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Building of a thermoresponsive cement

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ABSTRACT

A thermoresponsive copolymer solution is used to control the mechanical properties of a cement paste suspension. We use a comb copolymer consisting of a polymethacrylic acid (PMAA) backbone grafted with a polypropylene oxide (PPO) and polyethylene oxide (PEO) copolymer that possesses a low critical solution temperature (LCST). When the temperature crosses the LCST value, microphase separation occurs and the adsorption of the copolymer onto the cement particles is modified. We show that a control of the grafting ratio and of the graft chain composition allows monitoring of the transition temperature as well as the viscosity of the paste in the low and high temperature phases.

1. Introduction

Cement suspensions should fulfill antagonistic requirements: low viscosity to facilitate its placing, and high yield stress to avoid sedimentation during setting. Here, we propose to use a thermoresponsive adsorbing polymer to control their rheologicalproperties. Cement pastes are aqueous concentrated suspensions of reactive mineral particles, composed of a mixture of calcium silicate and aluminate phases. Immediately after dispersion in water, a strong ionic dissolution of surface layers of the cement particles occurs. This dissolution is followed by a period of low reactivity, called the induction period. During this period, calcium and sulfate hydrates nucleate and grow to form the so-called CSH phase. Then, the hydration process becomes faster, the rigidity of cement paste increases and a sol/gel transition is observed [4]. Whereas the gel phase must be as concentrated as possible, the initial dispersion must be fluid and as a consequence not so concentrated, in order to allow for the handling of the paste at early ages. Ideally, the initial paste should be fluid but should posses a yield stress high enough to prevent sedimentation of the cement particles. At high concentrations, cement suspensions have a yield stress due, on the one hand to jamming [5–9] and on the other to attractive interactions between cement particles, leading to particles aggregation [10,11]. But both phenomena also lead to high values of the viscosity of the suspension. The aggregation may be controlled by the addition of polymers that adsorb onto cement particles. Few polymers can be distinguished in function of their mechanism of action [12] (Fig. 1):

- polysulfonates, adsorb chemically by reaction with cations (Na^+ or Ca^{2+}) on the surface of cement particles and inducing an electrostatic repulsion. Indeed, some studies showed that lignosulfonate polymers form complexes with cations [13].
- polycarboxylates,also adsorb chemically by reaction with cations but resulting in steric hindrance [14–16]. These polycarboxylates are often composed of a linear backbone adsorbing on cement particles, for example polymethacrylate. Non adsorbing side chains, like polyalkyl oxides, generate the steric hindrance, reducing, or even suppressing, interparticle attractive forces. [17–20][21–24]

However, although the apparent viscosity of the suspension decreases when the particles are well dispersed, the yield stress also decreases [25,26]. As a consequence, sedimentation or crackling [11,27] of the cement paste may occur during the induction period, raising difficulties in the use of the suspension [28]. A compromise between low viscosity and high yield stress may nevertheless be looked for, and the addition of a second polymer is used to increase the viscosity of the continuous aqueous phase, for instance PolyPropyleneOxide (PPO) polymer [29,30].

We propose in this article a new strategy, in which the polymer properties are tuned up to control the rheological properties of cement suspensions. The sensitivity of a complex system to a control parameter, such as temperature, pH, or illumination, may be greatly enhanced by using the change of solubility of a polymer solution. For example thermoresponsive microgels [1] or emulsions [2] have been devised. One may even control colloidal interactions [3]. As a consequence of a change in the colloidal interactions, self-assembly may be changed, but also macroscopic properties, such as rheological

