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## Synthesis and Characterization of Polyelectrolyte Complexes and Assessment of Their Use as Filler Binders for Improving Paper Strength in High-filled Paper

*Master of Science Thesis in the Master Degree Programme, Materials and  
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## Abstract

In order to improve optical properties, reduce the usage of cellulose fibres and save costs, fillers are usually added into furnish in the production of fine paper. However, the addition of fillers will have a negative influence on some paper properties such as paper strength.

In this project, polyelectrolyte complexes (PECs) made from a highly charged anionic carboxymethyl cellulose (CMC) and a lowly charged cationic polyacrylamide (CPAM) were introduced to the filler slurry prior to addition to the furnish aiming at maintaining the paper strength.

The produced PEC solutions were characterized by different techniques such as particle charge detector, optical microscopy, viscosity measurements, static light scattering, zeta potential, optical density, total organic carbon content, nuclear magnetic resonance, cryogenic transmission electron microscopy (cryo-TEM), flow cytometry, etc. In the end, several kinds of PEC solutions were used in filler slurries to produce paper sheets and these paper sheets were evaluated by internal bond strength and tensile strength measurements.

The produced PEC particles were around 500nm to 1µm and it was observed that by adding CPAM to CMC, more and more PECs were made until a certain ratio had been achieved, but after that, PECs stop to be formed. CPAM and CMC then seem to form a loose network in the solution surrounding the PECs. From the final paper characterization, it is evident that PEC particles have a big influence on the paper strength.

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## 1. Introduction

In the paper industry, there is an ever increasing need to find an approach to maintain paper qualities in the most economic way. One of the most common and convenient ways is to add fillers into the paper to substitute cellulose raw materials.

One of the fillers commonly used in paper industry is calcium carbonate, in the form of either ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). PCC is the most commonly used one thanks to its beneficial properties such as purity, narrow size distribution, uniform shape and large specific surface area. In addition to that, PCC can provide good brightness, opacity etc. Therefore, in this project, PCC was used as the filler. (G. Renaudin, July 2008)

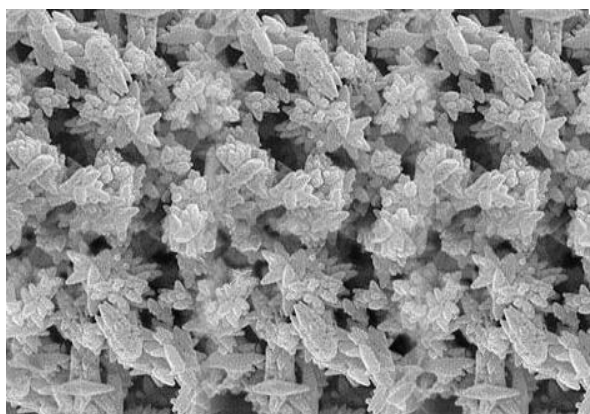


Figure 1. Structure of scalenohedral precipitated calcium carbonate (chememan.com, 2010)

Although the fillers are cheaper than cellulose fibers, the filler addition will negatively influence paper properties such as dry and wet strength. Generally, a cationic strength polymer is added in the wet end to increase the binding between fibers. In order to avoid detrimental influence of high filler contents on the strength of the fiber network, a filler pretreatment can be made and various approaches have been tested the last few decades. This work intended to assess a novel approach of using net anionic polyelectrolyte complexes (PECs) consisting of carboxymethyl cellulose (CMC) and cationic polyacrylamide (CPAM) as a binder together with cationic fixation agents. The idea was to form strong flocs of the filler particles to avoid a weakening of the fiber network. Moreover, cationic retention polymers in combination with silica nanoparticles were used to retain the filler flocs.

This diploma work was performed at Eka chemicals in Bohus as a continuation of a previous bachelor degree diploma work (Holmgren, 2010). Polyelectrolyte complex solutions were produced and characterized by different techniques, such as viscosity measurement, zeta potential, static light scattering etc. Moreover, lab manufactured paper sheets using PECs were also evaluated.

## 2. Materials

Carboxymethyl cellulose (CMC) with a weight average molecular weight of 340000g/mol and an average degree of substitution of 0.83 (Akucell AF 1985 from AkzoNobel) was used as the anionic polyelectrolyte in this project. Two different cationic polyacrylamides (CPAM) were used as cationic polymers and both of them consisted of 95 mol% acrylamide and 5 mol% diallyldimethylammonium chloride (DADMAC). The differences between these two polymers were the monomer residual, molecular weight and viscosity. In this diploma work, they are called CPAM1 and CPAM2, respectively. For CPAM2, only half of the added DADMAC monomers ended up in the polymer (making up 5 mol% of the monomer content in the polymer) while for CPAM1, all the DADMAC monomers stayed in the polymer during synthesis process. The molecular weights (Mw) of CPAM1 and CPAM2 were claimed to be 500,000g/mol and 1,000,000g/mol, respectively. However, the viscosity results (Section 4.4) indicate that CPAM1 has a much lower Mw than 500,000g/mol. In the following report, the PEC solutions made from CPAM1 and CMC are called PEC1 while the other ones made from CPAM2 and CMC are referred to as PEC2. The theoretical charge density of CMC is 3.6meq/g and the one of CPAM is 0.65meq/g. Close to these values, the experimental value of CMC was 4.14meq/g, and the ones of the two CPAMs were 0.71meq/g and 0.66meq/L, respectively.

