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Adsorption of polyelectrolytes and rheology of suspensions of calcium carbonate

R. MORINI^a, J. PERSELLO^a, P. BOUSTINGORRY^b, G. BOSSIS^a

a. Laboratoire de Physique de la matière condensée (LPMC), Université de Nice-Sophia Antipolis
Parc Valrose, 06108 NICE

b. Chryso, 7 rue de l'Europe - Z.I., 45300 SERMAISES DU LOIRET LOS ANGELES

Abstract :

This study focuses on the superplasticizers which allow to increase the concentration of the particles (cement) of a concrete while maintaining good handling. The superplasticizers analyzed here are polyelectrolytic: polymethacrylates grafted with side polyethyleneoxide chains (PEO) of different lengths. We present a study of these molecules in solution, including the influence of OH⁻ ions on the PEO chains. We analyse the effect of the superplasticizers on the rheology of suspensions of CaCO₃ particles of micron and nanometer size ranges..

keywords : Suspension rheology, plasticizer, adsorption isotherm

1 Introduction

The use of fluidizer molecules is a key factor to lower the viscosity of concentrated suspensions of mineral particles like cement or concrete and consequently to improve their workability, principally in construction industry. In this paper we shall focus on the understanding of the effect of some polyelectrolytes on the rheology of suspensions of calcium carbonate. This mineral was chosen as a model of more complex materials like cement. Polyelectrolytes are polymer which become ionized in the presence of water and adsorb on the surface of mineral particles by means of electrostatic interactions between opposite charges. This polymer coating reduces the attractive forces between the particles and consequently their aggregation, which results in a strong reduction of the viscosity of the suspension. In this study we shall correlate the effect of these molecules on the rheology with the chain length, their affinity with water and also with the morphology of the calcium carbonate particles.

2 Experiments

2.1 Materials

We have used two kinds of calcium carbonate particles having quite different sizes and morphology..The first one was synthesized in our laboratory from the reaction between carbon dioxide and very pure lime CaO; their shape is more cubic than spherical and they are quite monodisperse with an average diameter of 100nm (FIG.1a). The second one was obtained from milling of a natural mineral (supplier Omnya, commercial name BL200) the particles are polydisperse with irregular shape(FIG.1b) and an average diameter of 5µm measured by light scattering (Mastersizer Malvern). The density of the particles is 2525 kg/m³. and the measurement of their specific surface by BET gave respectively 0,88 m²/g for the BL200 and 21,2 m²/g. for the synthesis. The superplasticizer, currently called PCP, is a comb like polymer(FIG. 2). based on a polymethacrylate backbone and side chains made of polyethylene oxide(PEO). The molecules we have studied have a molar mass between 15000 and 35000 g/mol. A segment of the PCP molecule is defined by four carboxylic and one PEO side chain groups. This PEO side chains contains p units ;with p = 17, 25, 45 and 114 and the respective molecules will be called PCP17, PCP25 etc...

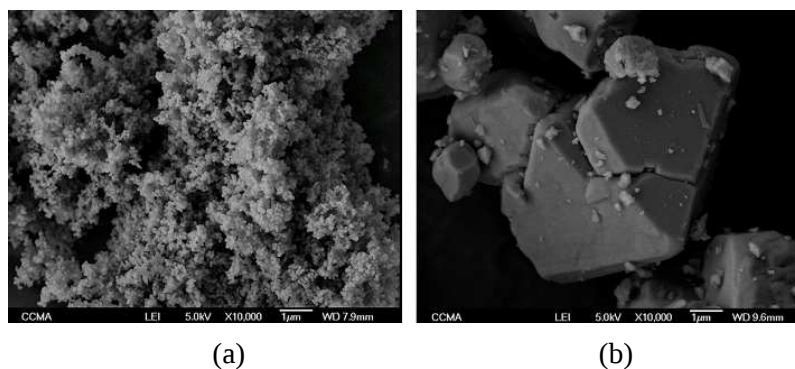


FIG. 1 – MEB picture : (a) Laboratory synthesis: agregates of small monodisperse particles: $d \sim 100$ nm, (b) BL200 :strong polydispersity $\langle d \rangle = 5 \mu\text{m}$

