Effect of Polymer Powder Addition on Well Cement Properties

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Abstract

Polymer powder / cement composites present good mechanical and durability properties, so they would be good candidates for oil well applications, which require high durability under aggressive environment. The rheology of the slurries, that has to be characterized for those applications, is studied here for polymer powder/cement composites : they present a shear-thinning behaviour in permanent shear and a transition from a gel to a liquid behaviour in oscillatory shear. The replacement of cement particles by polymer particles induces a decrease of the viscosity in the liquid state and of the storage modulus in the gel state. Solid state NMR (^{29}Si , ^{27}Al) and DSC (Differential Scanning Calorimetry) were used to understand the influence of the polymer addition on the hydration/ hardening of the slurry. Depending on the temperature and on polymer chemistry, polymer addition may strongly influence the hydration reactions of the materials and their kinetics.

1 Introduction

The selection of an optimal cementitious material is critical to maintain zonal isolation for the lifetime of oil and gas wells not only for primary cementing but also for well abandonment. Cementitious materials used in oil well industry have to permanently isolate the subsurface formations penetrated by the well or to durably fill up the wells when they have to be abandoned. Therefore, they have to present good mechanical and durability properties. Polymer powder/cement composites are known to have higher flexural strength, deformability, adhesion, waterproofness and durability than standard cementitious materials [1] since polymer latex promotes improved adhesion and flexibility to the hardened cement paste. For this reason, polymer-modified cements are used in the construction industry as, for example, repairing materials, anticorrosive coatings or tile adhesives. Besides, adding polymer is a way to lighten slurries without degrading their mechanical and durability properties [2]. All these reasons make polymer powder/cement composites potentially interesting materials for oil well cementing.

Many studies of the mechanical or durability properties of these composite materials can be found in the literature [3-11]. However, only a few authors [12-14] have studied the rheology of the composite pastes. Such studies are necessary for the oil well applications since the slurries are injected into the wells by pumping. So the first matter of this work is to characterize the effect of polymer addition on the rheological properties of

the slurries. Moreover, for the application, the setting time has to be very well-known and controlled. Some authors showed that adding latex or redispersible powder delays the hydration reactions [14-16]. We therefore performed calorimetry on the composite pastes. Indeed this technique allows to follow the hydration kinetics, since the hydration reactions are exothermic. Besides, it has been described that adding polymer modifies the cementitious matrix : there seems to be a diminution of the amount of portlandite [16-17] and ettringite [18] due to the presence of the polymer. So we characterized the C-S-H by ^{29}Si NMR and the aluminate hydrates by [27] Al NMR.

2 Materials and methods

The cement powder used is a class G Portland cement according to the American Petroleum Institute standards. It contains 51% of C3S, 27% of C2S, 14% of C4AF, 2.3 % of C3A and 5.7 % of gypsum. It was characterized by LASER granulometry: the powder particles are very polydispersed in size, with an average number diameter of 0.6 μm and an average volume diameter of 20 μm. The cement slurries are prepared by adding the powder to deionized water in a Waring blender, mixing at a speed of 4000 rpm during 3 min and 35 s at 12000 rpm.

Cement pastes having solid volume fractions ϕ comprised between 0.39 and 0.51 were studied, which corresponds to W/C ratios between 0.35 and 0.5. The corresponding W/C and ϕ are given in table 1.

Table 1: Correspondence between mass water to cement ratios (W/C) and solid volume fractions of cement pastes without polymer (ϕ_{cw})