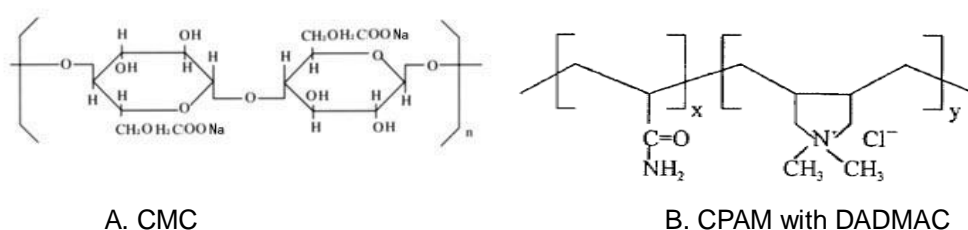


Figure 2. Structure of A. CMC (Carboxymethyl cellulose) (hengshui jiamu chemical co.,ltd, 2005-2010); B. CPAM (polyacrylamide) with DADMAC (diallyldimethylammonium chloride) (Li Ming Zhang, 2000)

The CMC solutions were made by adding the chemical in dry powder form into deionized water under agitation by a propeller and then the solution was filtered by filter paper to remove any undissolved polymer. CPAM stock solutions were diluted in deionized water to obtain the target concentration.

### 3. Methods

Most of the PECs in this project were made from 1wt% CMC and 2 wt% CPAM solutions but some other polymer concentrations were also studied. The PECs were generally prepared by pumping 2 wt% CPAM solution into 1 wt% CMC solution up to different final ratios (weight based) under propeller mixing using a syringe pump fitted with a plastic tube on the end of which a pipette tip was placed.

Other ways of making PECs were also tested, such as pumping 1 wt% CMC into 2 wt% CPAM, changing concentrations of both polymers, making PECs at different salt concentrations, etc.

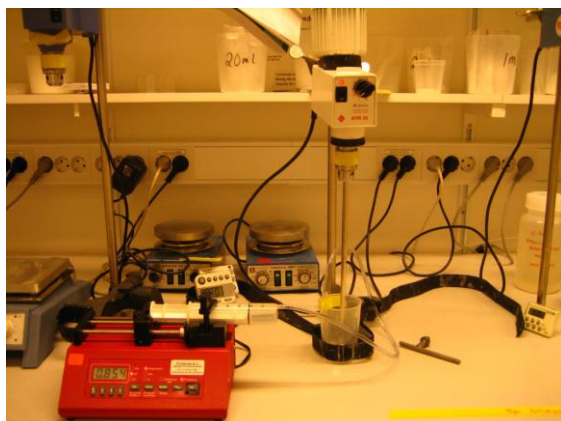


Figure 3. Setup for PEC production

#### 3.1 Particle charge detector (PCD)

A particle charge detector is used to measure the charge density or concentration of a polymer or a particle. The charge of a polyelectrolyte can be obtained by titrating in an oppositely charged polymer and, based on the quantitative electrostatic interaction between these two polymers, the neutralization point of the polyelectrolyte titration can be detected by a particle charge detector (PCD). A PCD equipment contains a reciprocating piston moving in a cylinder. The movement of the piston creates a current between two electrodes. When the polyelectrolyte in the solution is neutralized, its charge density can be calculated by the added amount of titrand.

In this project, poly (diallyldimethyl ammonium chloride) (PDADMAC) was used as the cationic titrand and PES-Na (sodium polyethylene sulphonate) as the anionic titrand.

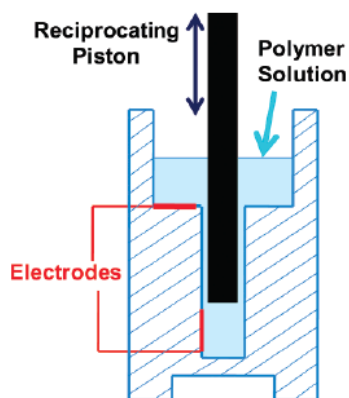


Figure 4. Diagram of particle charge detector (Robert Pelton, 2007)

#### 3.2 Microscopy

An optical microscope (CX41 Olympus) with a UPlan SApo 20X lens and equipped with a CCD camera and computer was used to study the visible polyelectrolyte complexes. Kromasil

particles (Kr-SiO<sub>2</sub>) of a well-defined size (3.5 µm in diameter) were chosen to be compared with the size of the polyelectrolyte complexes.