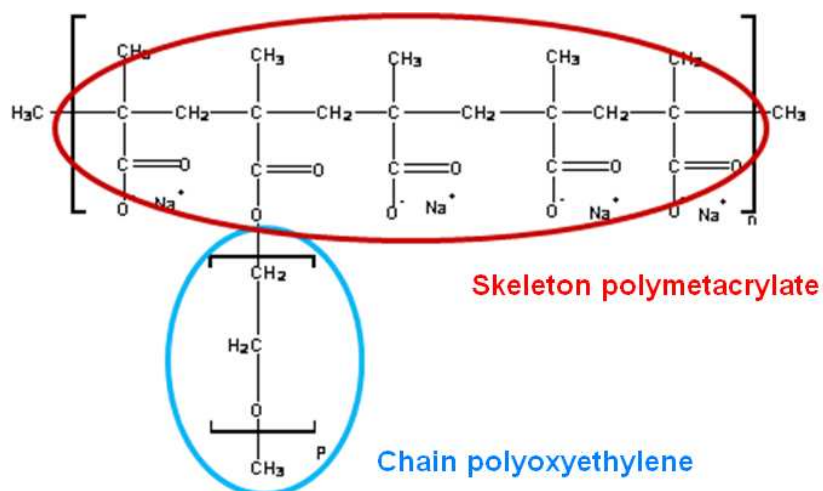


FIG. 2 : Schematic representation of PCP

.We shall mainly study the PCP45 with a grafted PEO chain of molar mass 2000 g/mol. and ten of these chains, the total molar mass being 25000g/mol. The two parts of the molecule have a different role. The backbone part will adsorb on the surface of the particle thanks to the electrostatic attraction between the groups COO^- of the molecule and the calcium on the surface of the particles; the side chain will extend in water and it is the entropy of these side chains which generate a repulsive force between two particles approaching each other at a distance smaller than two times their gyration radius [6].

2.2 Adsorption isotherm of PCP on calcium carbonate

The energy of adsorption of the polymer as well as its surface fraction will determine its efficiency as a fluidizer[2, 3, 4]. The adsorption isotherms that we shall present are obtained from the measurement of the total organic carbon (TOC) remaining in the supernatant after the adsorption on the particles. The initial solution of polymer is mixed with the particles under agitation on a vibrating table during 12h before analysis. The part of the molecules which is adsorbed on the surface is given in number of segments per nm² and the one remaining in the supernatant in gram per liter of solution. It is shown in FIG.(3) for the adsorption of PCP45 on the two types of particles presented in FIG. 1. These isotherms were realized at pH= 9,3 (imposed by the calcium carbonate). It appears that the adsorption plateau are very close to each other and equal to $0,13 \pm 0,01$ segment per nm², although the morphology of the two types of particles was very different. Taking into account the gyration radius of the PCP45 measured by light scattering (Zetasizer from Malvern) this density corresponds to a surface fraction of 0.95, so to a dense monolayer of the polymer on the surface of the particles. It is also worth noting that, for a same surface fraction of polymer its concentration in the solution is much higher for the nanoparticles, meaning a smaller adsorption energy for the nanoparticles than for the microparticles.

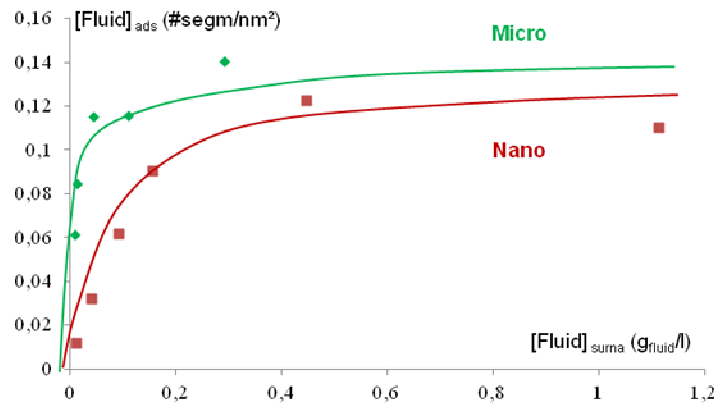


FIG. 3 : Adsorption isotherm of PCP45 on micrometer (upper curve) and nanometer (lower curve) particles

2.3 . Rheology of suspensions of calcium carbonate adjuvanted by PCP

In this part we aim to study the parameters which can change the efficiency of the superplasticizer with respect to the decrease of the effective viscosity of the suspension. We shall mainly use the micrometric particles because with these particles it is easy to reach high volume fractions with $\phi_v = V_{CaCO_3}/V_{tot}$ equal or larger than 0.6. This is not the case with nanoparticles where volume fractions higher than 0.42 can't be reached even in the presence of PCP molecules; the comparison micro-nano will still remain meaningful at this lower volume fraction.