ϕ_{cw}	0.39	0.44	0.47	0.51
W/C	0.50	0.40	0.36	0.30

The redispersible powder used was obtained from a styrenic acrylic latex, having a glass temperature transition T_g around 60°C. These polymer particles are also very polydisperse in size, with a number average diameter of 0.5 μm and a volume average diameter of 150 μm. Polymer and cement powders were first mixed in a 3-dimensional mixer for 10 min. The powders were then added to deionised water in a blender, with the same mixing protocole as for cement slurries. To characterize the composite suspension compositions, we introduce a volume ϕ_{cw} ratio equivalent to the weight W/C ratio (Eq.1) :

$$\phi_{cw} = \frac{V_c}{V_c + V_w} \qquad (1)$$

with V_w and V_c the respective volumes of water and cement ; for the suspensions studied, ϕ_{cw} ranged from 0.39 to 0.47. For a given value of ϕ_{cw}, different amounts of polymer were added ; when it was possible, we added a volume of polymer (V_p) up to a fraction of $V_p/V_c = 0.79$ (in weight,

it corresponds to a ratio of P/C = 0.25). The corresponding values of the volume ratio V_p/V_c and the mass ratio P/C are given in table 2.

Table 2 : Correspondence between mass polymer to cement ratios P/C and volume polymer to cement ratios V_P/V_C

V_P/V_C	0.16	0.32	0.47	0.63	0.79
P/C	0.05	0.10	0.15	0.20	0.25

The composite paste composition is fully determined by the two ratios (ϕ_{cw}; V_p/V_c), which will be used in this paper. These volume ratios are more relevant parameters than their equivalent weight ratios (W/C ; P/C) for the observed properties of the pastes. Rheological measurements were made using a stress controlled Haake RS150 rheometer, at 20°C. To avoid slipping at the walls, a four blade vane geometry and a grooved stator were used [19]. The suspensions were first pre-sheared at 1000 s^{-1} for 3 min and then let at rest until no more settling was observed, which lasted 30 min. The minimum settling height of the tested suspensions, which was obtained for cement suspensions having a solid volume fraction of 0.39 was of 0.94 of the total height, and we neglected the modifications of the volume fraction due to settling. After these two first stages, oscillatory shear and steady shear stress steps experiments were performed. In an oscillatory test, a sinusoidal stress of amplitude τ^0 is applied at a frequency ω. The resulting sinusoidal strain of amplitude γ^0 can be separated into a response in phase with the stress related to the storage or elastic modulus G' and a response out of phase with the stress related to the loss or viscous modulus G". Then we can define a complex modulus G* such that (Eq.2):

$$\tau^0 = |G^*|\,\gamma^0 \qquad (2)$$

where |G*| is magnitude of the complex modulus. G* is a complex number with G' as its real and G" as its imaginary parts, respectively (Eq.3 and 4)

$$G^* = G' + i\,G'' \qquad (3)$$

and

$$|G^*| = (G'^2 + G''^2)^{1/2} \qquad (4)$$

We can also defined the magnitude (or modulus) of the complex viscosity (Eq.5) :

$$|\eta^*| = (\eta'^2 + \eta''^2)^{1/2} = [(G''/\omega)^2 + (G'/\omega)^2]^{1/2} = |G^*|/\omega \quad (5)$$

Where η' is the dynamic viscosity and η'' the elastic part of the complex viscosity η^*. In steady shear experiments, a stress step τ_0 is applied and the strain or the rate of straining or shear rate $\dot{\gamma}$ is recorded versus time. Sufficient time is allowed to achieve a steady shear rate $\dot{\gamma}_\infty$. Thus the steady-state shear viscosity η is defined as (Eq.6):

$$\eta = \tau/\dot{\gamma}_\infty \qquad (6)$$

Calorimetry measurements were made using a Setaram C80 calorimeter. After mixing, cement pastes were poured into pyrex vessels that were introduced in the calorimeter vessels. Isothermal steps were applied, with a pressure of 90 bars of nitrogen. The heat flow was measured during 48h and extrapolated to 5 days of hydration. After that period of hydration, the heat flow becomes too low to be measured with this method.

The observation of fractures and polished sections of set cement pastes was performed by SEM. We also observed the pastes before setting by cryo-SEM [20].

For ^{29}Si and ^{27}Al solid state NMR measurements, a Bruker ASX500 spectrometer (11.7 T) was used. Single-pulse experiments were carried out, with $\pi/2$ pulses for ^{29}Si spectra and $\pi/12$ pulses for ^{27}Al spectra. Hardened cement pastes were ground and the powder were placed into ZrO_2 rotors of 7 mm for ^{29}Si spectra and 4mm for ^{27}Al spectra. The spinning rate of the 7 mm rotors was 5 kHz and the one of the 4 mm rotors was 14 kHz.