### 3.3 Viscosity measurements

Viscosity measurements are used to study the relation between an applied stress and the resulting flow of fluids. Viscosity is the internal resistance of a fluid to external shear forces. Greater internal resistance of the material requires greater forces to shear the fluid. Viscosity properties will generally be affected by several factors such as temperature and shear rate.

In this project, a rotation rheometer (Universal dynamic spectrometer, Physica UDS 200) with a cylindrical measuring system (Z2) was used to measure the viscosity of fresh samples (PECs, CMC and CPAM). The parameters were set as follows: temperature: 25°C, shear rate: from 1-1000 1/s and 1000-1 1/s.

### 3.4 Static light scattering

Static light scattering is a technique used to evaluate the size of particles in a dispersion. The basic principle in static light scattering is that the intensity of the light scattered by particles that are small enough is strongly dependent on the size of the particle. By measuring the intensity of the scattered light at various angles, information about the size of the particles scattering the incident light can be gained (E Vanden Bussche, 2004).

In this project, the instrument used was a Mastersizer Microplus from Malvern Instruments. The PEC solutions tested were freshly prepared and filtered with a 3µm syringe filter followed by degassing in vacuum. The solution was diluted in isotonic NaCl solution (with the same conductivity as the PEC solution) to maintain the obscuration (the percentage of light that does not pass) around 10% to 15%.

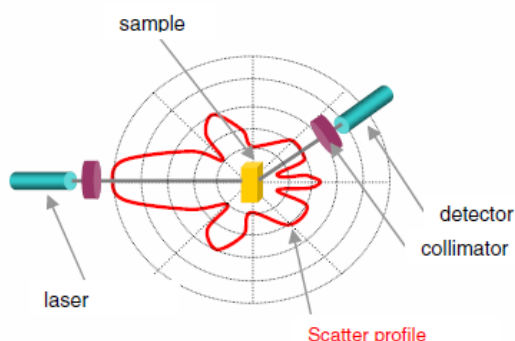


Figure 5. Basic principle of static light scattering (E Vanden Bussche, 2004)

### 3.5 Zeta potential

Zeta potential is the electrostatic potential at the slipping plane of a particle. This is dependent on ionization of surface groups, adsorption of counterions and the ion gradient out from the surface (Figure 6). The properties of the layer with these charges around the particles are different from the bulk surrounding, and it can move with the particle through the bulk solution. By measuring the velocity of the particles in an electrostatic field, the zeta potential value can be calculated (malvern.com, 2011). Highly charged particles will move faster than less charged ones in one direction.

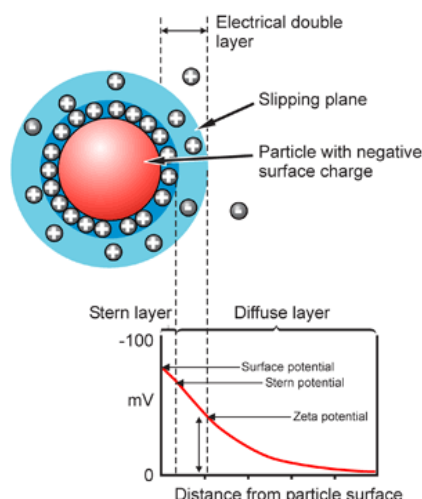


Figure 6. Scheme of Zeta potential (malvern.com, 2011)

A Zeta master from Malvern Instruments was the instrument used in this thesis work. PEC solutions were diluted 10 times in isotonic NaCl solution and the pH of all the samples is around 7.5.

### 3.6 Centrifugation

Centrifugation is a very common way to separate materials of different densities. A high spinning speed creates an external centrifugal force to force denser material to move towards the bottom of the centrifuge tube and the rest of the solution becomes supernatant (Clarke, 2009). The speed of rotation and time of centrifugation are the major parameters affecting the centrifugation.

PEC solutions were diluted for 5 times or 10 times in isotonic NaCl solution and centrifuged for certain times to obtain pure PECs with less free polymers by using a centrifuge from Hettich Rotixa.

### 3.7 Optical density

Optical density is a way to measure the absorption and scattering of light through a sample. It can be used to estimate the relative amount of particles in a solution between two samples with the same components. The optical density is otherwise influenced by parameters such as particle structure and size (learnquebec.ca, 2011).

### 3.8 Total organic carbon

Total organic carbon is a way to determine the content of organic carbon in the sample by oxidation. Carbon dioxide formed by carbon in the sample diffuses into the indicator solution and then the change of the color in the indicator will be evaluated and transformed into carbon concentration in the sample (hach-lange.co.uk, 2011).

Due to the limited range of analysis (30-300mg/L), all the samples were diluted 10-100 times with deionized water.

### 3.9 Flow Cytometry

Flow Cytometry is a technique to characterize particles, commonly used for cells. The sample is carried by a solution through a flow chamber where it passes a laser beam. Generally, the samples need to be diluted in order for the particles to pass through a light beam one by one, see Figure 7. The emitted signal will be collected and transferred to an electric signal in the computer. Relative particle sizes and number of particles in the solution can be studied (Akzonobel).