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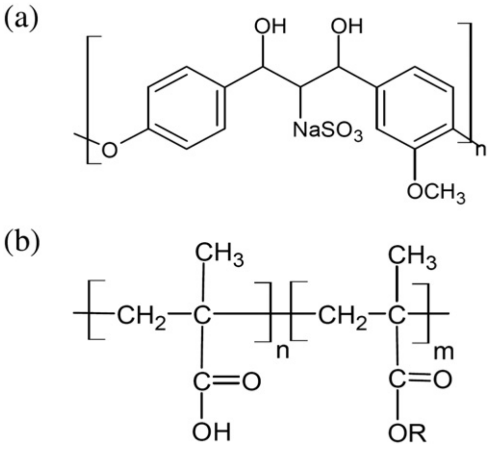

Fig. 1. Chemical structure of the sodium lignosulfonate polymer (a) and of the (b) polycarboxylate chains.

properties. Here, we propose the use of a copolymer brush, whose backbone adsorbs on the cement surface, and is in good solvent conditions, whereas the grafted chains exhibit a Lower Critical Solution Temperature (LCST), so that they are in good solvent at low temperatures, but form a microprecipitate above a critical temperature [31,32]. The temperature of the suspension thus becomes a control parameter. The critical temperature of the grafted chains is chosen so that the copolymer is in its good solvent conditions at ambient temperature, and stabilizes the particles. Under these conditions, the suspension is fluid, and the flow of the paste requires low amount of energy. On the contrary, at high temperatures, microprecipitation of the grafted copolymer chains induces a yield stress, and prevents the sedimentation of the cement particles. We chose to use polycarboxylate backbone polymers, grafted with PolyEthyleneOxide (PEO)/PolyPropyleneOxide (PPO) chains. The LCST temperature of PEO appears between 100 °C and 150 °C in function of molecular weight, and that of PPO chains is around −55 °C, so that, by controlling the ratio PEO/PPO chains, we are able to tune the overall microprecipitaion temperature of the copolymer. Previous experiments have been realized with copolymer carboxylate/PEO [33] and showed that the temperature could be used to control rheology of the dispersed phase. Nevertheless, the obtained transition temperatures were too high to make the system workable.

Here, we design new brush copolymers that precipitate at high temperature, and show that the rheological properties of the polymer/cement paste may in consequence be controlled by a change of temperature. We first detail the synthesis of polymer and techniques used to study cement/polymer mixtures. Then, we present the rheological properties of the synthesized copolymer in aqueous solution. We will thus be able to determine the amount of polymer necessary to induce a sol/gel transition. Lastly, we study the rheological properties of cement/polymer pastes and correlate these results with polymer adsorption experiments.

2. Materials and methods

2.1. Polymer synthesis

The synthesized copolymer is composed of a hydrophilic backbone of polymethacrylic acid and thermoassociative side chains of amino PPO/PEO copolymer. Polymetracrylic acid of molecular weight 150,000 g/mol was purchased from Polymer Source. Amino PPO/PEO copolymer was purchased from Huntsman and has a molecular weight of 2000 g/mol. The formula of grafted polymers is described in Fig. 2.

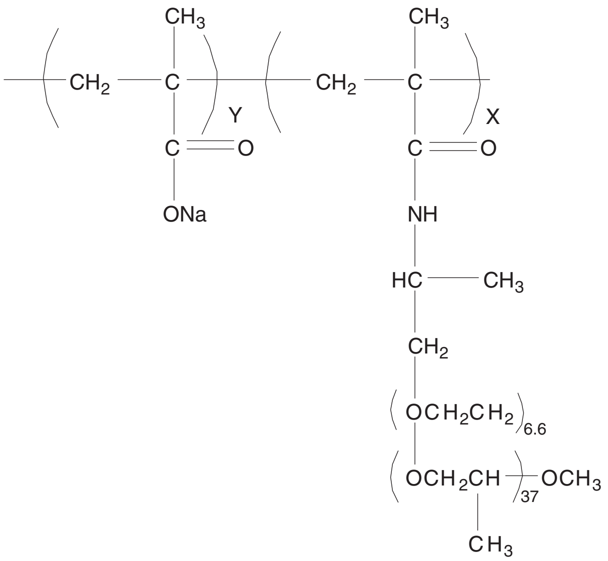

Fig. 2. Formula of one of the synthesized polymer, PMAAPOPGX. *X* is the grafting ratio and the POP/POE ratio is equal to 83%.