3 Results and discussion

3.1 Rheology

Figure 1 shows the variation of the elastic modulus G' and the viscous modulus G'' with the amplitude τ^0 of the applied shear stress, at a given frequency of 1 Hz. Figure 1a was obtained with a polymer free cement paste of a solid volume fraction of $\phi=\phi_{cw}=0.44$ and figure 1b was obtained with a polymer powder/cement composite having a composition of ($\phi_{cw}=0.39$; $V_p/V_c = 0.32$). In both cases, the two curves G'(τ^0) and G''(τ^0) are characterized by a sharp fall-off from a high-modulus plateau at low shear stress to a relatively gradual levelling-off towards a low-modulus asymptote at high shear-stress. The sharp drop of typically four to five decades, corresponds to the transition between a solid-like behaviour at low shear stress and a liquid-like behaviour at high shear stress. In the gel state, the suspensions can be characterized by the value of the elastic modulus G'$_{gel}$ which is proportional to the energy needed to break the gel. In the liquid state, they can be characterized by the asymptotic value of the complex viscosity modulus η^*_l, which does not depend on the frequency applied [21].
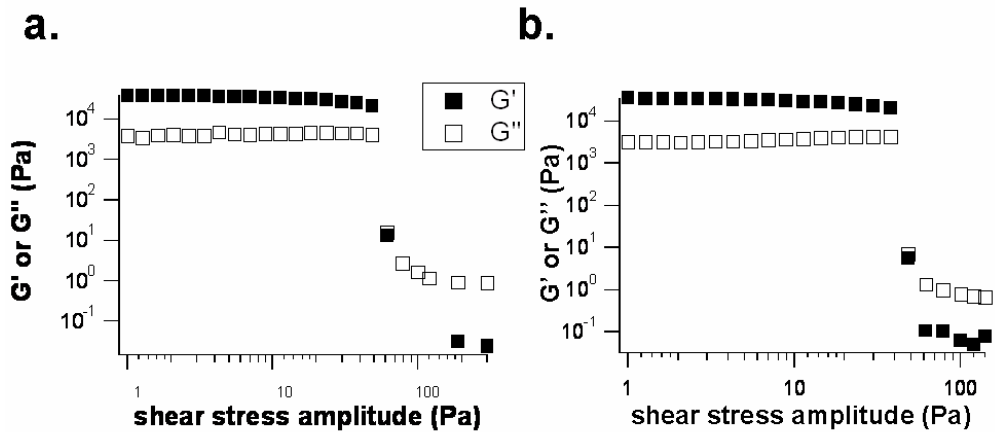
Figure 1: Elastic modulus G' and viscous modulus G'' as functions of the shear stress amplitude. a : polymer free cement suspension, having a solid volume fraction of 0.44 ; b : polymer/cement composite suspension of composition (ϕ_{cw}=0.39; V_p/V_c=0.32)

