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Large, viscosity-enhancing polyelectrolyte complexes and an assessment of their contribution to dry strength in paper

Diploma work

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Abstract

In this diploma work, the aim was to elucidate whether preaddition of polyelectrolyte complexes (PEC) to the filler slurry could improve the paper strength when a filler called precipitated calcium carbonate (PCC), that has a rough surface, is used. The approach was to make polyelectrolyte complexes of three different high-charge anionic carboxymethyl cellulose (CMC) and three different low-charge cationic polyacrylamides (CPAM). Preferably, big complexes (400-800nm), rich in water, would be formed with the intention to make them adsorb to the surface of filler without vanishing in the straggling structure.

The produced PEC solutions were characterized and analysed mainly by rheological measurements but also with microscopy and dynamic light scattering. One of these PEC solutions was also used in sheet forming experiments and evaluated for its effects on paper strength.

The results from the different measurements showed that big PECs are produced already at low additions of CPAM and just get more numerous when further CPAM is added. A significant viscosity increase is also observed for the PEC solutions in comparison to CMC. The size of the produced PECs could be estimated to 500-600 nm. Despite this, no significant effects on the paper strength could be observed.

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1 Introduction

This project was performed as a ten week diploma work at the department of Product Development Pulp and Paper at Eka Chemicals in Bohus, where polyelectrolyte complexes (PECs) have been generated, studied and evaluated for their performance in fine paper. This is of great interest because it could reduce the content of cellulose fibre in paper manufacture which can lower the raw material cost and is also an advantage in environmental aspects.

To make the paper strong, a cationic strength polymer is added to the stock where it binds to the negatively charged fibre surfaces. To make these polymers bind well to the filler as well, a cationic fixation agent may be added to the filler slurry along with anionic carboxymethyl cellulose (CMC). The cationic strength polymers have a high affinity for cellulose and for this reason adhere the CMC-covered filler to the fibres. Cationic retention polymers further improve upon the retention of the CMC-covered filler.

In terms of paper strength assessment, this work focussed on comparing plain CMC with PECs consisting of highly charged anionic CMC and lowly charged cationic polyacrylamides (CPAM). The aim was to make the complexes big (400-800nm) and rich in water with the intention to make them adsorb to the surface of the filler precipitated calcium carbonate (PCC), se figure 1. Thanks to the net negative charge of the PECs, they should also make a good substrate surface for the cationic strength polymers.

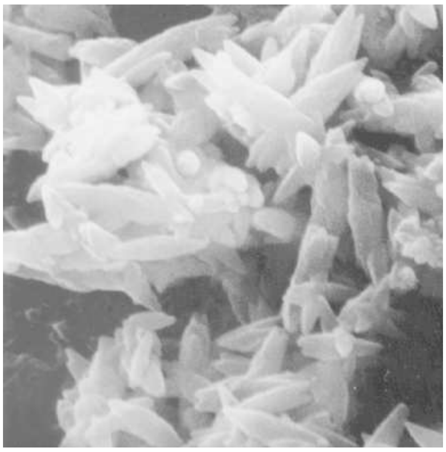


Figure 1: The filler precipitated calcium carbonate PCC (scalenohedral). [1]

The work was partly based on the findings in the article “Viscosity properties of homogeneous polyelectrolyte complex solutions from sodium carboxymethyl cellulose and poly(acrylamide-co-dimethyldiallylammonium chloride)”of Zhang et al. [2] where the viscosity properties of polyelectrolyte complex solutions were investigated. In this article, sodium carboxymethyl cellulose with an average degree of substitution of 0.8 and a weight-average molecular weight of 5.0×10^5 g/mol in complex with the cationic polyelectrolyte (poly(acrylamide-co-diallyldimethylammonium chloride), PAM-co-DADMAC) with a stated weight-average molecular weight of 3.2×10^4 g/mol and 3 mol% DADMAC was studied [2]. The authors report up to a 25-fold viscosity increase when PEC solution was compared to an imaginary polymer blend solution with no interactions between oppositely charged polyelectrolytes. They get a viscosity decrease with increased shear rate, but there is nothing said about salt concentrations in the solutions.

The produced PEC solutions were characterized and analysed mainly by rheological measurements but also with microscope and attempts were made to use dynamic light scattering to determine the size of the complexes. One of these PEC solutions was then evaluated in terms of its performance in paper by internal bond strength tests and tensile strength measurements.

2 Materials and Methods

This chapter describes the material and the different analytical methods that were used to produce and characterize the PECs. Techniques used were rheometry, microscopy, dynamic light scattering, charge titration along with sheet-forming and internal bond and tensile strength index determination.

2.1 Materials

The polyanions used in this project were anionic carboxymethyl celluloses (CMC), Akucell AF (AkzoNobel), with weight-average molecular weights of 140000, 340000 and 860000 g/mol and an average degree of substitution of 0.83. These are from now on referred to as CMC1 (140000 g/mol), CMC2 (340000 g/mol) and CMC3 (860000 g/mol).

Three different cationic polymers were also used. Two of them were polyacrylamides (with 97% and 94% acrylamide monomers, respectively) with 3 mol% and 6 mol%, respectively, of the cationic monomer acrylate dimethylaminomethyl methylchloride (CPAM with ADAM MeCl), obtained from the polymer manufacturer SNF Floerger, with a weight-average molecular weight of ~ 40000 g/mol. These are from now on referred to as CPAM1 (3 mol%) and CPAM2 (6 mol%). The third cationic polymer that was used was a polyacrylamide (with 95% acrylamide monomer) with 5 mol% diallyldimethylammonium chloride (CPAM with DADMAC), also obtained from SNF Floerger, with a weight-average molecular weight of ~ 1×10^6 g/mol. This is from now on referred to as CPAM3.

From these CMCs and CPAMs, solutions of 1% and 2%, respectively, were prepared in deionized water. CMC was dissolved by adding dry powder to water in less than one minute under stirring, upon which it was stirred for an hour and then put to rest over night. If anyway some undissolved CMC was left, the solutions were filtrated through filter paper (pore size >20µm) before it was used. The CPAM samples were received as water solutions and were diluted to the appropriate concentration using a magnet stirring device.

When the polyelectrolyte complexes (PECs) were produced, CPAM solution was added to CMC solution with the assistance of a pump with a constant addition rate of 3 ml per minute under constant stirring, resulting in a total volume of 120ml, see figure 2. This was made with different weight proportions of the polyelectrolyte solutions (10:110-80:40; the amount of

CPAM first), concentration (0.3-1% CMC (w/w), but CPAM always with double the concentration of CMC) and different combinations of CMC and CPAM.

Figure 2: Production of PECs by adding CPAM solution to CMC solution under constant stirring and addition rate.

2.2 Rheology

Rheology is the learning of the relationship between the deformation and flow of materials when exposed to an external force. To measure the rheological behavior, a well-defined force is applied under a given time and the results describe parameters such as strength, stiffness and viscosity of the material [3].

In this project, these experiments were aiming to show the viscosity properties of the solutions. The viscosity is the flow-resistance in a fluid as a reaction to a tension. If a fluid is “thick”, it has a high viscosity in contrast to “fine” fluids that have a low viscosity. Some fluids are shear-dependent, which means that their viscosity changes with increased shear rate. One problem that can occur when measurements are made at low viscosities is that the flow becomes turbulent which can give misleading results.

The viscosities of each polymer component, CMC and CPAM, and the polyelectrolyte complexes (PECs) have been studied in a rotation rheometer (Universal dynamic spectrometer, Physica UDS 200) using a concentric cylinder measuring system (Z2). The temperature was set to 25°C and the shear rate was varied from 1-1000 1/s and 1000-1 1/s. The PEC measurements were made on fresh solutions and, in some cases, solutions that had been resting for approximately 20 and 60 hours. The results from the viscosity measurements are presented and discussed later on.

2.3 Microscopy

An optical microscope (CX41 Olympus) connected to a charge-coupled device camera (CCD) was used to study the polyelectrolyte complexes (PECs). The images of the PECs were also compared to images of CMC and CPAM solutions in 40 and 100 times enlargement. To estimate the size of the observed structures, well-defined Kromasil particles (Kr-SiO_2) of 3.5 µm in diameter, were added to the solutions.

To investigate the bacteria content in the PEC solutions an ATP test was performed. ATP, or adenosine triphosphate, is an energy carrying molecule found only in and around living and dead cells. To measure the ATP content an enzyme is added to the sample. The enzyme will react with the ATP molecule and during the reaction light is produced. The amount of light is equal to the amount of biological energy present in the sample and indirectly equal to the bacteria content.