2.3.1 Rheology versus adsorption

In FIG. 4 is presented ,on the left, the rheological curves for different concentrations of PCP45 in weight of polymer relatively to the weight of particles and on the right the adsorption isotherm. Since, on the abscissa axis, it is the mass of polymer remaining in the supernatant which is reported and not the mass ratio of polymer with respect to the particles, this last quantity is reported on the isotherm curve in order to see the correspondence with the different rheological curves.

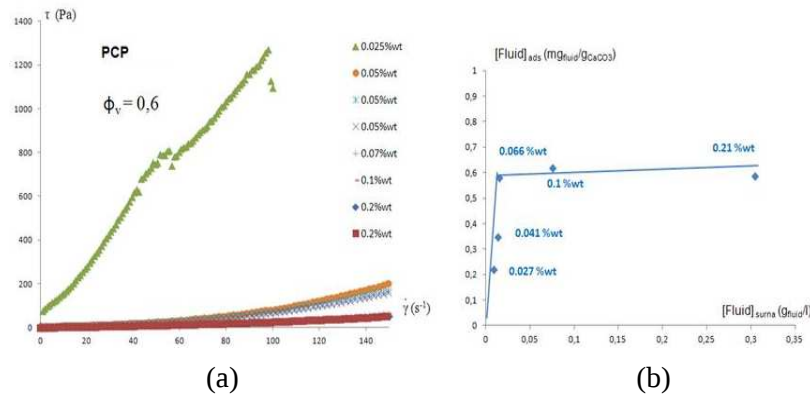


FIG. 4 : Correlation between adsorption isotherm of polymer on CaCO₃ (right) and stress versus shear rate curves (left) on a suspension of microparticles ;

We first observe a very strong decrease of the shear stress between $c = 0,025\%wt$ ($\eta_{0,025\%wt} \sim 12 \text{ Pa.s}$) and $c = 0,05\%wt$ ($\eta_{0,05\%wt} \sim 0,3 \text{ Pa.s}$) which well corresponds to a strong increase of the adsorption with a surface fraction of polymer increasing from 35% to 71%. It indicates that it is the steric repulsion between PEO chains which play the major role since electrostatic repulsion would vary in a more progressive way with the surface fraction of polymer. Actually this preponderance of entropic repulsion for polycarboxylate fluidizers was also found in previous work [2]. On the other hand between 0,1% and 0,2% of polymer there is no improvement of the rheology which is well correlated with the fact that the surface of the particles is already totally covered by the polymer (FIG.4b). Now, since the repulsive force between particles come from steric interactions between the PEO chains ,we expect that increasing the length of these chains will increase the

fluidizing effect.

2.3.2 Influence of the length of the PEO chain on the rheology

Four molecules with different lengths of the PEO chain were used, namely: 17, 25, 45 and 114 groups per chain. For each molecule we used a weight fraction relatively to the mass of CaCO_3 which is slightly above the one corresponding to the adsorption plateau ($c > 0,1$ %wt).

