultrasonic treatment. It is well-known that the zero shear viscosity of polymer solution increases with the polymer molecular weight [39]. Thus the viscosity reduction evidences depolymerization [40]. The shear thinning behavior becomes less dramatic when ultrasonic degradation time increases (Fig. 2). This is explained by a decrease of the entanglement because of depolymerization and thus molecular weight reduction [39]. Additionally, it is worth to note that the rate of viscosity reduction is unalike according to the polymer studied (Fig. 3). In the case of HPG, a sharp drop is observed in the first moments, until reaching a plateau. By way of contrast, HPMC 2 exhibits a higher initial viscosity and a slower viscosity reduction than HPG. Indeed, HPMC 2 sample presents a relatively high viscosity even after 120 min of degradation without slowdown of viscosity reduction. For HPMC1, a weak initial viscosity is observed. Then, the viscosity decreases gradually with time.

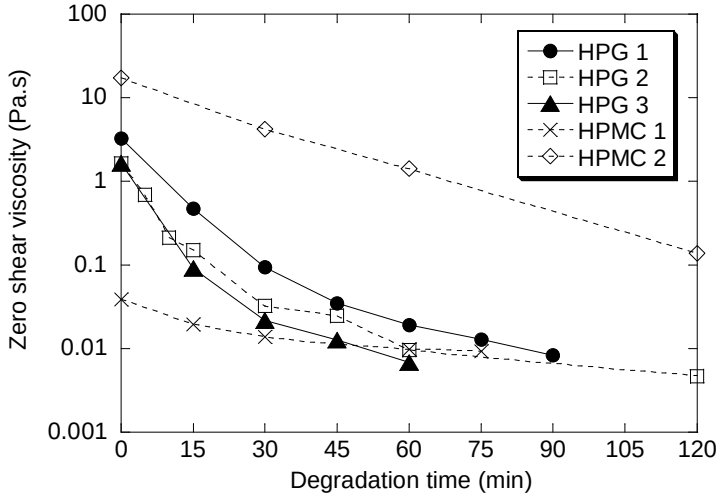

Fig. 3: Viscosity reduction due to ultrasonic degradation

Moreover, the degradation has been investigated by SEC. On a SEC chromatogram, higher is the elution time, lower is the molecular weight. Fig. 4 presents typical chromatograms, obtained for HPG 3 after 0, 15, 30, 45 and 60 min of ultrasonic treatment. Thus a qualitative molecular weight reduction is obviously observed for HPG 3. This observation is identical for each polymer.

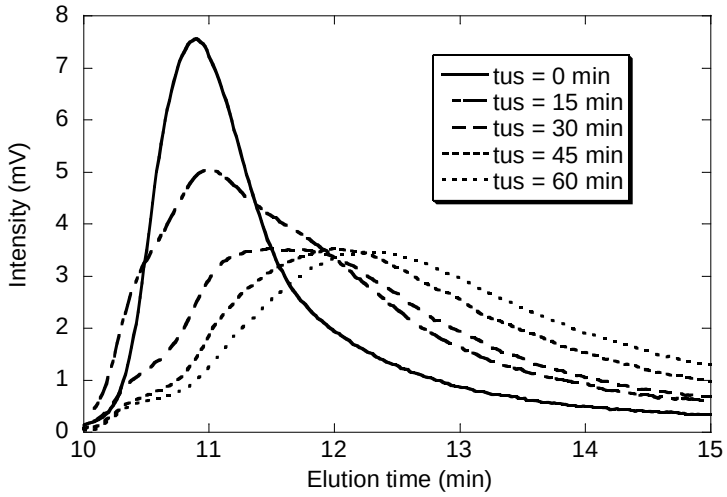

Fig. 4: Qualitative molecular weight reduction – SEC chromatograms of HPG 3

3.1.2 Characterization of the molecular weight reduction

The molecular weight reduction of polymer sample due to ultrasonic degradation was characterized by SEC. Thanks to the calibration curve, it is possible to determine the quantitative molecular weight reduction. According to the literature, the shape of these degradation profiles should be an exponential decrease, until reaching a limiting molecular weight (M_{lim}) [26,28].