2.4 Dynamic light scattering

Dynamic light scattering is a method that estimates the size of particles (or other light scattering entities) in a solution. It measures the relaxation times of the scattering entities and in the case of a particle solution translates these into rates at which the particles are diffusing. This is done by having the sample exposed to a laser light, which the particles scatter and the intensity of the scattered light will fluctuate with the movement of the particles. Large particles move slowly which leads to a slow change of the intensity of the scattered light, in contrast to smaller particles that have a more rapid movement, which results in a rapid fluctuation of the light.

With the knowledge of the viscosity of the sample and an assumption that the particles are spherical, the distribution of the sizes of the particles can be calculated. The intensity of the scattered light is proportional to the diameter of the particles raised to the power of six ($I \alpha d^6$). This means that if there are e.g. large dust particles, this will have huge consequences for the signal of the scattered light and also for the calculated particle size [4].

In this project the PECs were tested in three different ways. First, the samples were tested in the original concentration, then diluted 100 times and then also by adding salt to a concentration of 10mM in the diluted samples. The instrument used was a Malvern Zetasizer Nano ZS.

2.5 Particle charge detector

With a particle charge detector, or PCD, measurements of the charge carried by e.g. particles or polymers can be made and charge density can be calculated if the concentration of the sample is known and vice versa.

In this project, a Mütek PCD 03 (and a Mettler DL21 titrator) was used where a piston is moving up and down creating an electrical potential difference between two electrodes. If the analyte is an anionic polymer, the titration should be made with a cationic polymer and the other way around. The titration goes on until the isoelectric point, where the sample is neutral and the potential difference is equal to zero, is reached. By knowing the concentration and the amount of the titration solution added to reach neutralisation, calculation of the charge in the sample can be made. See the equation below.

$$q = (V_t * C) / V_p \tag{1}$$

Here, q is the charge concentration of the sample (eq/l), V_t is the added volume of titration solution (l), C is the concentration of the titration solution (eq/l) and V_p is the volume of the sample (l) [5].

In this project, PCD was used to investigate whether the PECs were adsorbed on to the surface of the filler during the filler slurry preparation or not. The solutions were centrifuged and the supernatant was saved for titration. The investigated solutions were PCC+fixation chemicals and PEC+PCC+fixation chemicals.

2.6 Paper production

In the evaluation of the performance of the polyelectrolyte complexes in paper, only one complex was chosen and added to the paper stock due to the time limits of the project.

Paper consists of cellulose fibres (the raw material), fillers (to increase the whiteness of the paper, opacity and for cost and environmental reasons) and other performance chemicals (fixation agents, cationic strength polymers and retention chemicals).

The first step in making paper is to prepare a stock which contains fibre, fillers, chemicals and water. The stock is then distributed on a web where the water is removed by suction and the paper is beginning to form. The paper is then separated from the web and passes through a press before it reaches the last drying section. Here, the dry content is increased to 95% by drying with hot air [6].

The sheet former used in this project was a dynamic sheet former. The strength of the paper was tested by different methods of assessment, like internal bond strength and tensile strength index measurements. These methods are described later on in chapter 2.7.1 and 2.7.2.

2.7 Paper strength

The strength of the paper was tested by different methods of assessment, like internal bond strength and tensile strength index measurements, and also the bulk development was determined. The bulk development is calculated from measurements of the thickness and the weight per area of the paper.

2.7.1 Internal bond

Internal bond strength tests, (also called Scott bond), are measurements of the delamination strength in a paper. It defines the required energy to split a paper strip into two parallel sheets in the z-direction of the sheet [7].

The experiment preparation implies placing the sample between two layers of double coated tape on a metal block with an L-shaped piece on top under relatively high pressure. A pendulum is then released and knocks off the upper metal piece and the paper sample is then split into two sheets. The energy loss of the pendulum is translated into a scale that can be read (J/m^2). See figure 3 below.

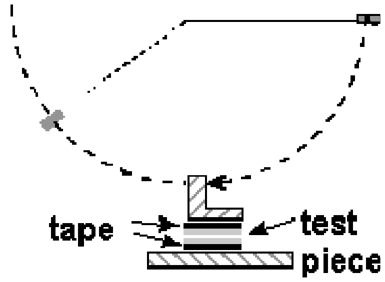


Figure 3: Internal bond strength experiment [8]

The test was repeated five times for every sample and the result is thus an average value.

2.7.2 Tensile strength index

This test determines the force required to tear a paper strip apart, see figure 4. Some properties vary with direction and hence the measurements are made in two different directions; machine direction (MD) and cross direction (CD). MD is the same as the fibre direction and CD is perpendicular to the MD [9].

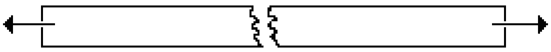
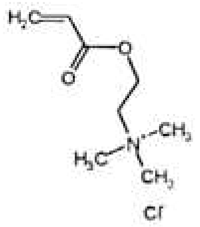


Figure 4: A paper strip is ripped apart in a tensile strength index test.

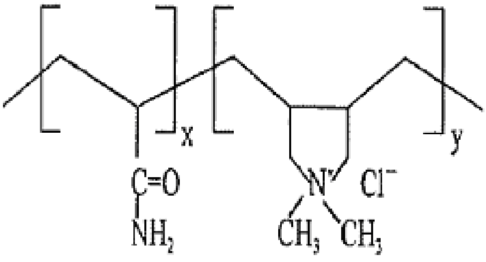
The experiment was repeated five times in MD and six times in CD for each paper sample. From the compiled values, an average result was calculated and expressed in kN/m.

3 Results and Discussion

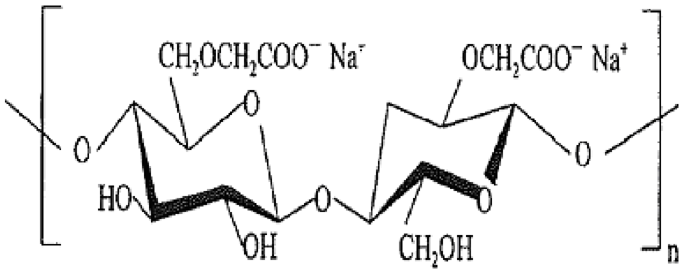
In this project, PECs were produce by adding low-charge CPAM to high-charge anionic CMC, see figure 5. The aim was to make these complexes big (400-800nm) and rich in water with the intention to make them adsorb to the surface of PCC. The PECs were characterized mainly by rheological measurements, but also by microscope, and attempts were made to use dynamic light scattering to determine the size of the complexes. One of these PEC solutions was then evaluated in terms of its performance in paper by internal bond strength and tensile strength measurements.



ADAM MeCl



CPAM with DADMAC



NaCMC

Figure 5: Structures of the cationic monomer ADAM used in CPAM1 and CPAM2, CPAM with DADMAC monomers (CPAM3)and CMC [2].

The three different CMCs that were used are from now on referred to as CMC1, CMC2 and CMC3, where the one with the lowest MW is number 1 and the one with the highest MW is number 3 (140000, 340000 and 860000 g/mol). The three different CPAMs are referred to as CPAM1, CPAM2 and CPAM3. CPAM1 and 2 has the same MW, ~40000 g/mol, but 1 has a charge of 3 mol% and 2 who has a charge of 6 mol% and CPAM3 is the one with the highest MW, ~1x10^6 g/mol, and a charge of 5 mol%.

The PECs were made with different weight proportions of the polyelectrolyte solutions, 10:110-80:40, where the amount of CPAM is the first number.

3.1 Rheology

In the article of Zhang et al., the viscosity properties of polyelectrolyte complex solutions were investigated. The authors report up to a 25-fold viscosity increase when PEC solutions were compared to an imaginary polymer blend solution with no interactions between oppositely charged polyelectrolytes [2]. Viscosity measurements were for this reason used to study the viscosity properties of the produced PEC solutions. The desired effect for the PECs was an increase in viscosity compared to CMC, which might indicate that the complexes were big and had a loose structure, rich in water.

In the viscosity diagrams presented, the curves represent the raw data from the measurements. However, since the effects of even small dilutions of CMC are substantial, especially at high molecular weights and high concentrations, dilution effects should be taken into consideration in the interpretation. Thus, the viscosity enhancement factors at a shear rate of 1s^{-1} are given in table 1, calculated according to equations 3 and 4 in Zhang et al [2]:

The viscosity of an ideal blend solution (theoretically assuming no interactions between the polymers) is taken as

$$\log \eta_B = \Sigma W_i \log \eta_i \qquad (2)$$

where η_i is the solution viscosity of the *i*th component, η_B is the solution viscosity of the blend solution and W_i is the weight fraction of the *i*th component. The viscosity enhancement factor, V_m, is then calculated as

$$V_m = (\eta_{obs} / \eta_{calc}) - 1 \qquad (3)$$

where η_{obs} is the measured viscosity of the PEC solution and η_{calc} is the "ideal" viscosity calculated according to equation 2.