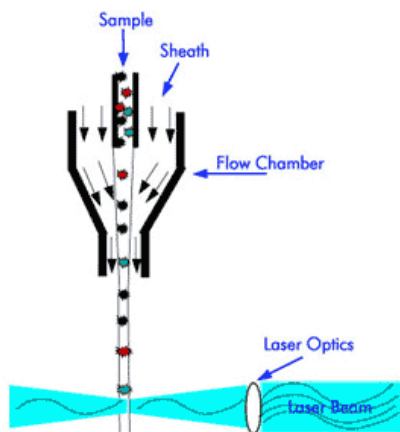


Figure 7. Scheme of flow cytometry (Akzonobel)

There are two detectors to detect the scattered light, a forward scattering light detector (FSC) and a side scattering light detector (SSC). As Figure 8 suggests, both SSC and FSC are related to the size of the particles while SSC may also give information about the internal structures and granularity.

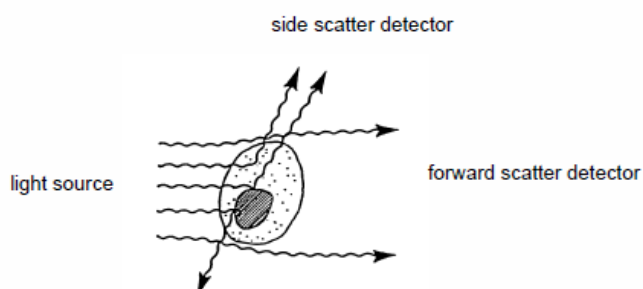


Figure 8. Scheme of light scattering (Introduction for Flow Cytometry: A Learning Guide, 2000)

Various dyes can associate with particles to make them fluorescent and thus absorb light in a certain range of wavelength and emit light at a longer wavelength. Therefore, the specific particles can be detected and characterized by the intensity of the fluorescence. A 1ml diluted PEC2 sample with an addition of 20µl propidium iodide (40ppm) was studied. The dilution ranged from 10 times to 100 times.

### 3.10 Nuclear magnetic resonance (NMR)

NMR is a technique based on the absorption and re-emission of electromagnetic radiation by magnetic atomic nuclei of molecules in a magnetic field to study the chemical structure (muniche.linde.com). These experiments were performed in the Swedish NMR Center in Gothenburg using a Varian INOVA 800 NMR spectrometer.

### 3.11 Cryogenic-Transmission Electron Microscopy (Cryo TEM)

Cryo TEM is a technique to characterize the structure of a specimen, especially for sensitive samples such as colloidal and biological samples. In cryo TEM as in all TEM techniques, an electron beam passes through the sample and then the image is collected by a computer. The unique feature of Cryo TEM is that the sample is frozen (extremely rapidly) and thus the natural environment of the sample can be kept and it does not require the sample to be fixed and/or stained by other chemicals.

The sample is prepared by deposition onto a holey membrane film. The sample will be embedded into the holes and the excess of liquid can be absorbed in a wipe to obtain a thin

sample film. Then the sample is vitrified at a very low temperature (e.g. in liquid nitrogen) (Bagshaw)

### 3.12 Dynamic sheet former

A dynamic sheet former is a device to produce paper sheets in laboratory scale. The principle of the dynamic sheet former is similar to paper machines in the industry. In this work, a stock consisting of cellulose fibers, filler slurry, fixation agents, a cationic strength polymer and retention chemicals was first prepared and then sprayed onto a plastic web in a rapidly rotating drum. The paper sheet is formed on the plastic web as most of the water is drained through this web in the machine. After that, 2 and 6 bar pressures were applied on the paper sheet in between blotting papers to further dry the sheet, enable separation from the plastic web and also to increase the paper's density. In the end the paper sheet was dried in an oven to get the final dry paper sheet.

Due to the slightly non-uniform distribution of furnish on the plastic web, the same section of each paper sheet was characterized and compared with each other.

### 3.13 Ash content determination

Ash content determination is used to measure the filler content in the paper sheet. The paper sheet is placed in an oven at 105°C to get rid of all the water followed by another oven at 925°C. This high temperature will burn all the material except the filler, thereby allowing the filler content to be calculated.

### 3.14 Tensile strength

A tensile strength test measures the maximum load that a material can withstand before rupture in the axial direction under an applied force. Due to the variation of tensile strength in the different directions of the paper sheet, paper samples are measured in both the machine direction and the cross direction and the test is repeated several times (6 times for machine direction and 5 times for cross direction) to get the average values.



Figure 9. Scheme of tensile strength experiment

### 3.15 Internal bond strength (Scott Bond)

The internal bond strength test is a method to test the strength of the paper in the z direction (perpendicular to the plane of the sheet), which is an important property in fine paper. A test sample was pressed between a metal block and an L-shaped metal piece and between two double sided adhesive tapes (see Figure 10). The paper sheet was delaminated by the L shaped piece when knocked by a released pendulum. The internal bond strength is calculated from the loss of potential energy in the pendulum and expressed with the unit J/m<sup>2</sup>. Each sample is cut and used to perform 5 tests.