Figure 2 represents the steady-state shear viscosity measured, as a function of shear rate. Figure 2a was obtained with a polymer free cement suspension, of $\phi=\phi_{cw}=0.44$ and figure 2b was obtained with a polymer powder/cement composite of ($\phi_{cw}=0.39; V_p/V_c = 0.32$). Like in oscillatory shear, the rheological behaviour observed in permanent shear is qualitatively the same for polymer powder/cement composites as for polymer free cement pastes: they present a shear-thinning behaviour at shear rates smaller than about 1000 s^{-1}, followed by a shear-thickening behaviour at high shear rates. This behaviour can be explained by the formation of particle aggregates in the slurry, the size of which depending on the shear rate applied. At about 1000 s^{-1}, the viscosity reaches its minimum value η_{min} , which is very close to the modulus of the complex viscosity characteristic of the liquid state $|\eta^*|_l$. The apparent static yield stress τ_s was determined by applying decreasing shear stress steps.
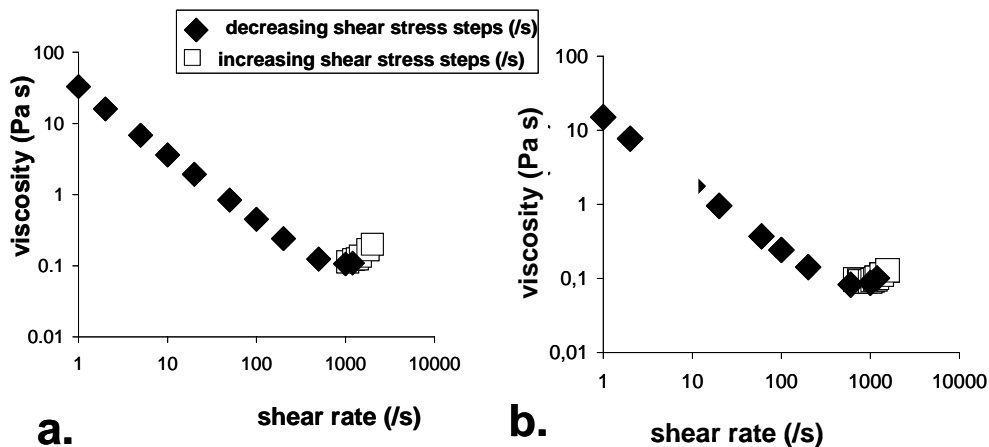

Figure 2: Shear viscosity as a function of shear rate. a : polymer free cement suspension, having a solid volume fraction of 0.44 ; b : polymer/cement composite suspension of composition (ϕ_{cw}=0.39; V_p/V_c=0.32)

Even if it does not modify the rheological behaviour, adding polymer modifies the values of the characteristic parameters. For example, the storage modulus in the gel state, which characterizes the cohesion energy of the gel, is represented as a function of the solid volume fraction in figure 3a, for different cement suspensions, with or without some polymer powder. When some polymer is added to a cement suspension, the ϕ_{cw} parameter being constant, the modulus increases, because of the increase of the solid volume fraction. But at a given solid volume fraction, replacing cement particles by polymer particles induces a decrease of the modulus, because the interactions between polymer and cement particles are weaker than those between cement particles. Figure 3b shows the variation of the apparent yield stress τ_s, measured in permanent shear, with solid volume fraction. This parameter being also related to the cohesion of the gel, it varies in a similar way as the storage modulus in the gel state.

Figure 4 shows the variation of the complex viscosity modulus $|\eta^*|_l$ (Fig. 4a) and of the minimum shear viscosity η_{min} (Fig 4b) as functions of the solid volume fraction. These two parameters have very close values. When some polymer is added to a cement suspension, the ϕ_{cw} parameter being constant, the viscosities $|\eta^*|_l$ or η_{min} increase, because of the increase of the solid volume fraction. But at a given solid volume fraction, replacing cement particles by polymer particles induces a decrease of $|\eta^*|_l$ or η_{min}. It can be explained by the fact that polymer particles are less hydrophilic than cement particles, so they entrap less water within the aggregates. Then replacing cement particles by polymer ones leads to a higher quantity of water in the bulk, which facilitates the flow.
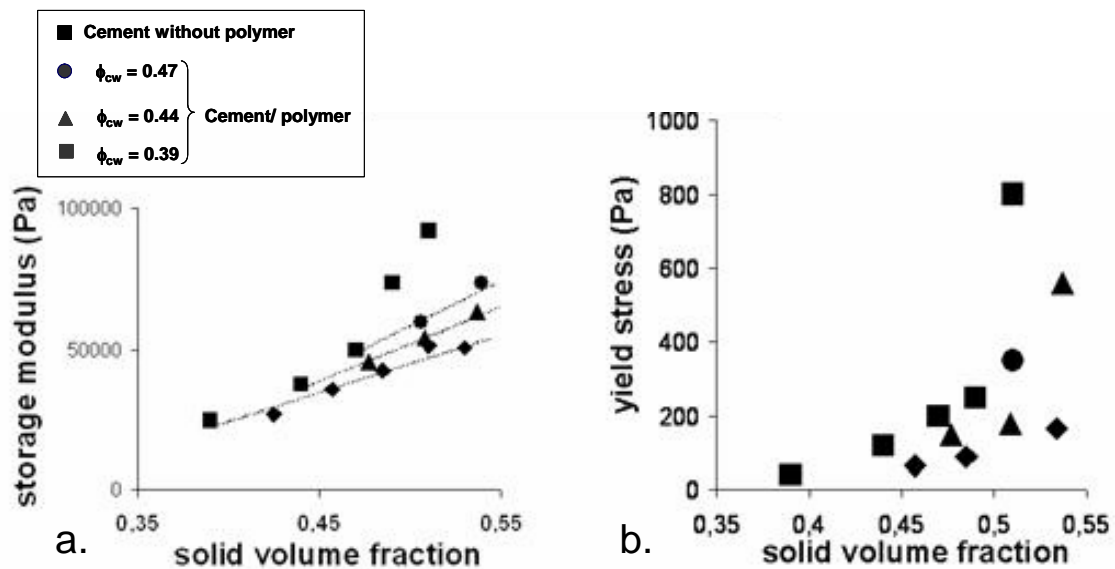