The first measurements were made on CPAM1 and CPAM2 in association with CMC2 and CMC3. Evaluating these results, the conclusion could be made that they do not correlate with those of the work of Zhang et al and did not show any significant increase of the viscosity upon adding CPAM to CMC. However, it was realized that the stated weight average molecular weight of the CPAM used in that study could not possibly be correct since in one of the tables, the viscosity of that CPAM was listed as ~53 mPas (at 1.2% concentration and a shear rate of 5.4s^{-1}). Therefore, a bigger CPAM, CPAM3 with a MW of ~1x10^{6} g/mol and with a charge of 5 mol%, was tested. The results for the samples of CPAM1 and CPAM2 are shown in figures 11-12, and discussed in the end of this chapter. The results from CPAM3 forming PECs with, CMC2, CMC3 and CMC1 are shown in figures 6-10 below.

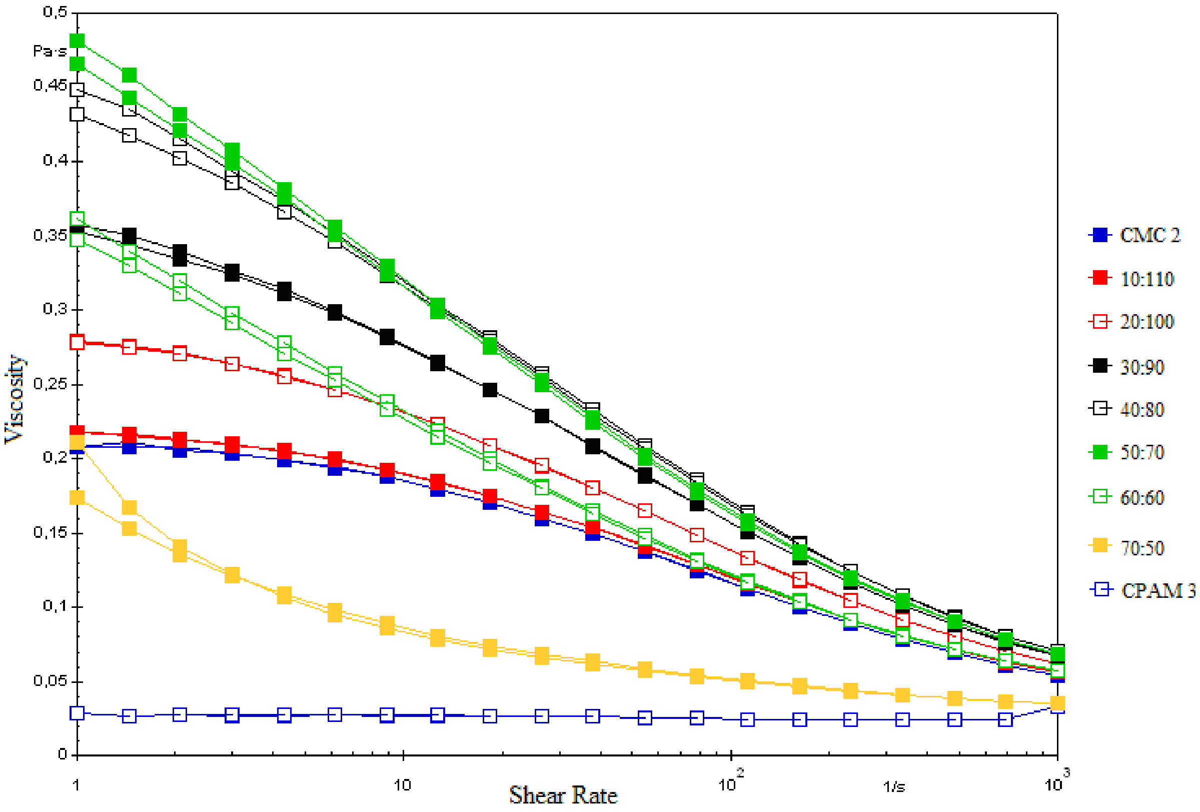


Figure 6: The results from rheological measurements for CPAM3:CMC2 with a concentration of 1% CMC

In this diagram, a viscosity increase is observed for all ratios except 70:50, where the highest ones are 40:80 and 50:70. The largest viscosity enhancement factor (6.18, see table 1) is obtained for 50:70. For all ratios up to 40:80, the curves have the same shape as CMC. This suggests that free CMC is present in the sample and has a significant effect on the viscosity properties of the samples. When additional CPAM is added to the sample, the shape of the curves is changed. This suggests that the CMC content in the sample has decreased and that the PECs now dominate the viscosity properties. In the samples 40:80 to 70:50, the curves differ somewhat on the way forwards and backwards, i.e. they show thixotropic behaviour. This is an indication that the shear breaks some structure in the sample which does not recover fully on the timescale of the experiment.

To assess the concentration effects on PEC formation, PECs made of CPAM3 (0.6%) and CMC2 (0.3%) were tested. As observed by microscopy (chapter 3.2) on the PEC solutions at high and low concentrations (1%-0.3% CMC), the PECs looked the same but decreased in number when the concentration was decreased.

Sample	$\mathbf{V_m}$
CPAM3:CMC1 (2%:1%)	
20:100	0.26
30:90	0.52
40:80	0.70
60:60	0.51

Sample	$\mathbf{V_m}$
CPAM3:CMC2 (2%:1%)	
10:110	0.41
20:100	1.32
30:90	2.73
40:80	4.67
50:70	6.18
60:60	5.27
70:50	3.19
CPAM3:CMC2 (0.6%:0.3%)	
40:80	6.18
60:60	4.27

Sample	$\mathbf{V_m}$
CPAM3:CMC3 (2%:1%)	
40:80	9.96
60:60	17.76
CPAM3:CMC3 (0.6%:0.3%)	
10:110	0.60
20:100	2.15
30:110	4.95
40:110	8.14
50:110	11.53
60:110	14.44
80:110	17.03
100:110	10.99

Table 1: Viscosity enhancement factors for various PEC preparations, calculated according to equations 2 and 3.

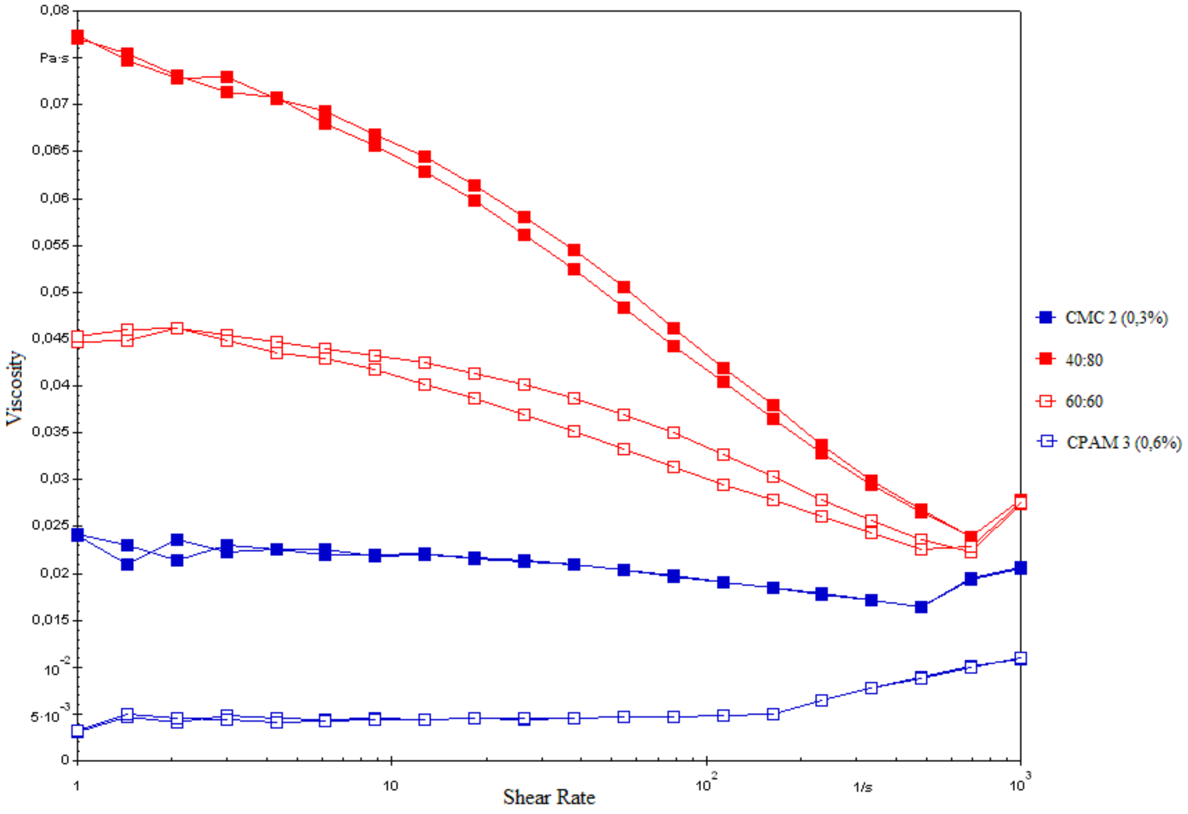


Figure 7: The results from rheological measurements for CPAM3:CMC2 with a 0.6%:0.3% concentration.