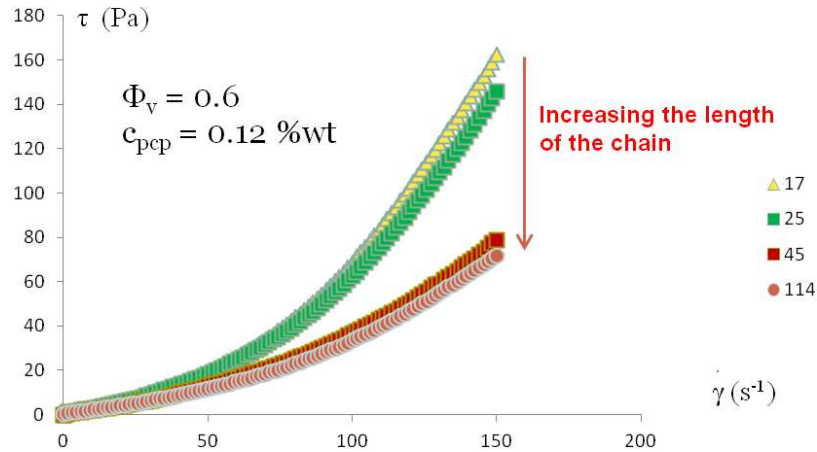


FIG. 5 : Influence of the length of the PEO chain on the rheology

The stress versus shear rate curves for these four molecules are plotted in FIG. 5. It is clear that increasing the length of the side chains decrease the viscosity, but the change appears mainly between 25 and 45 groups and even a large increase from 45 to 114 groups has a little effect on the rheology. These results demonstrate that the length of the chain has an important effect but only in a restricted range and that above 45 groups the improvement is very low. This observation can be explained with the help of the scaling law for the gyration radius: $R_g \sim bN^v$. The exponent v can vary from $3/5$ for a good solvent to $1/2$ for a θ solvent, and to lower values for a poor solvent. If we compare the gyration radius for the PCP114 in a good solvent to the one in θ solvent it drops from 8.75 to 5.45nm that is to say close to the one of the PCP45 which is 5.0nm. It is likely that the increase of the number of oxyethylene groups contributes to decrease the affinity of the chain for the solvent hence, the saturation effect with the length of the chain. This affinity for the solvent can also be modified by the ions which are present in the solvent like OH^- and CO_3^{2-} [1]. In the following section we shall show, with the help of turbidity measurements, that actually, increasing the pH leads to a precipitation of the polyelectrolyte.

2.3.3 Influence of the affinity polymer / solvent on the rheology

The collapse of the PEO chain leads to a phase separation and to the formation of large aggregates of molecules which scatter the light and strongly increase the turbidity. We have measured the turbidity of a solution of PCP45 in pure water versus the pH. The turbidity is obtained from a phototrode (Malvern), which measures the intensity, I , of the transmitted light, through the well known relation:

$$T = \frac{1}{c} \ln\left(\frac{I_0}{I}\right)$$

where c is the weight concentration of the polymer and I_0 the transmitted intensity of pure water. The pH was changed with a solution of NaOH 1M; the results are shown in Fig.6 for two weight fractions of PCP45. We have plotted the turbidity versus the ratio $[\text{OH}^-] / [\text{OE}]$ and we see that, for the two concentrations of polymer, the turbidity presents an abrupt increase for a ratio $[\text{OH}^-] / [\text{OE}] \sim 0,06$. It is noticeable that this polymer is quite sensitive to the pH and in suspensions of calcium carbonate, where a pH of 9 is imposed by the dissolution of calcium carbonate in the presence of CO_2 , we are close to this transition. Furthermore the ions CO_3^{2-} in the suspension also contribute to the precipitation of the PEO chains[1], so it is likely that the increase of the length of the chains, which is known to decrease its affinity with the solvent, will be enough to provoke its precipitation.

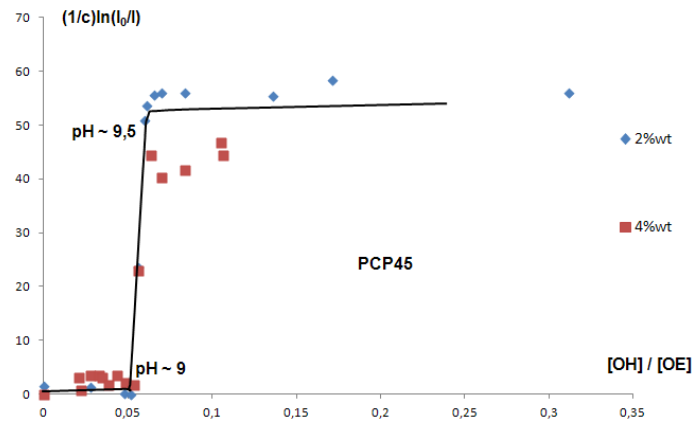


FIG. 6: Turbidity of a solution of PCP45 at 2% and 4%wt versus the ratio $[OH]/[OE]$

As the affinity of the PEO chain for the water depends strongly on the pH, it is interesting to see how it will interfere with the fluidizing effect of these molecules. In Fig.7 are presented the stress versus shear rate curves for different pH between 8 and 12. for a volume fraction $\Phi_v=0.55$ of calcium carbonate and a concentration of 0.3% of PCP45. There is almost no influence of the pH at shear rates below 30 s^{-1} but a clear increase of viscosity at higher shear rates with a transition taking place between $\text{pH}=8$ and $\text{pH}=10$ which is quite well correlated with the turbidity curve. So, here too, we have a correlation between the affinity for the solvent and the rheology, with a decrease of the efficiency of the fluidizer when its affinity for the solvent decreases. Nevertheless at low shear rates, where the hydrodynamic forces, proportional to $\eta\dot{\gamma}d^2$, are still small, the extension of the polymer layer in the solvent remains high enough to prevent the aggregation.