Figure 3: for cement suspensions with or without polymer, storage modulus in the gel state measured in oscillatory shear (a) or yield stress measured in permanent shear (b) as a function of solid volume fraction.
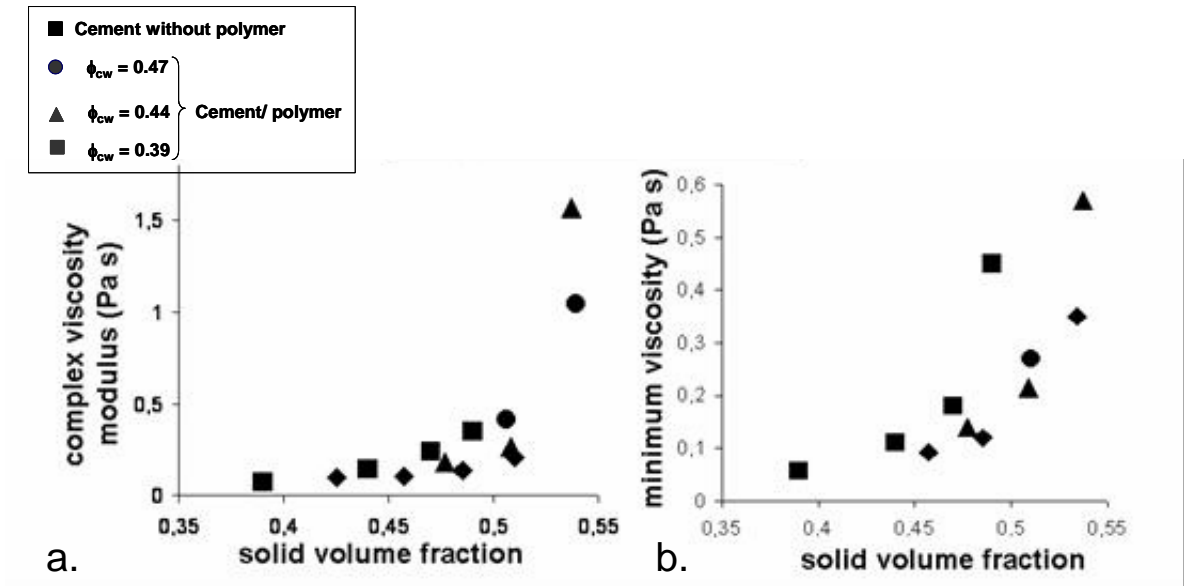
Figure 4: for cement suspensions with or without polymer, complex viscosity modulus in the liquid state measured in oscillatory shear (a) or minimum viscosity measured in permanent shear (b) as a function of solid volume fraction.