These PECs, see figure 7, give an increase in viscosity relative to free CMC, but also some turbulence is observed at high shear rate. When comparing the two PECs, CPAM3:CMC2 with concentrations of 2%:1% and 0.6%:0.3%, similar viscosity enhancement factors were obtained. For the PEC solutions, thixotropic effects are observed.

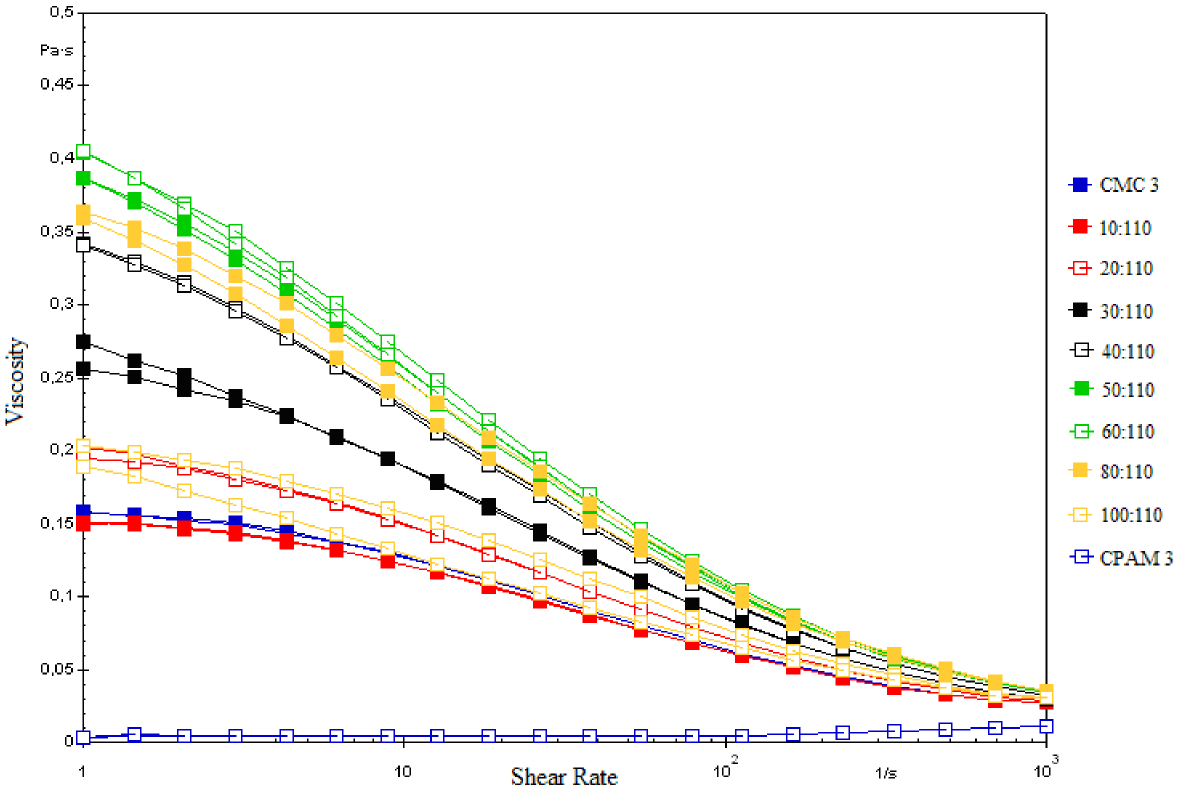


Figure 8: The results from rheological measurements for CPAM3:CMC3 with concentration of 0.3% CMC

As in the results for CPAM3: CMC2, a large viscosity increase is observed for CPAM3:CMC3, where all PECs except 10:110 have a higher viscosity compared to the CMC sample, see figure 8. All the curves, except 100:110, have the same shape which might indicate that the samples have similar structure. All ratios from 60:110 to 100:110 show thixotropic behaviour.

Also in this case the concentration effects were tested by analyzing an increase from 0.6%:0.3% to 2%:1%.

In contrast to the samples with the lower concentration, this does not give any viscosity increase compared to the CMC sample (figure 9), but looking at the V_m values obtained (see table 1), it is obvious that the CPAM3:CMC3 PECs at both low and high concentration cause a significant increase in viscosity, higher than for CPAM3:CMC2.

In the rheological measurements of PEC solutions of CPAM3:CMC2 and CPAM3:CMC3, the viscosity increases at low additions of CPAM. It continues to increase up to a certain CPAM:CMC ratio. After this point, the viscosity decreases again. This is not easily explained, but knowing that the CMCs of these molecular weights at these concentrations due to entanglements form transient network structures, it could be argued that the PECs formed up to a certain CPAM addition level act as cohesive anchoring points in this transient network structure. Then, at this point, the net effect on viscosity of losing free CMC, and thus further decreasing the level of entanglements between free CMC, to build more PEC anchoring points, will be negative.

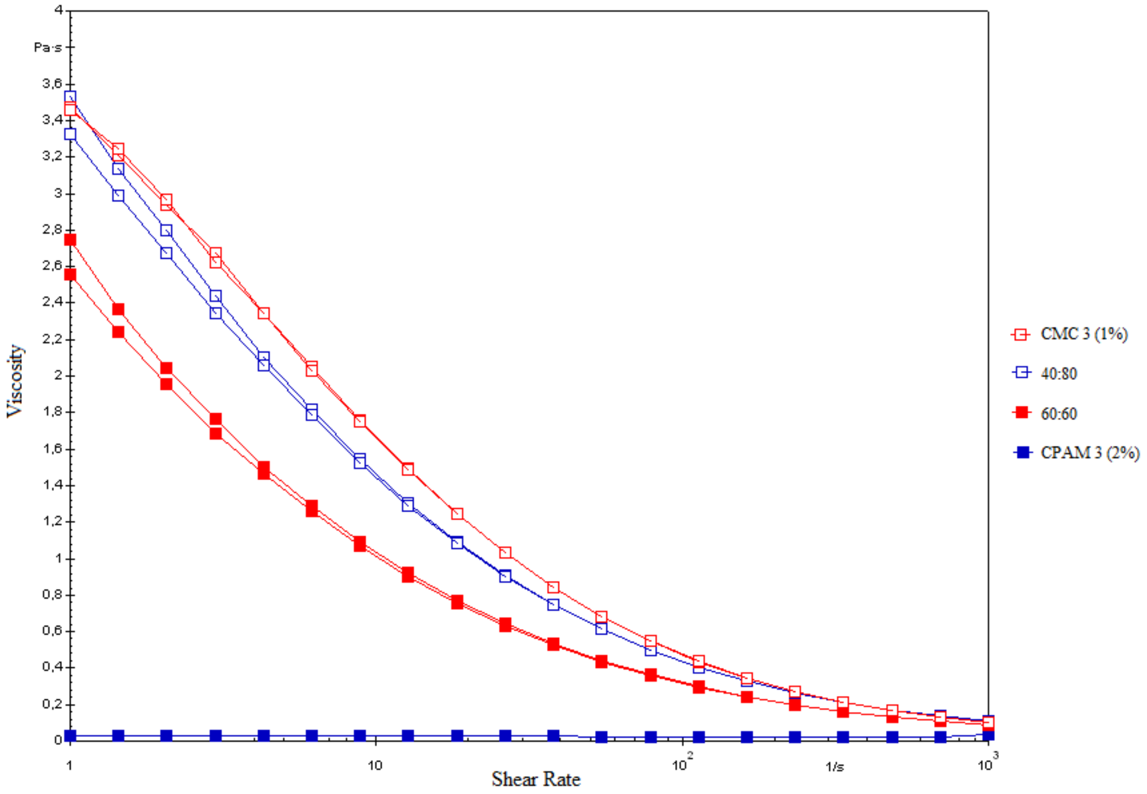


Figure 9: The results from rheological measurements for CPAM3:CMC3 with a 2%:1% concentration.