The grafting protocol is described below. First, polymethacrylic acid (PMAA) as PPO/PEO copolymer is dissolved in N-Methyl Pyrrolidone. Both are then mixed at 110 °C in the presence of a coupling agent : N,N′-dicyclohexylcarbodiimide. The grafting reaction occurs for 8 h. The copolymer is then precipitated with sodium hydroxide (details in Supplementary Materials). We synthesized polymers with six grafting ratios (cf. Supplementary materials) [34,35]. In the rest of the article, polymer notation will be the following: PMAA-POPGX with X: grafting ratio of thermoassociative polymer in percent.

2.2. Cement

The studied cement is a Portland cement CEM I from Italcementi Group. The clinker concentration is as high as 95 − 100% in this cement type. It is also rich in the CaO phase. The chemical composition of this cement is described in Table 1.

Cement physical characteristics have been also studied. Cement density is evaluated at 3.19 and specific surface measured with Blaine is 3540 cm^2/g. An analysis of cement particle size has also been conducted and is given in Supplementary Materials.

2.3. Rheometry

To obtain rheological measurements, the apparatus used is AR1000 TA Instrument rheometer. The used geometry to study cement pastes was a helicoidal geometry. The cement powder was mixed with water (or with the water/polymer solution) inside the geometry and flow experiments were performed immediately after mixing. The measurements lasted less than 20 min whereas the

Table 1
Chemical composition of used Portland cement CEM1.

Element	Weight percentage
CaO	63.29%
SiO_2	20.23%
Al_2O_3	4.52%
MgO	4.2%
Fe_2O_3	2.23%
Alkali	0.85%
Sulfates	2.9%

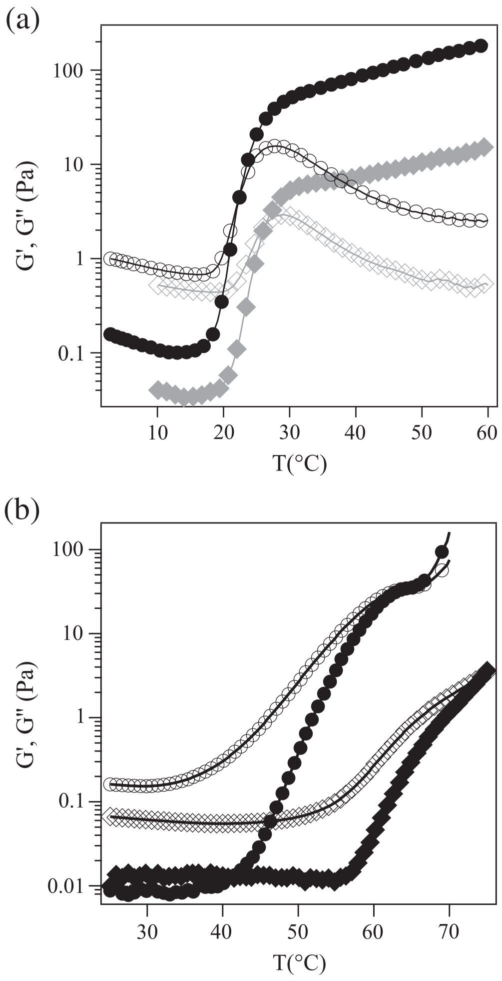

Fig. 3. Elastic modulus G′ (full symbols) and loss modulus G″ (open symbols) of PMAA-POPG10 (a) and PMAA-POPG1.5 copolymers(b) at two concentrations: 2.5% (◆) et 5% (●). Measurements are peformaed at the frequency $\nu = 1s^{-1}$ and amplitude $\sigma = 0.6$ Pa.

setting time was larger than 1 h, at all studied temperatures. This geometry is not a conventional geometry (Fig. 3). However, it is possible to find a Couette equivalent geometry [36,37] by calibration with a newtonian oil of known viscosity. The equivalent Couette geometry has an inner radius equal to 6.8 mm and an outer radius of 10 mm. The length of helix is 20 mm. In the case of polymer solutions, a 40 mm diameter cone-plate geometry was used with an angle of 2°.