Fig. 5 shows effectively a decrease of the molecular weight with the degradation time for HPMC samples (a) and HPG samples (b), which is consistent with qualitative results (Section 3.1.1). Molecular weights of HPMC 1 and HPMC 2 decrease from 240 x 10^3 to 95 x10^3 and from 950 x 10^3 to 570 x 10^3 g.mol^{-1}, respectively, after 60 min of ultrasonic treatment. The M_w of HPG 2 was reduced from an initial value of 2100 x 10^3 to 550 x 10^3 g.mol^{-1} after 60

min degradation. For HPG 1 and HPG 3, M_w decrease from 1700 x 10^3 and 1800 x 10^3 to 800 x 10^3 and 615 x 10^3 g.mol^{-1} after exposure to sonication for 60 min.

Degradation profiles of HPG samples (Fig. 5b) are closed while degradation profiles of HPMC samples (Fig. 5a) are totally different. For polymers sharing the same polymer backbone, a common M_{lim} should be reached [26]. This phenomenon was observed in this study and would explain the low sensitivity of HMPC 1 to ultrasonic degradation (66 % of loss after 75 min) compared to the loss observed for HPMC 2 (95 % after 210 min). Indeed, the initial molecular weight of HPMC 2 is much further of M_{lim} than the initial M_w of HPMC 1. On the contrary, initial molecular weights of HPG are very similar, so the degradation profiles are similar and tend towards the same M_{lim} which is consistent with literature. As the only difference between HPG 1, 2 and 3 is the degree of substitution, no significant effect of the DS on HPG degradation was observed too, as announced by Schittenhelm and Kulicke [26] with starches and cellulose derivatives.

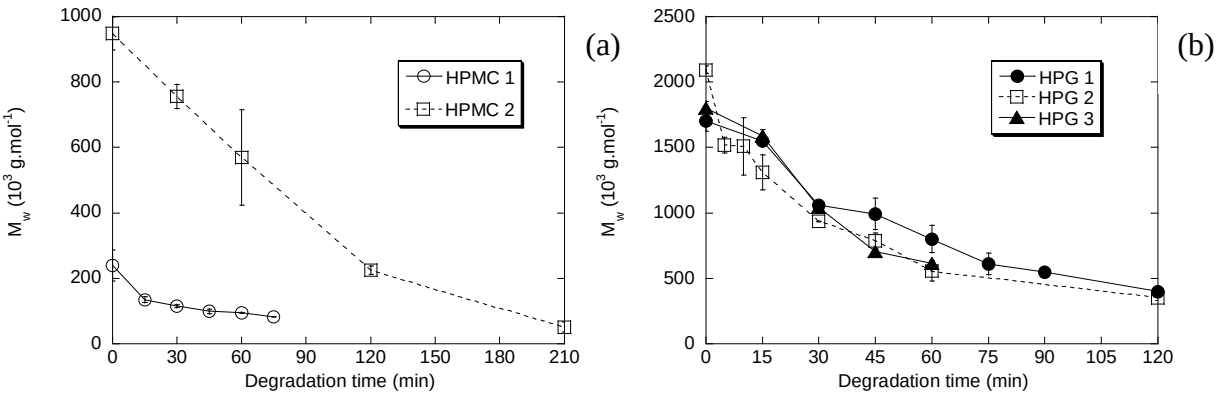

Fig. 5: Quantitative molecular weight reduction due to ultrasonic degradation for HPMC and HPG samples