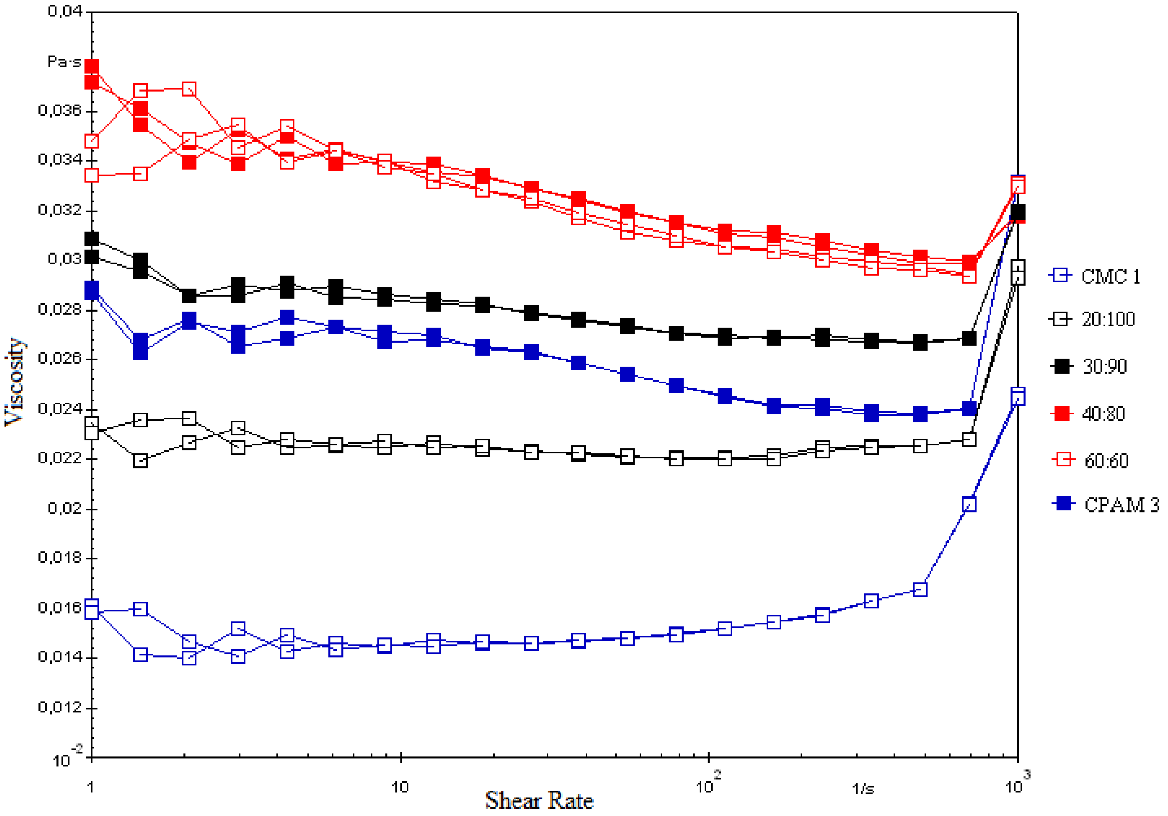


Figure 10: The results from rheological measurements for CPAM3:CMC1 at 2%:1% concentration.

The results on CPAM3:CMC1, see figure 10, indicate that the PEC structures formed here do not give any significant viscosity enhancement and the microscopy images also demonstrate that they are quite different from the ones obtained with CMC2 and CMC3 together with CPAM3.

As mentioned in the beginning of this chapter, the first measurements were made on CPAM1 and CPAM2 in association with CMC2 and CMC3. These results are shown in figures 11-12 below.

The results CPAM1:CMC2, see figure 11, did not at all match the viscosities achieved in Zhang et al. The results for CPAM1:CMC3 follow the same pattern as these result.

The results for CPAM2 are the ones that show a tangible viscosity increase of the two smaller CPAMs. As shown in the diagram (figure 12), ratios up to 40:80 have a higher viscosity than CMC, regardless the shear rate. The results for CPAM1:CMC3 follow the same pattern as these results.

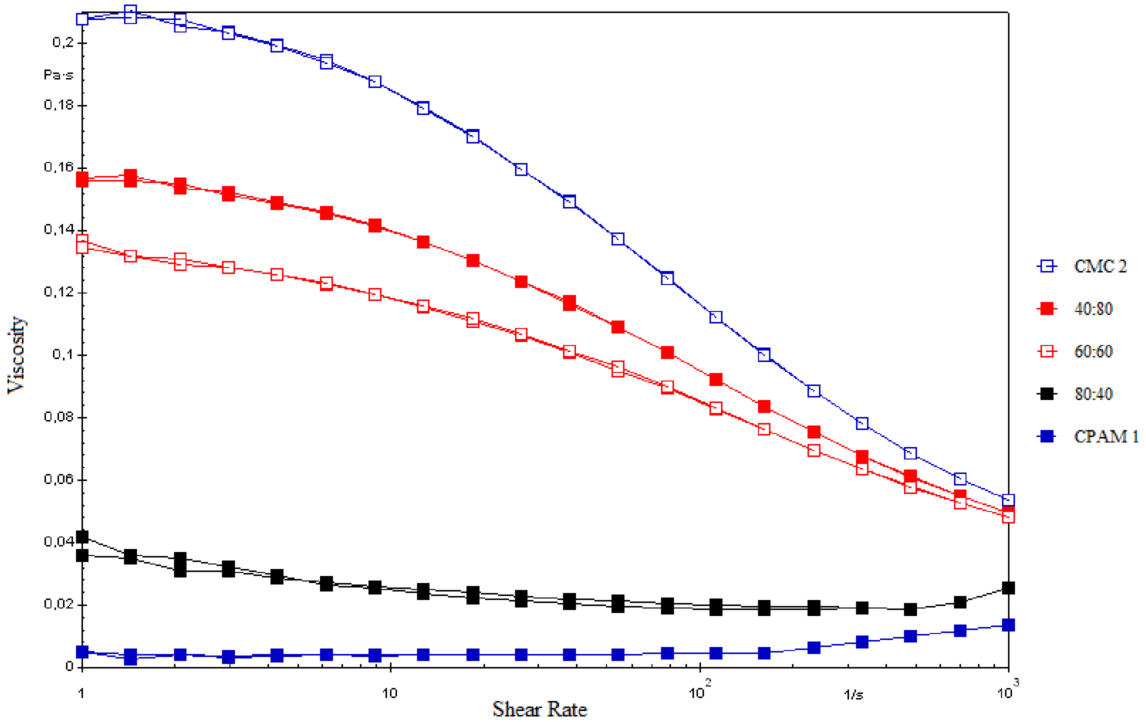


Figure 11: The results from rheological measurements for CPAM1:CMC2.

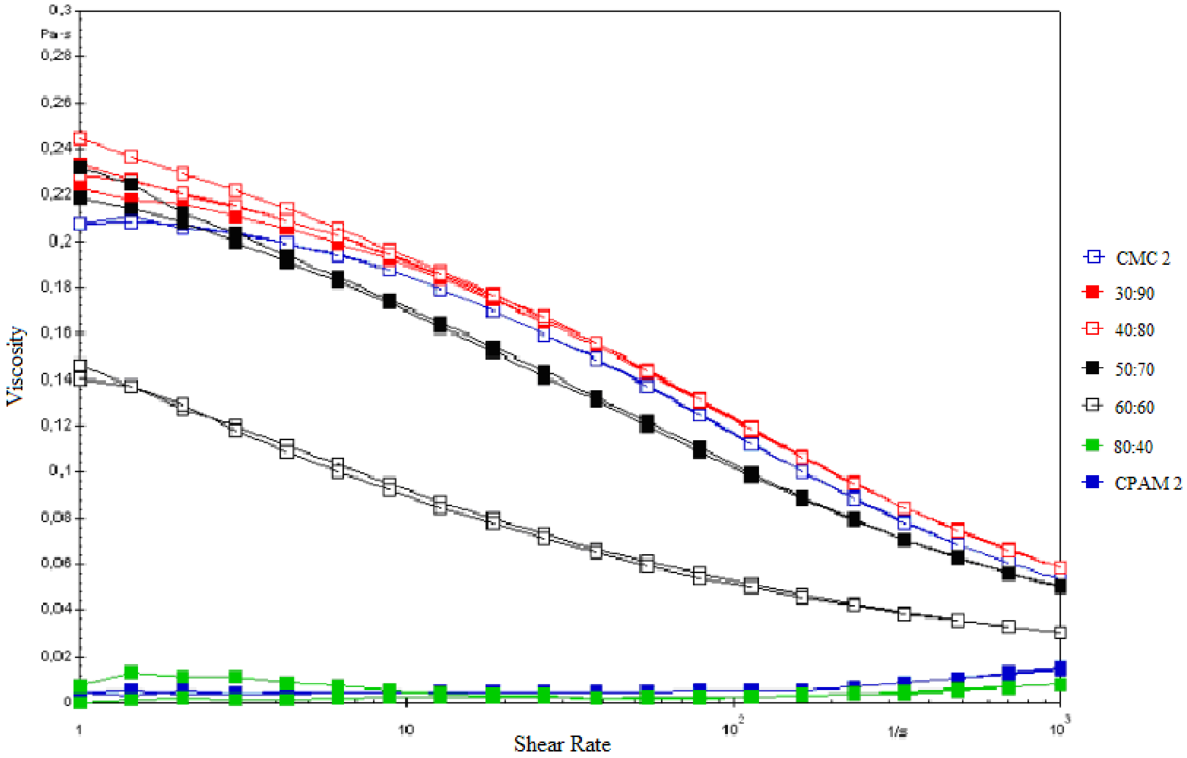


Figure 12: The results from rheological measurements for CPAM2:CMC2.