2.4. Adsorption measurements

Adsorption measurements have been performed by measuring the remaining quantity of polymer in the supernatant after centrifugation of a water/polymer/cement mixture. We measured the adsorption ratio of our polymers onto the cement suspension and it did not evolve significantly for mixing times comprised between 30 min and 3 h (see Supplementary Materials). We thus chose a mixing time equal to 1 h in the rest of the study. Samples were then centrifugated at 500 rpm for 10 min. The obtained supernatant was observed to be limpid after centrifugation. We measured the non-adsorbed polymer quantity in the supernatant phase with a Total Organic Carbone analyser. The adsorbed polymer quantity was as such deduced from the initial polymer concentration.

3. Rheological behavior of polymer in solution

The sol–gel transition of polymer solutions may easily be followed with mechanical measurements. For a semi-dilute solution, at low temperatures, the system is viscous and its loss modulus is higher than its elastic modulus. When temperature is increased, both moduli increase and the elastic modulus becomes larger than the loss moduli at the transition temperature. We have measured the transition temperature as a function of the copolymer concentration and of the grafting ratio (Eq. 3). At a concentration of 2.5%, the transition occurs at 74.7 °C for a grafting ratio of 1.5% and at 26.4 °C for a grafting ratio of 10%. In both cases, an increase of two decades of elastic modulus is observed at the sol/gel transition. The value of the transition temperature also depends on the polymer concentration. Thus, an increase of the polymer concentration induces a lowering of the transition temperature, and a higher increase of the moduli at the transition. This result had already been observed by Hervé [34] on a polymer composed of an hydrophilic backbone of poly(acrylic acid) (PAA) and grafts of PEO/PPO copolymers.

We also performed viscosity measurements under flow at different temperatures (Fig. 4), under a constant tangential stress $\sigma = 0.6$ Pa. These measurements do not allow such a precise determination of the transition temperature as measurements of the elastic and loss moduli, but we do observe a divergence of the viscosity above the previously determined transition temperatures.

The rheological behavior of copolymer with a hydrophilic backbone and thermoassociative grafts have been studied in detail [38–42]. In [38], it is shown that, at the transition temperature of a PAA polymer grafted with POE/PPO side chains, polyether chains association leads to an increase of the viscosity as large as several decades. Parameters controlling the association temperature are identified as: concentration, grafting ratio, polymer nature and length of grafts. This apparent viscosity increase with polymer concentration has also been observed by Volpert et al. [43]. In order to compare these measurements with the ones performed in the cement suspension, we also studied the transition as a function of sol/gel transition temperature for pH = 13 (Fig. 5(**a**)). We observe a decrease of the transition temperature and an increase of the viscosity of the gel phase when compared to previous measurements, performed at pH = 8. At pH = 8, 70% [44] of the carboxylic groups are dissociated, and further dissociation occurring at pH = 13 will contribute to the decrease of the transition temperature. Moreover, the increase of the ionic strength will also tend to decrease the transition temperature. Indeed, the screening of the electrostatic repulsions lead to a decrease of the transition temperature [45–47,39]. We thus performed a measurement of the variation of the viscosity with temperature at