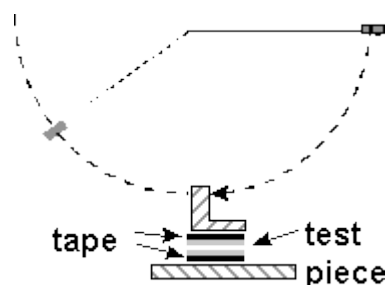


Figure 10. Scheme of internal bond strength experiment (Furst, 2011)

## 4. Results and discussion

This project was performed as a 20 weeks Master's Thesis work. In the first 2 months, only CPAM1 was available, so different kinds of PEC1s were prepared and characterized. However, this kind of PECs was very unstable, which will be discussed later in this chapter. In the latter 3 months, CPAM1 was replaced by CPAM2 to make PEC2s which were much more stable. In this chapter, both types of PECs are discussed.

The quoted ratios of polymer solutions to make the PECs are, unless otherwise stated, the grammages of 2% CPAM to 1% CMC solutions. For example 40:80 PECs means 40g 2% CPAM was pumped into 80g 1% CMC.

### 4.1 Microscopy

In a previous diploma work, PECs made from the same CMC and similar CPAM polymers had been proven to be bright spherical structures as observed in bright field microscopy (Holmgren, 2010). In this diploma work, PECs were also observed as bright spheres in the microscope. However, when the PECs get slightly out of focus, they turn into dark dots instead (see Fig. 11B). The irregular shadows seen were dust particles from slides and lens.

Different weight proportions of CPAM1 was pumped into CMC (2% CPAM: 1%CMC = 30:60; 60:60; 90:60; 120:60). Figure 11 shows that, by increasing the amount of CPAM1, more and more PECs were created until the ratio of 90:60. Instead gel-like structures appeared in the image, and at a ratio of 120:60, extensive aggregation of PECs had started. Therefore, it suggests that PEC1s were formed up to 60:60 and after that extra polymer becomes free polymers surrounding the PEC1s, or associates in structures invisible in the microscope, instead of forming more PEC1s. After a certain ratio has been achieved, aggregation appears. It may be explained by more and more CPAM1 binding to PEC1s, which lower the total charge of the particles and thus the electrostatic repulsion is reduced.