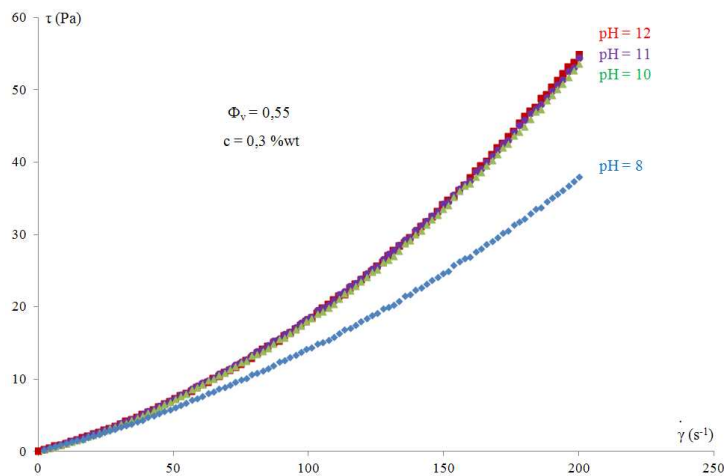


FIG. 7: Stress versus shear rate for different pH in presence of PCP45 ($\Phi_v = 0.55$ et $c = 0.3\%wt$)

After an analysis of how the different characteristics of the PCP molecule (adsorption energy, size, affinity for the solvent) are related to the rheology, we analyse in the next section the effect of the size of the particles for a same molecule: the PCP45.

2.3.4 Influence of particle size on the rheology with the same plasticizer

The micrometric particles can easily be densified, even above $\Phi_v=0.6$ in the presence of the plasticizer, but it is not possible to reach such high volume fraction with the nanoparticles because the yield stress varies as the invert of the diameter of the particles [5] (the number of contacts between two planes of particles is proportional to $1/d^2$ whereas the Van der Waals force is proportional to their diameter). Also the shear forces, which increase as $\dot{\gamma}d^2$ are less efficient to disaggregate small particles. The maximum volume fraction obtained by centrifugation at 20000 rpm was $\Phi_v=0.42$.

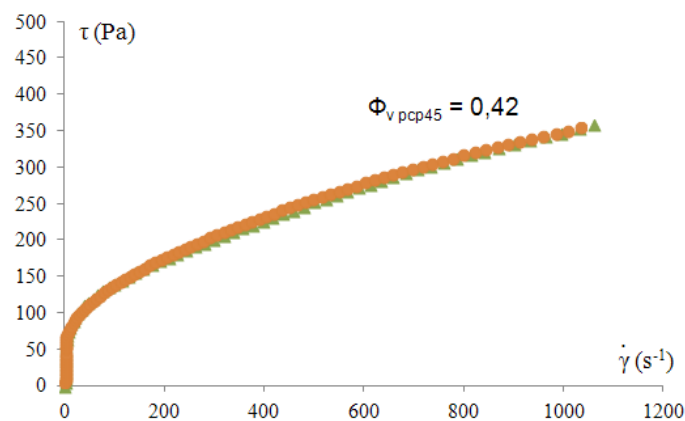


FIG. 8 : Stress versus shear rate for a suspension of nanoparticles (Fig 1b) in presence of PCP45 $c = 1,8\%$ wt

We actually see in Fig.8 an important yield stress even in the presence of a high concentration of plasticizer. This curve should be compared to the one in Fig.7 where, even in the presence of a much higher volume fraction ($\Phi_v = 0.55$), there is no measurable yield stress. The plastic viscosity is also larger : about 0.25 Pa.s for the nanoparticles against 0.1 Pa.s for the microparticles. It is likely that, besides the particle's size effect the difference in the energy of adsorption which is much smaller for the nanoparticles (cf Fig.3) also plays a rôle for decreasing the efficiency of the PCP on the nanoparticles.

3 Conclusion

This study has shown, that even on a simple system like calcium carbonate, several parameters must be taken into account to characterize the efficiency of the PCP plasticizer. With a careful correlation between the adsorption isotherm and the rheology, we have seen that the formation of a monolayer of PCP was a necessary and sufficient condition to obtain the maximum reduction of viscosity. The increase of the length of the PEO chain is an important factor to reduce the aggregation between particles, nevertheless an increase from 45 to 114 OE groups had no effect on the rheology, which is attributed to a decrease of the affinity of the longer chain with the solvent. The importance of the affinity with the solvent is also decreased when the pH is raised ; this is shown by turbidity measurement with a precipitation of the PCP45 arising at a pH close to 9.5 which is well correlated with an important increase of the suspension's viscosity between pH=8 and pH=10. On suspensions of microparticles, the yield stress is suppressed by the superplasticizer even at volume fraction as high as 0.6 whereas it remains important, even at much lower volume fraction for the nanoparticle suspension; the rôle of the difference of adsorption energy of PCP on these two systems will be addressed in a future work.

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