3.2 Calorimetry

When cement is added to water, immediate chemical reactions occur. After a few minutes, these reactions decrease and remain very low during the so-called "dormant period". The duration of that period, the induction time t_{ind}, was measured by calorimetry, for the different cement pastes. To analyse the effect of the polymer, we introduce δt_{ind}, defined by (Eq 7):

$$\delta t_{ind} = \frac{t_{ind} - t_{ind}^0}{t_{ind}^0} \qquad (7)$$

with t_{ind} the induction time of the composite paste and t_{ind}^0 the induction time of the cement paste without polymer, at the same temperature and pressure. It can be noticed that t_{ind}^0 does not depend on the W/C ratio of the cement paste. Figure 5 represents the variations of δt_{ind} with the polymer volume fraction, for the different temperatures studied, a nitrogen pressure of 90 bars being applied to the pastes. The effect of polymer is very different below and above its glass transition temperature T_g, which is about 60°C. Below its T_g, adding polymer powder decreases the induction time of the cement paste, proportionally to the polymer volume fraction. We can attribute this acceleration to the increase of alkali ion concentration induced by the polymer addition and its ability to fix calcium ions. Indeed, these phenomena increase the dissolution ability of the anhydrous particles of cement, which explain the acceleration of the hydration reactions observed when some polymer is added. The ability of the polymer to fix calcium ions is due to both the presence of adsorbed

surfactant on polymer powder particles and of acrylate groups formed by saponification of ester acrylate at high pH.
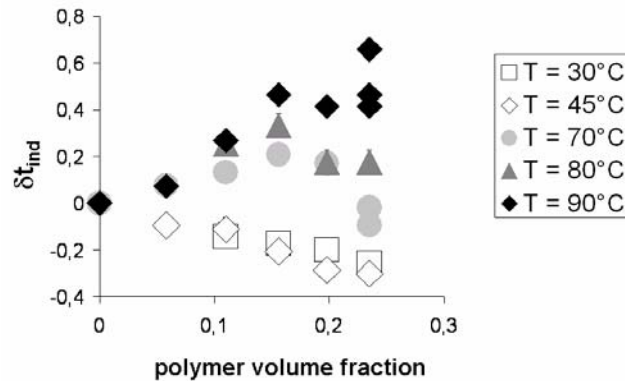

Figure 5: Variations of δt_{ind} with the polymer volume fraction, for composite slurries at different temperatures, under a nitrogen pressure of 90 bars.

At temperatures higher than the T_g of the polymer, adding some polymer powder increases the induction time. This retarding effect of the polymer, described in the literature [14-16], can be explained by the adsorption of polymer particles on cement particles. It is enhanced at temperatures above the T_g because the polymer is softened. The delay increases with the temperature due to the increase of the polymer softening. This phenomenon is in competition with the increase of the anhydrous particle dissolution, which explains the non-linear evolution of δt_{ind} with the polymer volume fraction: at the smallest polymer volume fraction, the delay phenomenon dominates, but for polymer volume fractions above 0.15, it is counterbalanced by the acceleration effect.