3.2 Microscopy

This way of studying the PECs was used to estimate the size and follow the formation of the observed structures. The studied PEC samples were CPAM3:CMC2, CPAM3:CMC3 and CPAM3:CMC1, in 40 and 100 times enlargement. These observations were also compared to images of pure CMC and CPAM solutions.

The PECs of CPAM3:CMC2 looked like spherical structures separated from each other. In figure 13 the PECs of 40:80 (with a CMC concentration of 1%) can be seen as the small brighter points.

Figure 13: PECs in CPAM3:CMC2 solution of ratio 40:80 with a CMC concentration of 1%

For CPAM3:CMC3, ratio 40:80, with a CMC concentration of 1%, the PECs were similar to the ones observed for CPAM3:CMC2, though possibly slightly bigger. See figure 14.

Figure 14: PECs in CPAM3:CMC3 solution of ratio 40:80 with a CMC concentration of 1%

At the tested concentrations of 1% for CMC1, 1% for CMC2 and 0,3% and 1% for CMC3 the PEC solutions are opaque. Microscopic analysis however indicate that this does not seem to affect the appearance of the structures when compared to the transparent solutions of 0,3% for CMC1 and 0,3% for CMC2. All the solutions with low addition of CPAM were stabile for weeks in contrast to the solutions with high addition of CPAM that were separated after a few days.

A number of different tests were made to make sure that the observed structures were really PECs. One sample was de-aerated to ascertain that the observed spheres were not air bubbles, but it did not make any difference. The microscope slides and cover slips were also thoroughly washed in distilled water and ethanol to see if any dirt was polluting the samples, but neither this had any influence. Furthermore, an ATP test (see chapter 2.3) was performed to determine whether the PEC solutions were contaminated by bacteria. The results from this test showed that the PEC solutions were free from bacteria. The most decisive test, however, was to compare samples at low and high ratios of CPAM:CMC. Then, it was evident that more and more spheres (of the same structure and size) were formed as the CPAM addition proceeds. From the results of these different tests, observations of the different PEC solutions (CPAM3:CMC2 and CPAM3:CMC3) and the comparison with images of CMC and CPAM solutions where the observed structures are not present, the conclusion could be made that PECs are produced.

In the images of CPAM3:CMC1, spherical aggregates of PECs were observed, see figure 15. This phenomenon was seen already at low addition of CPAM. When adding more CPAM to the solution these structures just seem to increase in number. At the ratio 60:60, the formation is changed and the PECs are no longer in spherical aggregates but in unsymmetrical clusters.

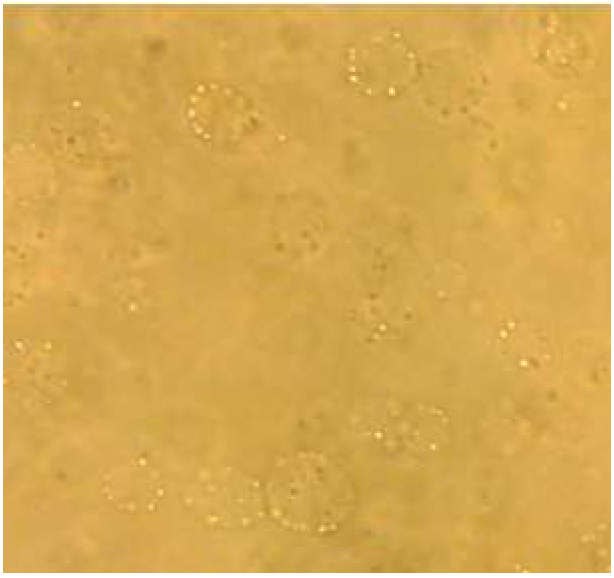


Figure 15: Pictures of CPAM3:CMC1, ratio 40:80, in 40 times enlargement.

To estimate the size of the PECs, well-defined Kromasil particles (Kr-SiO_2) of 3.5 μm in diameter, were added to the solution. The observed image of the Kromasil particles was compared to images of the PECs and with the assistance of a computer program where measurements of the observed structures could be made, calculations of the real diameter of PECs could be estimated to 500-600 nm.

3.3 Dynamic light scattering

Dynamic light scattering is a method that determines the size of particles in a solution and was used for trying to estimate the PEC sizes. In figure 16 below, the results for CPAM3:CMC2 50:70 are shown. The green, red and the blue lines are just three different measurements on the same sample.

Considering the results from the microscopy observations, where estimations of the size of the complexes had been done, the peaks at ~1μm were roughly as expected for PEC solution of CPAM3:CMC2. However, when measurements were made on CMC solution, much larger sizes than expected were obtained (>500 nm). When the samples were diluted and an addition of salt were made the results were unchanged.

This can be due to restricted motion of the CMC polymers which make them appear much bigger than they actually are. This issue made the results from all DLS measurements hard to interpret. To be able to draw any conclusions from this analytical technique, additional measurements have to be made. The samples probably need to be diluted even more than they were here to come down to non-overlap conditions for the CMC [10]. Also, an even higher salt concentration might be used to further screen the electrostatic repulsions, but this will also probably influence the PECs themselves.