Fig. 5 shows also that the principal objective was achieved as a wide range of M_w was reached. Nevertheless, it is important to check if ultrasonic degradation does not create polydisperse samples (with initial long chains and degraded short chains) as announced in the literature [25–28]. Indeed, polydispersity of the sample, characterized by I_p, should be as low as possible to study the real impact of M_w on water retention. Nevertheless, it is noteworthy

that I_p of admixtures for building material are higher than I_p of pharmaceutical or food admixtures for example. Indeed, a very controlled molecular weight is required in these kinds of industries. Considering that most of the articles on ultrasonic degradation of polysaccharides are performed on pharmaceutical [28] and food [24] grade or laboratory samples [26], low polydispersity index are given in the literature. I_p of each sample considered in this study according to the degradation time are given in Fig. 6. For HPMC 1, I_p decreases with degradation time (from 11 to 4) which is consistent with the literature [26–28]. In the case of HPMC 2, I_p of the un-degraded sample is very high (19). Then, I_p increases for samples degraded for 30 and 60 min. For samples ultrasonically degraded for 120 and 210 min, the molecular weight polydispersity decreases until values less than 10. For all HPG samples, whatever the degradation time, I_p is very low (less than 5) and so roughly constant.

Thus the polydispersity index decreases with degradation time in good agreement with literature, except for HPCM 2. This unusual result could be attributed to the high viscosity of HPMC 2 solutions. Indeed, it is well known that it is more difficult to produce cavitation in viscous liquids [41–44]. Additionally, the effect of viscosity is emphasized by the low intensity of ultrasound used in this study in order to have a wide range of molecular weights. After 60 min of degradation, the viscosity of the solution is much lower due to depolymerization (equivalent to the viscosity of HPG solutions, Fig. 3), thus the ultrasonic degradation becomes more efficient and I_p begins to decrease.

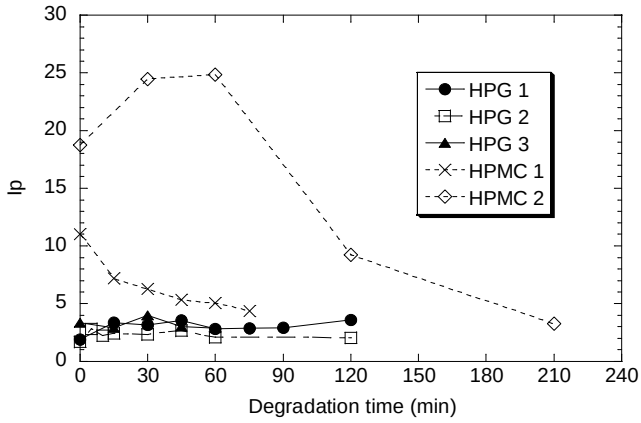

Fig. 6: Polydispersity of the degraded samples

3.1.3 Water retention of mortars mixed with degraded admixture solutions

Water retention capacities of mortars mixed with un-degraded and ultrasonically degraded polymer solutions are presented in Fig. 7. The value found for the control (mortar without admixture) is also included in Fig. 7 and plotted as horizontal dotted line (WR=62.6%).

Except for HPMC 1, water retention induced by un-degraded admixture solution is very high (>99%). Then, water retention decreases, according to the admixture, towards control value with the increase in degradation time.

Water retention induced by HPMC 2 is the less sensitive to ultrasonic degradation (WR > 84 % after 210 min of ultrasonic degradation). For HPG, water retention capacities of HPG 2 and HPG 3 decrease sharply and reach value closed to the control after 60 min of degradation, while WR of mortar admixed with HPG 1 seems to be less sensitive to its ultrasonic degradation. Thus polymers studied do not exhibit the same behavior in terms of water retention capacities versus ultrasonic degradation times.