With calorimetry experiments, we also measured the released energy during 5 days of hydration: indeed the hydration reactions are exothermic, and measuring this energy is a way of following their evolution. Figure 6 represents the thermal energy as a function of the solid volume fraction, for cement pastes with or without some polymer powder. The released thermal energy increases with temperature, which is due to the fact that hydration reactions are activated by temperature. This increase is enhanced by the fact that after 5 days, the hydration reactions are far from being finished, especially at the lowest temperatures: even if after 5 days, the heat flows become too low to be measured by calorimetry, hydration reactions continue, as can be seen with other techniques, such as solid state NMR. We shall go back to that point later. Figure 6 also shows that the energy decreases with solid volume fraction. It can be explained by the fact that adding some solid particles leads to decrease the amount of water available for the dissolution of the reactants and the nucleation/precipitation of hydration products [22]. It can be observed that, for all the temperatures studied, adding polymer or cement particles seems equivalent: the decrease of capillary space seems to dominate the other effects linked to the addition of polymer.
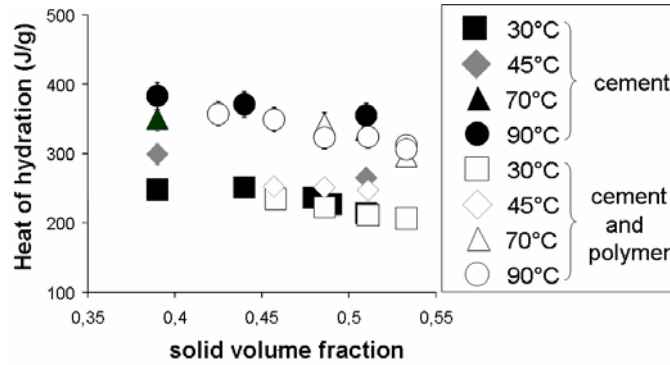
Figure 6: Heat after 5 days of hydration as a function of solid volume fraction, for cement pastes with or without some polymer powder, at different temperatures, with a nitrogen pressure of 90 bars

3.3 Solid state NMR

Figure 7 shows the [29]Si spectra obtained with cement pastes hydrated in sealed conditions during 5 days at 30°C (Fig. 7a) and during 1 year at room temperature (Fig 7b). In both cases, one of the paste contains no polymer, it is a cement paste with a cement volume fraction of 0.39, and the other contains the maximum possible amount of polymer powder, and has a composition of (ϕ_{cw} = 0.39; V_p/V_c =0.79). Three main peaks can be seen on these spectra: one, at -71 ppm, corresponding to the Q^0 species, which are the isolated silicate groups of the anhydrous calcium silicates. The presence of this peak shows that even after one year of hydration, some anhydrous particles remain in the cement paste. The other peaks, at -79 and -85 ppm, correspond to the Q^1 and Q^2 species that are found respectively to the end and at the middle of the silicate chains present in the C-S-H hydrates. The spectra obtained for pastes with or without polymer have been normalized with respect to the Q^0 peak so the amount of C-S-H can be directly compared. After one year of hydration (see Fig. 7b), this amount is smaller when some polymer is added to the paste. This result, in agreement with the results obtained by calorimetry, may be explained by the decrease of capillary space available. The spectra of cement pastes with or without some polymer powder hydrated during one month at 90°C, with a nitrogen pressure of 90 bars, lead to the same conclusion. However, figure 7a shows that after 5 days of hydration the spectra obtained for cement pastes with or without polymer are very similar: so the amount of C-S-H formed remains almost the same when the polymer is added. Nevertheless the calorimetry experiments show that there is a decrease of the released energy when the polymer is added (see Fig. 6) : this result can be explained by the decrease of the amount of portlandite, which was observed by Thermo Gravimetric Analysis. So after 5 days of hydration, the decrease of the hydration degree induced by polymer addition is due to the decrease of the amount of portlandite, not of C-S-H.
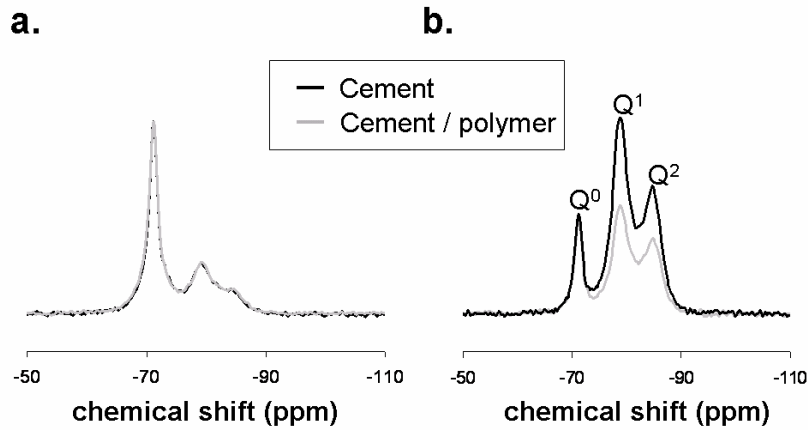
Figure 7: ^{29}Si spectra of a cement paste without polymer (ϕ_{cw} = 0.39; V_p/V_c=0) and a cement paste with or without polymer (ϕ_{cw} = 0.39; V_p/V_c =0.79) hydrated 5 days at 30°C (a) or 1 year at room temperature (b).