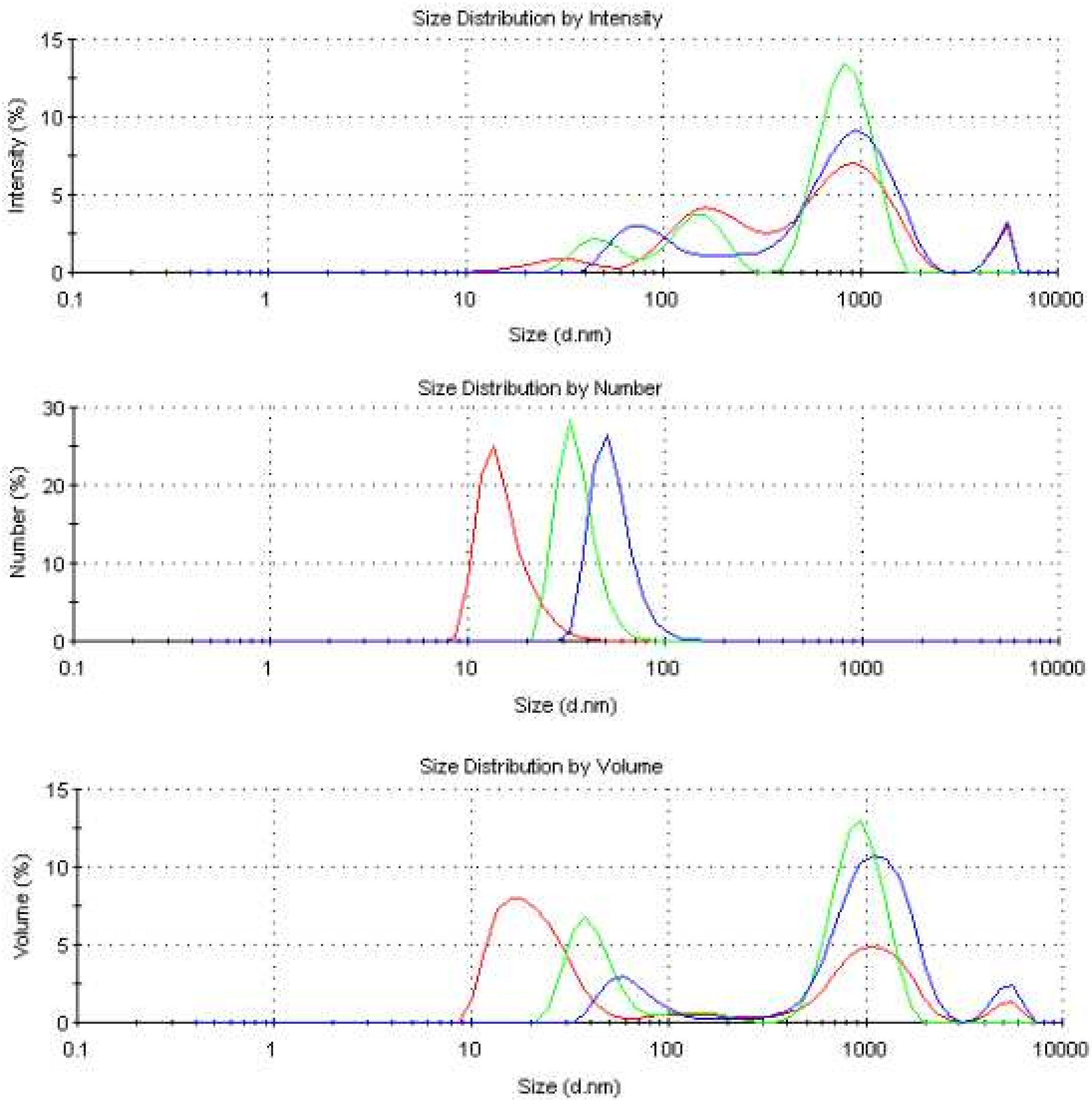


Figure 16: Results from measurements on diluted CPAM3:CMC2, 50:70, with a salt addition

3.4 Slurry preparation

To make the paper strong, a strength polymer is added to the pulp where it binds to the fibre surfaces. To make these polymers bind well to the filler as well, a cationic fixation agent and PEC solution is added to the filler slurry in this project. These complexes need to be big (hundreds of nanometers) and preferably rich in water to adsorb to the surface of PCC without vanishing into the straggling structure.

In order to make the PECs adsorb to the surface of PCC, polyamine (PA) was used as a cationic fixation agent. Separate experiments had shown that when PECs were added to a solution with low concentration of PA, the PECs were aggregated. To avoid that this occurs, the slurries must have as low content of free PA as possible. In the first particle charge detector (PCD) measurement, it was however found that at a PA addition of 1 kg/ton (dry PA on dry PCC) to a PCC slurry, a large excess of PA was found in the supernatant from the centrifugation. In attempts to overcome this issue, salt was added to help the adsorption of PA to the PCC surface. Concentrations of 0.2 M and 0.8 M NaCl were tried, but neither gave more PA adsorption than 0.35 kg/ton and the remaining 0.65kg/ton (65%) stayed in solution. It would thus seem that this is the point of surface saturation (although it seems a small figure, considering the estimated specific surface area of 6-14 m^2/g for PCC [11]) and that if a lower dosage would be applied, complete adsorption would occur. This also proved right, as when 0.2 kg/ton was dosed at a salt concentration of 0.2 M NaCl, no cationicity in the supernatant could be detected.

In order to determine the PECs' adsorption to PA-coated PCC, it first had to be elucidated whether the PECs would follow the naked PCC down in the pellet at centrifugation or not. By using a non-centrifuged PEC solution as a reference in the charge titration, it was found that for undiluted slurry, ~90% of the PECs would stay. Surprisingly, for a 10 times diluted slurry, only ~67% would stay and for a 100 times diluted slurry ~83% stayed in the supernatant. Unfortunately, when 0.2 kg/ton PA and 0.2M salt was added before PEC addition, there was no sign of a fixation effect on the PECs. Due to lack of time, where slurries had to be chosen for sheet-making, it was reasoned that this could possibly be due to the high salt concentration. It was determined to make three slurries out of this; one without fixation (CPAM3:CMC2 a), one with 0.2 kg/ton PA and 0.02 M NaCl (CPAM3:CMC2 b) and one with 1.0 kg/ton PA and 0.02 M NaCl (CPAM3:CMC2 c). These slurries were analysed after the sheet forming and the results indicated (when taking the polyamine charge into account) that ~10% for sample b and ~22% for sample c of the PECs had been adsorbed on PCC (or aggregated and followed the PCC down in the centrifugation). This has to be taken into consideration when interpretations of the results from paper strength measurements are made.

3.5 Paper strength evaluations

The desired effect of the PECs is that a high content of filler can be used while maintaining the paper strength. One of the produced PEC solutions was chosen and evaluated in terms of its performance in paper by internal bond strength tests and tensile strength measurements. These complexes were tested in three different slurry formulas and compared with three slurries of reference samples, a Ref., a CMCref and CMC2.
The "Ref." was a slurry consisting of only PCC filler. The "CMCref" contained CMC of a technical quality with a weight-average molecular weight of 250 000 g/mol and an average degree of substitution of 0.5. What differed between the two CMC samples, beside the different kinds of CMC, was that the CMC2 slurry had a higher content of fixation agent than the "CMCref". The three PEC-containing slurries were made from CPAM3:CMC2 PECs in ratio 40:80 and all three had the same amount of PEC solution. The first sample, a, had no fixation agent. Sample b contained 0.2 kg/ton PA and 0.02 M NaCl and to sample c, 1.0 kg/ton PA and 0.02 M NaCl was added.

The sheet former used was unfortunately unstable and somewhat irregular in the distribution of fiber on the web. This is a large disadvantage and means that the same section of each paper sample must be analyzed for the results to be comparable. Results from the assessment of three different properties; internal bond strength (figure 17), tensile strength index (figure 18) and bulk development (figure19), are shown and discussed here.

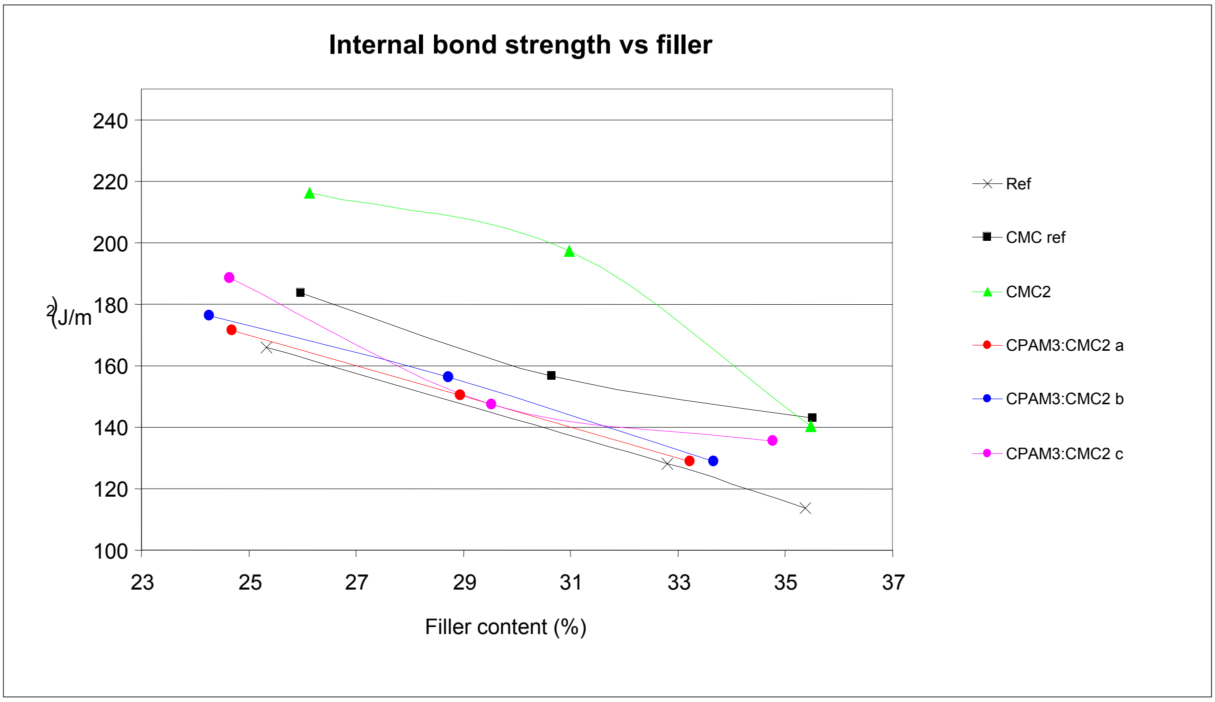


Figure 17: The results for the Internal bond

The results of the internal bond strength measurements do not show the same positive effects for PECs as for CMC2.