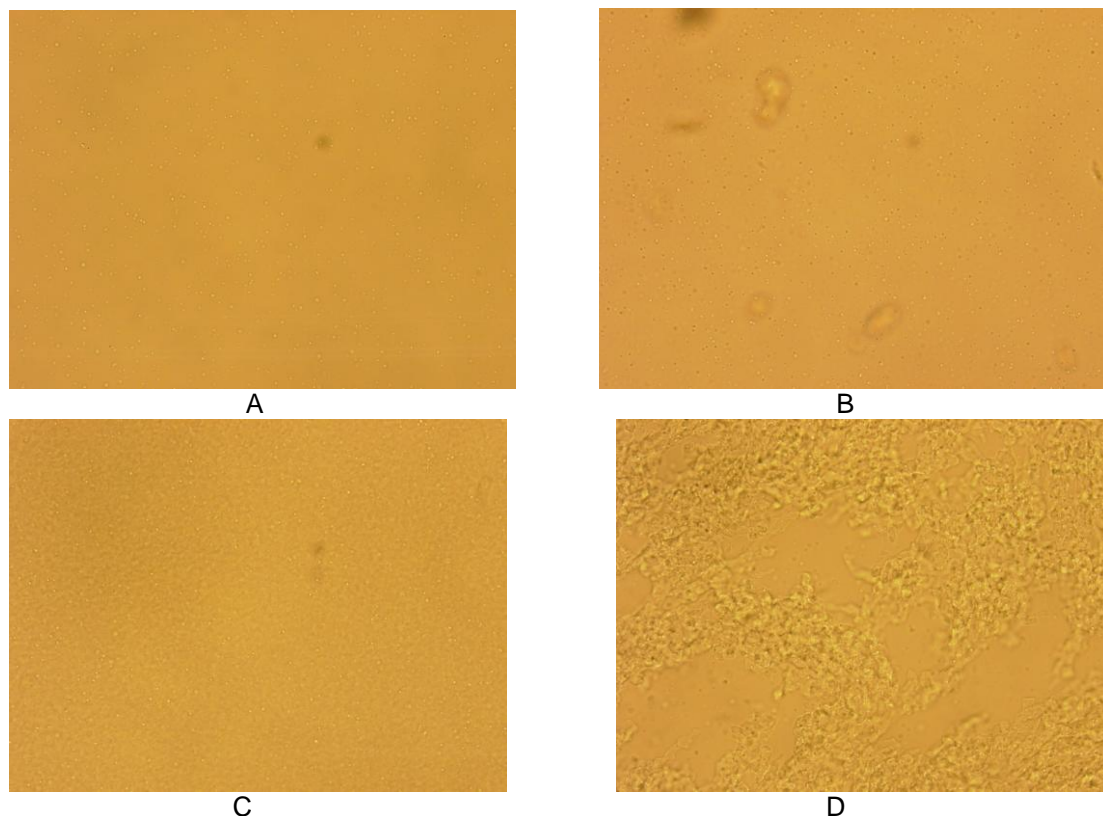


Figure 11. Bright-field microscopy pictures of PEC1s. Different ratios of 2% CPAM1: 1%CMC (A. 30:60; B. 60:60; C. 90:60; D.120:60)

In order to study the formation of PEC1s, various PEC1 production parameters were tried, such as changing pumping rate, propeller rate, pipette opening diameter and the pumping order of CMC and CPAM1. In contrast to the pumping rate and pumping order of polymers, propeller rate and pipette tip opening size did not influence the PEC1s size. Figure 12 shows the influence of various pumping speed to 60:60 PEC1s.

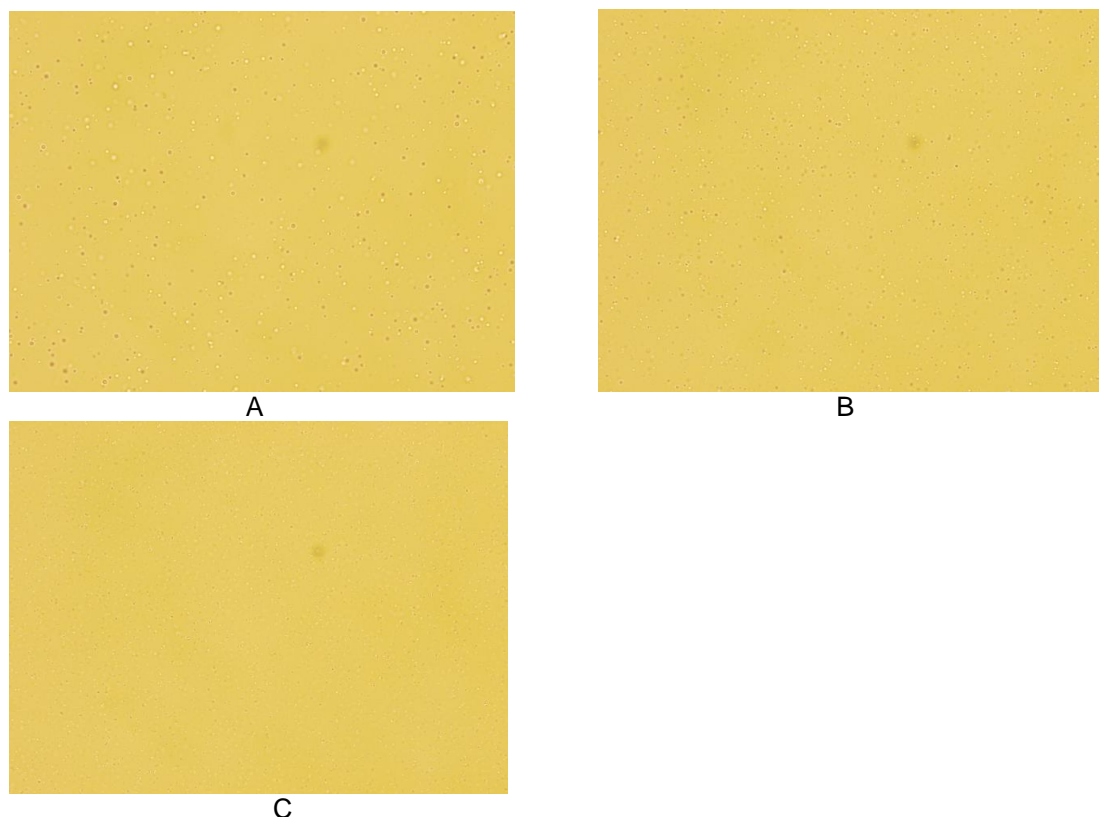


Figure 12. 60:60 PEC1s with different pump rates (A. 0.5ml/min; B. 3ml/min; C. 15ml/min)

From Figure 12, it is obvious that PEC1s becomes bigger with decreased pump rate. If CMC was pumped into CPAM1 (pump order was reversed), no PEC1s could be found in the microscope.

Among PEC1 samples, there exists a big problem that PEC1s would aggregate after a few hours. However, with a certain extra addition of CMC, the aggregated PEC1s returned to individual PEC1s again. It suggests that free CMC adsorbs to the PECs, thereby stabilizing them according to zeta potential results (section 4,3).