Figure 8 shows the ^{27}Al spectra obtained with a cement paste without polymer powder having a cement volume fraction of 0.39, and a composite paste of (ϕ_{cw} = 0.39; V_p/V_c =0.79) composition, hydrated during one year at room temperature. The two spectra are very similar which means that after one year of hydration, the polymer has little effect on the different aluminate hydrates after one year. On the ^{27}Al spectra, the anhydrous aluminate phases cannot be observed and the different peaks observed are listed in table 3 [23,24]. The same conclusions were drawn with spectra of cement pastes hydrated one month at 90°C.
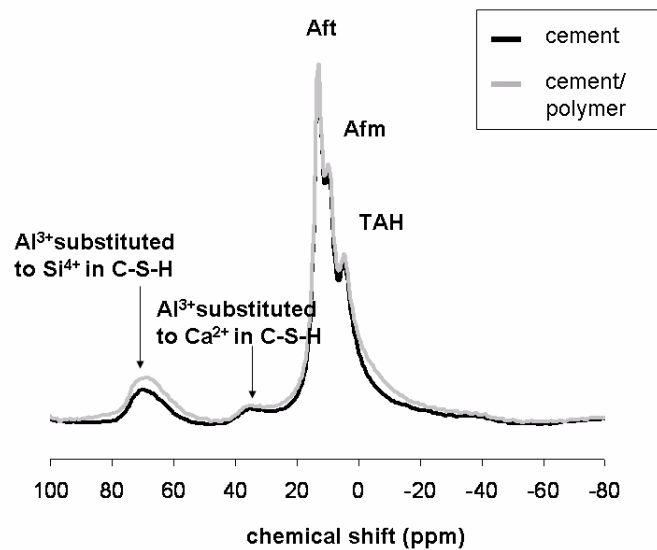

Figure 8 : ^{29}Si spectra of a cement paste without polymer (ϕ_{cw} = 0.39; V_p/V_c=0) and a cement paste with or without polymer (ϕ_{cw} = 0.39; V_p/V_c =0.79) hydrated 1 year at room temperature

Table 3: Phases corresponding to the NMR peaks

Chemical shift (ppm)	phase
70 ppm	Al^{3+} substituted to Si^{4+} in C-S-H
35 ppm	Al^{3+} substituted to Ca^{2+} in C-S-H
13 ppm	Ettringite Aft
10 ppm	Monosulfoaluminate Afm
4 ppm	Third aluminate hydrates: amorphous phase [25]

4 Conclusion

Adding polymer does not qualitatively modify the rheological behaviour of a cement slurry. However, at a given ϕ_{cw} (or W/C), it increases the storage modulus in the gel state and the viscosity in the liquid state, because of the increase of the total solid volume fraction. Replacing polymer particles by cement ones leads to a decrease of the storage modulus, due to the weaker interactions between cement and polymer particles (than those between cement particles), and to a decrease of the viscosity, because polymer particles are less hydrophilic than cement particles.

At temperatures below the glass transition temperature of the polymer T_g, adding polymer decreases the induction time, maybe because of the enhancement of anhydrous dissolution. Above the T_g, the adsorption of polymer on cement particles leads to an increase of the induction time. For field application, it means that polymer structure - properties relationships (composition and Tg) can be adapted to the required characteristics of the cement slurry for well depth and configuration (rheological behaviour and setting time). This will be published later.

At any temperature, the hydration degree of cement is lower when some polymer is added, which was observed by calorimetry and ^{29}Si NMR. ^{27}Al NMR shows that at long periods of hydration, the aluminate hydrates formed are the same with or without polymer.

5 Acknowledgements

6 References

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