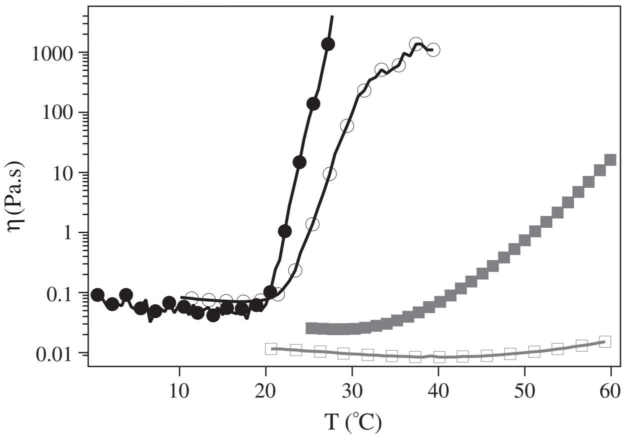

Fig. 4. Viscosity of PMAA-POPG10 (○) and PMMAPOPG1.5 (□) at volume fraction $\phi = 2.5\%$ (open symbols) and $\phi = 5\%$ (full symbols).

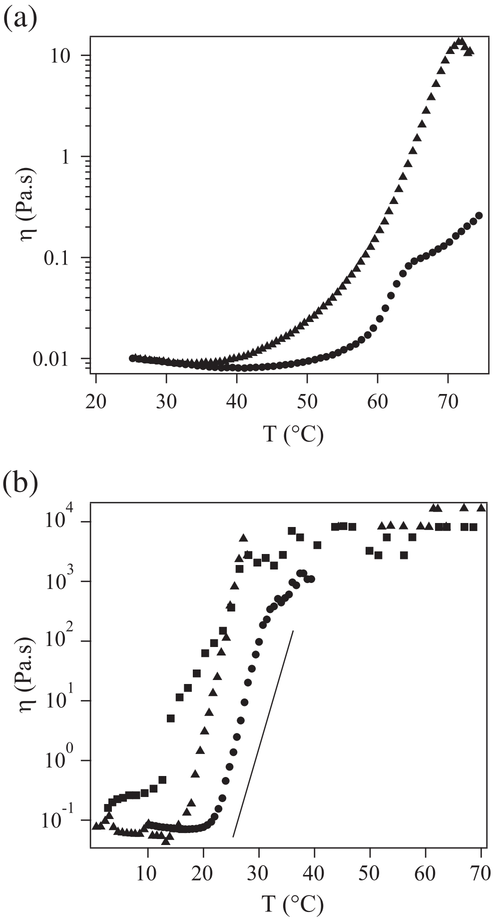

Fig. 5. Evolution of the viscosity as a function of the temperature for PMAA-POPG1.5 at a concentration of 2% (a), and of PMAA-POPG10 at a concentration of 2.5% (b), in water at pH = 8 (●), at pH = 13 (▲), and at pH = 8 with the addition of NaCl, 0.1 M (■).

pH = 8 after the addition of sodium chloride NaCl 0.1 M, corresponding to similar ionic concentration (Fig. 5(b)). An evolution of the viscosity was observed with the temperature similar to that observed at pH = 13 (although the transition occurs at a slightly lower temperature). The measured viscosities in the gel phase are the same in both cases.

As a conclusion, the grafting ratio has the largest effect on polymer thermoassociation, and we chose to keep the polymer concentration equal to 2.5% in the rest of the study.

4. Rheological behavior of cement/polymer pastes

4.1. Flow properties of the cement/polymer paste below the sol/gel transition

Firstly the flow properties of the cement/polymer paste are studied in the low temperature regime. In this sol phase, the polymer is in good solvent conditions and the viscosity of the polymer solution does not depend strongly on the grafting ratio (Fig. 4). A cement/polymer suspension is prepared by adding polymer to a 37.8% cement suspension (water/cement ratio = 0.5). The weight fraction of the polymer, relative to the amount of water is 2.5%. We studied two grafting ratios: 1.9% and 6%. With both copolymers, a decrease of the viscosity and of the yield stress is observed (Fig. 6). The lower ratio grafted polymer results in a stronger decrease of the viscosity at low shear rate of the suspension. Such a behavior cannot be due only to the change of viscosity of the continuous phase at temperatures lower than the gel transition (Fig. 5). It must be attributed to a change in the state of dispersion of the cement particles when the grafting ratio of the added polymer is changed. We thus measured the amount of adsorbed polymers (Fig. 7). The general evolution of the amount of adsorbed polymer as a function of its concentration in the continuous phase is in agreement with previous measurements on similar