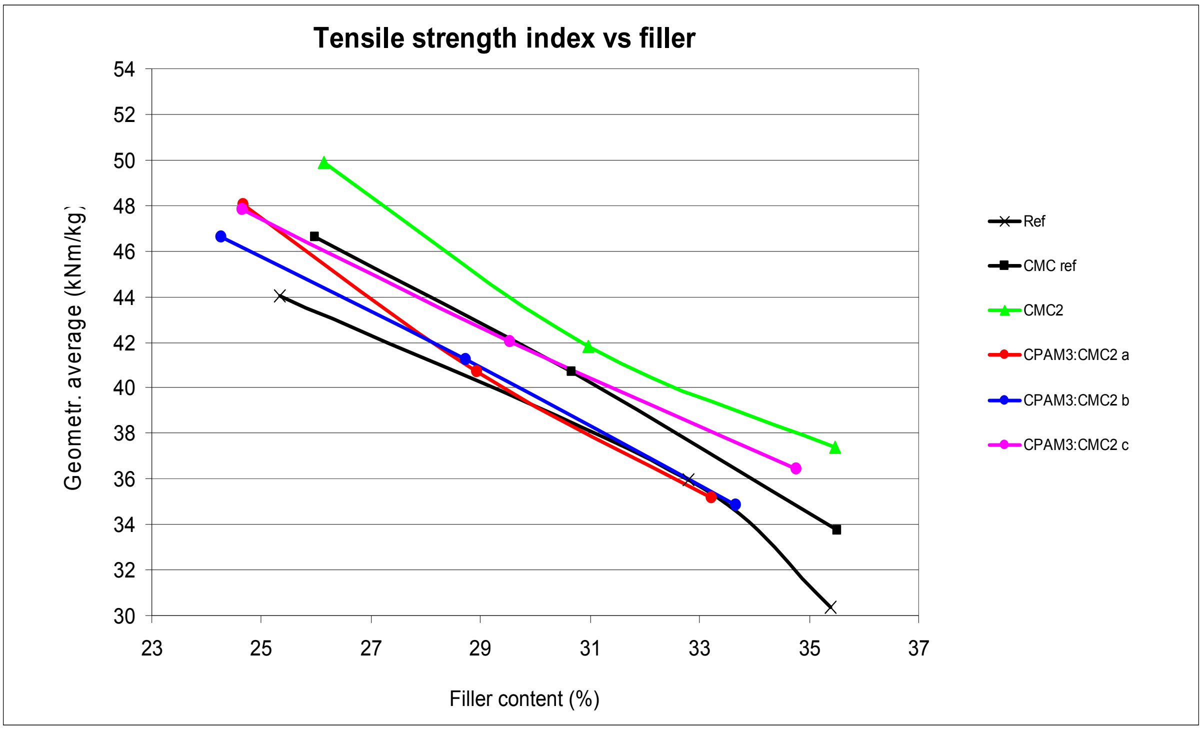


Figure 18: The results for the Tensile strength index

The tensile strength index for the PEC samples is lower than for the CMC2 sample. The PEC sample with the highest strength is CPAM3:CMC2c that has the highest fixation content. There is no significant increase in the tensile strength for the other two PEC samples compared to the reference that has no fixation agent present.

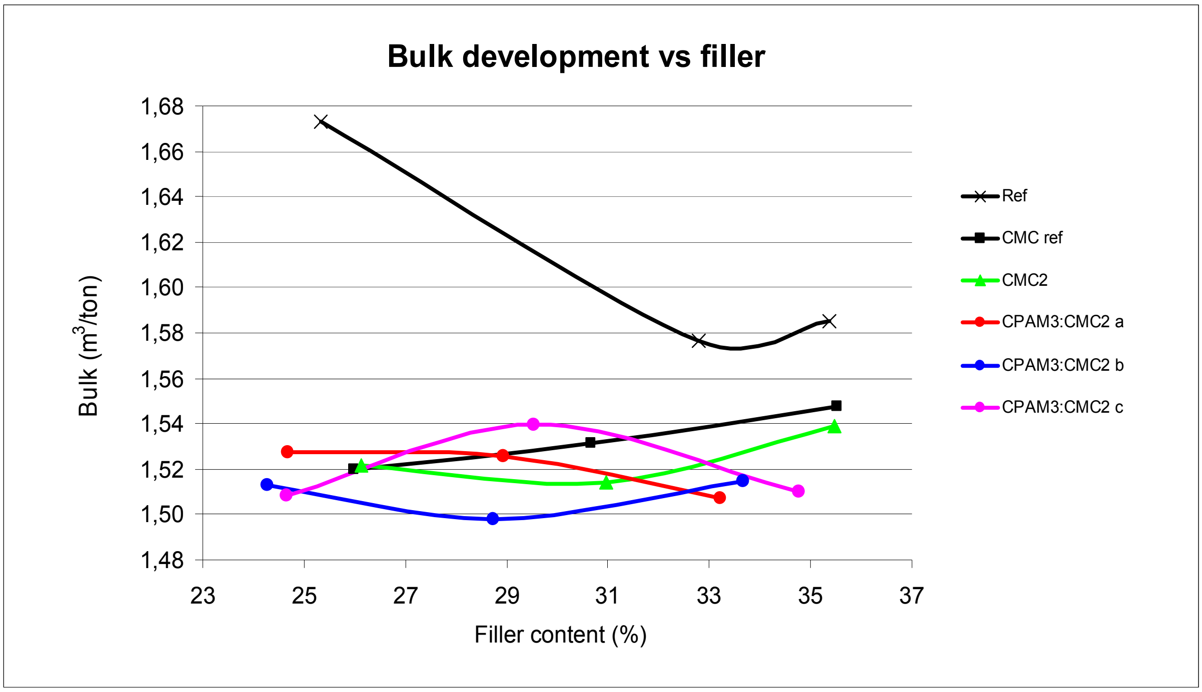


Figure 19: The results for the bulk development

Although some decrease of the bulk is unavoidable when introducing binders, it is preferable to lose as little bulk as possible during the paper production. These results of the bulk development measurement show a general decrease of the bulk content.

For all PEC solutions, the filler content was slightly lower than the calculated value. This can be due to that the complexes (and free CMC) not adsorbed to the filler disturb the retention system. Unfortunately, none of the results from the measurements of tensile strength index and internal bond strength in PEC-PCC paper indicated significant improvements of the paper strength properties. One explanation for this could be the results from the slurry preparation, that only ~10% for sample b and ~22% for sample c, of the PECs were adsorbed to the PCC surface.

4 Future work

Considering that this project was performed as a ten week diploma work, the experimental part had to be limited due to lack of time. The work has included a large amount of different methods, like viscosity measurements, microscopic observations, dynamic light scattering measurements, particle charge detector tests, sheet forming and paper strength evaluations. Despite this there is still a lot of additional work that have to be done to find the answer to all the remaining questions.

One of these things is additional characterization of the PECs to find out more about the size, structure and the charge of the complexes. This can implicate further microscopy observations where both lower and higher ratios are observed and also different concentrations of CPAM and CMC.

Another method that can contribute to an increased understanding of the PECs is diffusion NMR that can estimate the amount of free CMC in the PEC solutions. A dialysis membrane that separates free CMC from the PEC solutions can also be used for this purpose and for obtaining pure PEC systems. By studying PEC systems, and then adding CMC to the solutions in well defined portions, the influence that CMC has on the PECs can be determined. The same thing can be done for deciding the influence of salt.

G’ and G’’ can be decided by using an oscillatory rheometry. G’ is the storage modulus and is a measurement of the stored and recovered elastic energy in a sample as a result of an impact of a force. G’’ is the loss modulus and describes the dissipated energy of the sample [12]. These values can increase the knowledge of how free CMC and the PECs interact. Free CMC should not have a noticeable elasticity due to the entanglements (at least at low frequencies), but for the PECs that have a more stable network, some elasticity should be seen.

The PECs can be produced from other polymers like CMC with a different degree of substitution. The mixing of the polymers can also be done the other way around, where the CMC can be added to the CPAM.

How the PECs bind to the PCC and the fixation agent is still an unanswered question. Further experiments on how the PCC and the fixation agent influence the PECs and their adsorption have to be made. A PEC slurry with the same formula as was made for CMC2 can be produced to see how the PECs react to a higher content of fixation agent when it is used in the paper pulp.

The same slurries that were used in these experiments, which were centrifuged before dilution and titration, can instead be diluted before they are centrifuged, to see if the PECs follow PCC down to the pellet or stay in the supernatant. Also, the other PEC solutions of CPAM3:CMC1 and CPAM3:CMC3 can be of high interest to evaluate in terms of their performance in paper.

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