PEC2s have a smaller size and narrower size distribution in comparison to PEC1s. Using well-defined  $\text{KrSiO}_2$  particles as reference, the size of PEC2s could be estimated to range from 500nm to  $1\mu\text{m}$  while PEC1 had a much bigger size range, from  $1\mu\text{m}$  to  $2.5\mu\text{m}$ . These kinds of PEC2s can be stable for one week and then slight aggregation starts. The attraction between aggregated PEC2s was not as strong as for the PEC1s so the aggregated PECs could easily be disaggregated by stirring again.

Different ratios (60:60, 50:70, 40:80, 30:90, 20:100, 10:110, 2:118) of PEC2s were also made and diluted with isotonic salt solution (same conductivity as PEC2 solution) in order to make pure PECs (section 4.9). The results (Figure 13) show that in the very beginning of CPAM2 addition (2:118), blurry and big spherical PEC2s were formed first and then smaller and more distinct spherical PEC2s were formed up to a certain ratio (10: 110) (the PEC2s formed initially transformed into this structure as well). After that almost no more spherical PEC2s were formed.

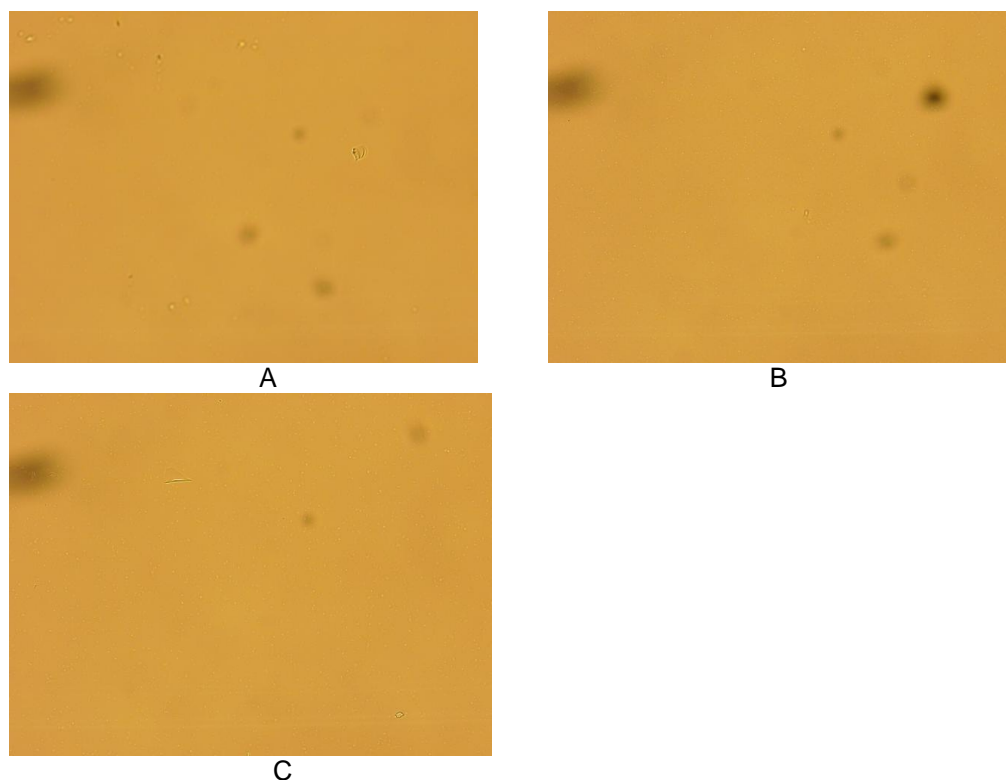


Figure 13. Different ratios of 2% CPAM2: 1%CMC (A. 2:118; B. 10:100; C. 40:80)

The size of the PEC2s at different ratios did not vary much and all the PEC2s could be diluted by isotonic salt solution except 60:60 and 50:70 ones (extensive aggregation). Different concentrations of salt solution were tried to dilute 60:60 and 50:70 PEC2s but none of them gave a satisfactory result. Compared to the PEC2s with other ratios, 60:60 and 50:70 PEC2s probably have less electrostatic repulsive forces.

In order to prove the assumption of the effect of free polymer, various amounts of CMC were added into the 60:60 PEC2 sample followed by dilution with isotonic salt water. After a certain amount of CMC addition, 60:60 PEC2 solutions can be diluted and individual PEC2s was observed in the microscope. It strongly suggests that free CMC may associate with PEC2 particles and then affect the charge of PEC2s.

To study the concentration influence on PEC2 formation, solutions from 0.2% CPAM2, 0.1%CMC and from 3% CPAM2, 1.5% CMC were prepared. The first solution had no visible PEC2 particles while the PEC2 particles from the second solution were of the same size and number as PEC2s with the ordinary concentrations of polymers, according to the microscopy.