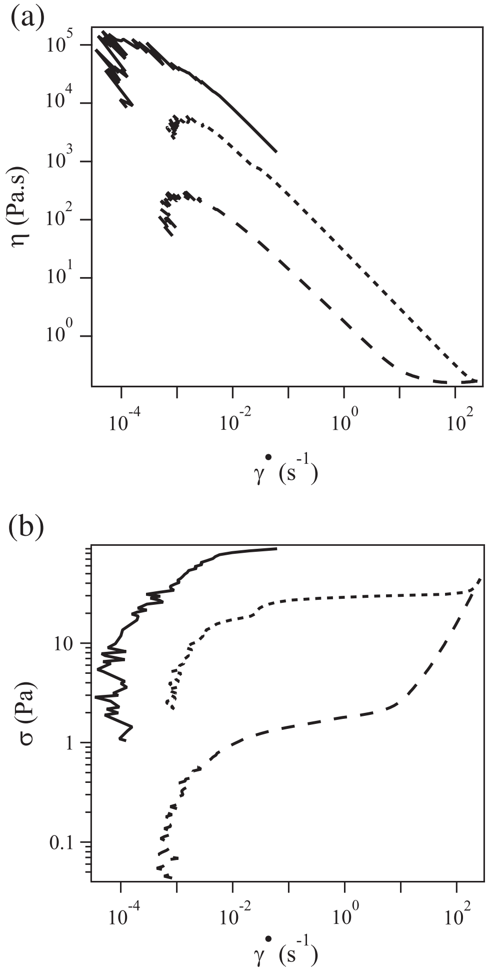

Fig. 6. Viscosity (a) and shear stress (b) of cement (continuous lines) and cement/PMAA-POPG mixtures with two grafting ratios: 6% (short dashed lines) and 1.9% (long dashed lines) at 20 °C as a function of the shear rate. The cement concentration is 37.8% and the polymer concentration is 2.5% in water (0.8%.).

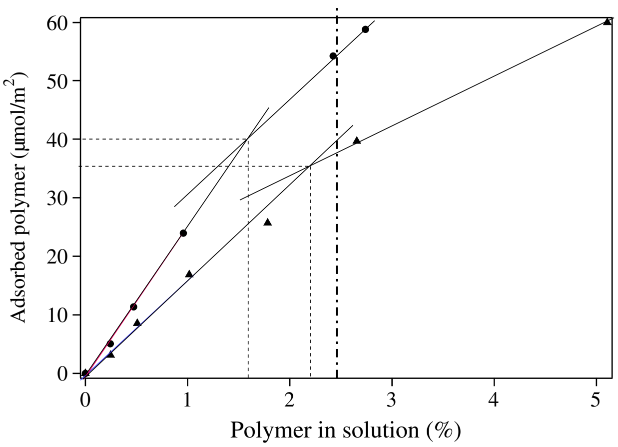

Fig. 7. Amount of adsorbed polymer PMAA-POPG as a function of the initial polymer concentration in solution, for $G = 1.9\%$ (●) and $G = 6\%$ (▲). Lines are guides to the eye.

systems [17,33]. First, a low polymer concentration regime is observed, in which the rate of adsorption is proportional to the amount of polymer. Then, adsorption continues but at gradually reduced rate. This behavior is generally attributed to the formation of a succession of layers. From the slope of the curve in the low concentration regime, one deduces the highest affinity of each polymer to the cement surface [48]:

$$K_a = \frac{[\text{Adsorbed polymer}]}{[\text{polymer in solution}]} \sigma \phi_w \tag{1}$$