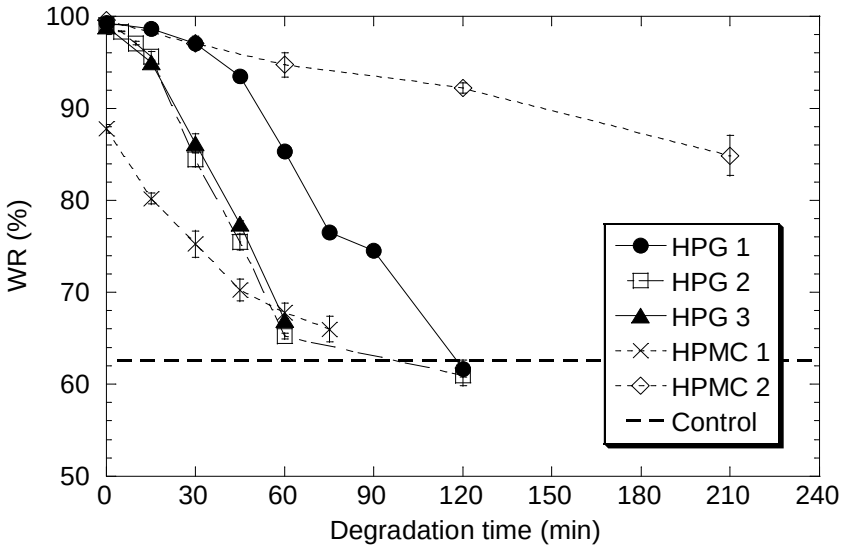

Fig. 7: Water retention capacities of degraded admixture solutions

According to these results, it emerges clearly that ultrasonic treatment is suitable to study the influence of admixture's molecular weight on properties of mortars. Indeed, by setting an appropriate probe sonicator power output and varying degradation time, we are able to obtain a wide range of polymer molecular weights, with low polydispersity.

3.2 Influence of the molecular weight on water retention

Fig. 8 illustrates the effect of the molecular weight of the 5 admixtures used on the mortars water retention capacities. Whatever the admixture, WR increases with M_w until reach a plateau with very high water retention values. Thus the capacity of admixtures to retain water in cement-based mortars is effectively link to M_w as first approximation.

Nevertheless, M_w of admixtures cannot explain alone the water retention induced by this kind of polymer. HPMC 1 presents a weak variation of M_w, but WR increases sharply from 66% to 88%. For HPMC 2, in despite of low M_w compared to HPG, high WR are obtained. HPG present equivalent initial molecular weight and structure. However, the curves obtained are not superimposed: the slope is stronger for HPG 1 than for HPG 2 and HPG 3 exhibits the weakest slope. Thus the plateau is reached for lower Mw for HPG 1, then HPG 2 and HPG 3. It appears that this remark is consistent with the MS values: for equivalent molecular weight, stronger is the MS, lower is the WR. However, it is not obvious to link the substitution degree with the water retention value.

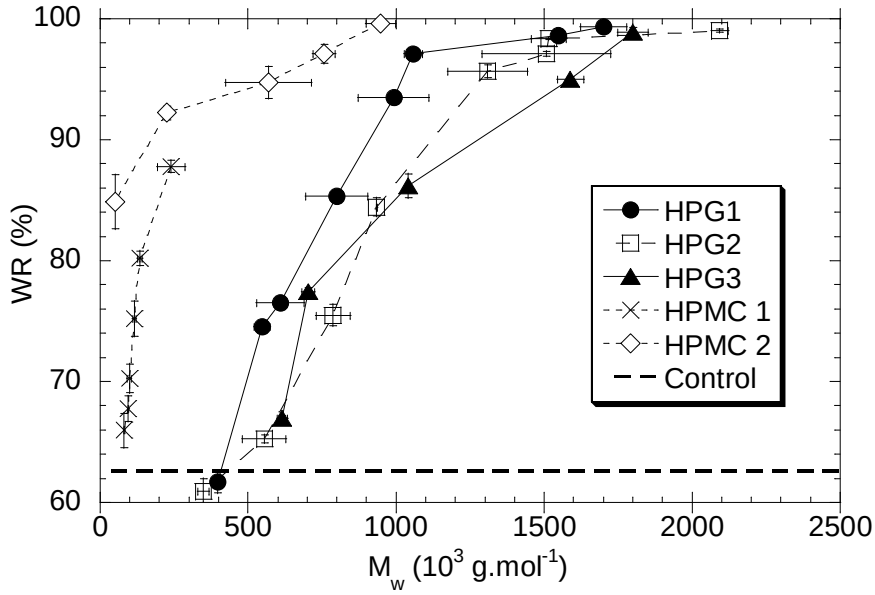

Fig. 8: Dependence of water retention on molecular weight of admixtures

Few specific points of Fig. 8 have been selected in order to highlight the water retention induced by polysaccharides with similar molecular weights for a same family. For HPMC

(Fig. 9a) and HPG (Fig. 9b), it appears that similar molecular weight does not induced similar water retention to the mortar. Indeed, HPMC 2 and HPG 1 have greater water retention capacity than HPMC 1 and HPG 2-3, respectively. HPMC 2 and HPG 1 seem to be inherently more favorable to keep the water within the mortar, regardless of the molecular weight. The high value of I_p in the case of HPMC 2 can explain partly this result by arguing that chains with high molecular weight remain in solution and enhance water retention. However, in the case of HPG, ultrasonic degradation results in a narrowing of molar mass distribution and the polydispersity index are similar.

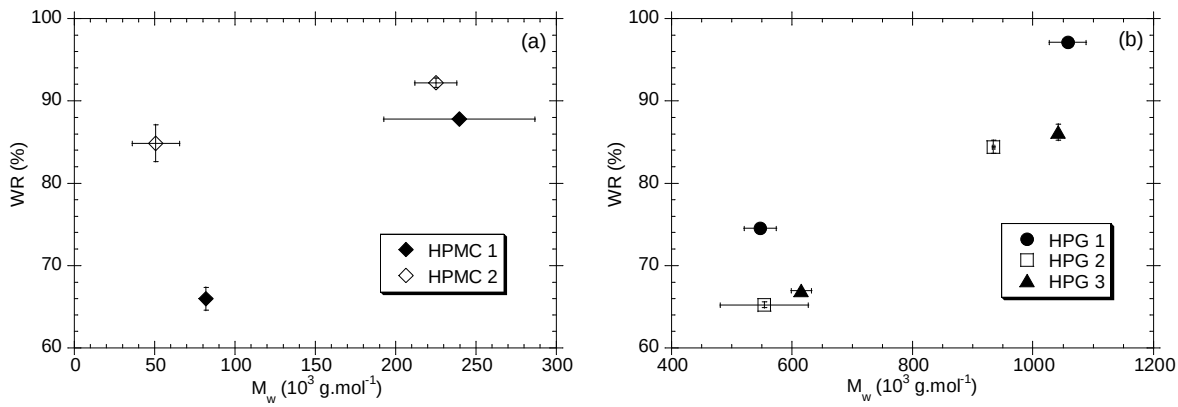

Fig. 9: Water retention of mortars admixed with similar molecular weight HPMC (a) and HPG (b)

Hence there is clear evidence that the molecular weight of the admixtures cannot be the only parameter driving the water retention capacity of the mortars induced by these molecules. These results are reliable since there are obtained from the decomposition of one native polymer sample and not from different commercial grades of admixtures.

It is worth mentioning that the main goal of this paper is to provide a useful methodology to study the influence of polysaccharidic admixtures on mortar properties. Nevertheless, results obtained show that M_w is not the main parameter affecting WR, which is a quite surprising and interesting result. As described for cellulose ethers [10,13,14], a physical effect may be responsible for WR (*i.e.* a jamming effect). The working mechanism of HPG as WR agent will be the specific topic of an incoming paper.

4 Conclusions

This paper shows that ultrasonic degradation could be applied to polymeric admixtures for establishing the impact of the molecular weight on macroscopic properties of cement-based materials. Indeed, the preparation of samples with a wide range of molecular weight, low polydispersity and exactly the same molecular structure was successful thanks to this simple method. Polysaccharidic admixtures used in mortars as water retention agent were studied.

From a single polymer, both viscosity and molecular weight reductions were observed according to the ultrasonic treatment duration. In good agreement with literature, the degradation profiles obtained reach a same limiting molecular weight for polymers belonging to the same family, independently of the initial molecular weight. Moreover, degradation process was found to be influenced by the viscosity of the solution but not by the substitution degrees of the studied polymer.

Dry mortars were then mixed with ultrasonically degraded admixture solutions in order to quantify the impact of molecular weight on the water retention capacity of fresh mortars. As expected, WR increases with M_w for a same admixture. Nevertheless, plotting WR versus M_w shows that, at similar molecular weight, different WR values were obtained according to the admixture. It seems that stronger is the DS, lower is the WR. Anyway, effectiveness of polysaccharides as water retention agent is not linked only to their molecular weight.

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