where the concentrations of adsorbed polymer and polymer in solution are expressed respectively in $mol.m^{-2}$ and $mol.l^{-1}$, σ is the specific surface ($\sigma = 1.189$ g.cm^{-2} as obtained from BET measurements) and $\phi_w = 2$ the weight ratio of cement in the solution. We obtain an affinity $K_a = 1913$ for PMAA-POP2.5 and and $K_a = 1472$ for PMAA-POP10. The increase of affinity with the decrease of grafting ratio may be explained by the high affinity of PMAA carboxylic groups with calcium ions adsorbed onto the cement particles. The polymer concentration chosen for the rheological study is equal to 2.5%, higher than the concentration required for the formation of the first polymer layer, for both studied grafting ratios.

4.2. Flow measurements at high temperature

Above the gelation temperature, at 60 °C, an increase of the yield stress and viscosity of cement/polymer pastes is observed (Fig. 8). Nevertheless, the rheological properties of the cement pastes depend strongly on the grafting ratio. At high grafting ratio the gel phase due to polymer association leads to a high value of the viscosity in the low shear rate regime, ten times higher than the viscosity of the naked cement suspension, although the particles are better dispersed.The temperature induced viscosity increase for this polymer is equal to 10^3 Pa.s. At low grafting ratios however, the viscosity of the suspension is similar to the one of the naked cement paste. But, reminding that the viscosity of this well dispersed suspension was much lower than the viscosity of the cement suspension at low temperature, and an increase of viscosity when low grafting ratio polymer is added causes it again to be equal to 10^3 Pa.s.

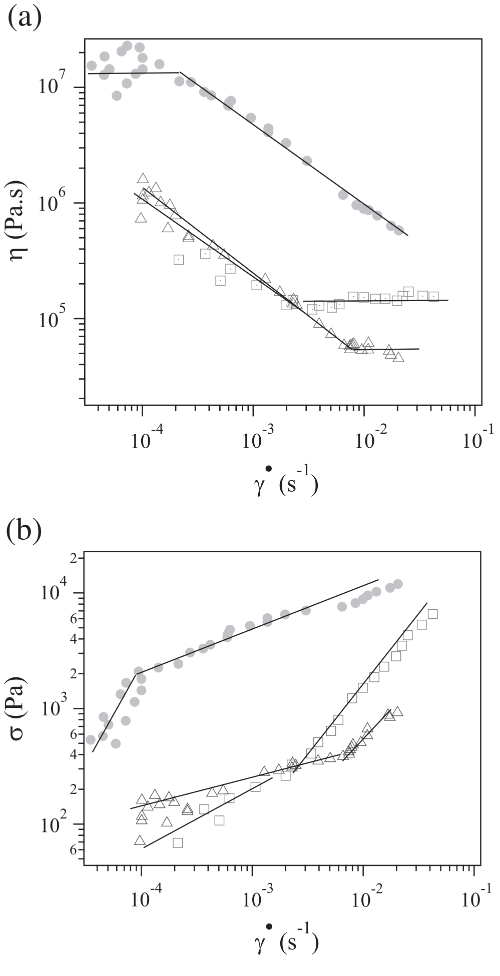

Fig. 8. Viscosity (a) and shear stress (b) at 60 °C as a function of shear rate for cement paste (△) and cement/PMAAPOPG1.9 paste (□) and cement/PMAAPOPG6 paste (●). Lines are guides to the eye.

5. Conclusion

Copolymer made of a polycarboxylate backbone grafted with polyalkyl oxides have already been used as dispersants [17]. Nevertheless, sedimentation of the cement particles results from the reduction of the viscosity of the paste. We have shown that the use of POE/POP grafts allows the use of the temperature as a control parameter to induce microphase separation of the grafted chain. The rheological properties of the paste can thus be controlled. The graft chain composition, the grafting ratio, and the polymer concentration, all need to be finely tuned. This first creation of a thermoresponsive cement/polymer paste opens the route to a fine tuning of cement pastes rheological properties.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at doi:10.1016/j.cemconres.2011.05.005.

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