Different salt concentrations in the PEC2 solutions were also tried, in order to find an efficient way to increase the yield of PEC2 particles in the solution. A higher concentration of salt in the solution was obtained by dissolving CPAM2 and CMC in 0.06mol/L and 0.2 mol/L NaCl solutions instead of deionized water. Moreover, a dialysis tube was used to get salt free CMC and CPAM2 solutions. The solutions made from polymers in the 0.2mol/L NaCl solution had no visible PEC2 particles. This may come from too high salt concentration weakening the attraction between oppositely charged polyelectrolytes. The one made from polymers in the 0.06mol/L NaCl had gel-like PEC2 structures but strangely, after dilution, individual PEC2s were found. Moreover, the ones made from dialyzed polymers had also the same amount of visible individual PEC2 particles as in the non-dialysis case.

#### 4.2 Cryogenic -Transmission Electron Microscopy (Cryo TEM)

The Cryo-TEM method was used to characterize the structures of a PEC2 solution. Here, PEC2s with the ratio 40:80 was studied. From the Cryo TEM images, a clear contrast between the surrounding water solution, the “free” polymers and PEC2 particles can be seen (Figure 14A and B). This is probably due to polymer-adsorbed counterions. The black polygon



is regarded as PEC2, although it is not as spherical as the one in the microscope, which is likely due to the low resolution of the optical microscopy. Figure 14A suggests that PEC2 particle has a loose structure (contain a lot of water) since the polymer network can be seen though PEC2 particle. Moreover, there is a network structure around the PEC2s, probably originating from surplus CMC and CPAM2. Because of the Cryo-TEM sample preparation process by drying out of the water, some parts of this network are more concentrated than the others. The size of the PEC2 particles is around 600nm.

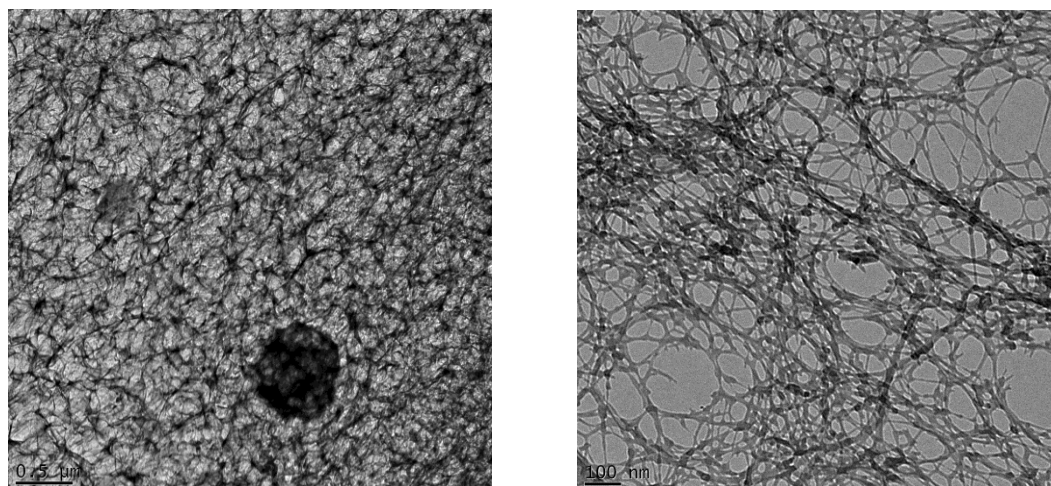


Figure 14. Cryo-TEM images of A: 40:80 PEC2 particle; B. associated polymer network

#### 4.3 Zeta potential

Zeta potential measurements are a way to estimate the charge of PEC particles by measuring the velocity of the particles in an electric field. The zeta potential is dependent on parameters such as ionic strength and pH.

Due to the relation between zeta potential and repulsive forces between particles, this technique can also be used to characterize the stability of the system. A higher charge will give a more stable colloidal system and vice versa.

The PEC1s exhibit a moderate zeta potential value (-25mV) and with addition of CMC, the value increased to -41.7mV. This also agrees with the microscopy observation carried out regarding the stability. PEC1s with CMC addition were more stable than the ones without CMC addition.

PEC2s have higher values in comparison to PEC1s, as seen below (Table 1), which is the reason why they are more stable. Moreover, the zeta potential decreased by increasing the ratio of CPAM to CMC in the PEC2 solution. It tells us that the proportion of CMC and CPAM2 in the PEC is related to the original addition of CMC and CPAM2 in the PEC solution.

sample	Mean(mV)	Cond(ms/cm)
PEC2 =20:100	-58,6	1,612
PEC2=30:90	-55	1,614
PEC2=40:80	-53,5	1,632
PEC1=60:60	-27,4	1,727
PEC1 with CMC addition	-41,7	1,74

Table 1. Zeta potential values of PECs

#### 4.4 Optical density

Optical density measurements can be used to compare the amount of polyelectrolyte complexes in the solution provided that PEC samples have the same properties. The more turbid the solution is, the more polyelectrolyte complexes are present in the polymer solution. Figure 15 describes the optical density at different ratios of PEC2s. In the beginning of CPAM2 addition to CMC, the optical density is very low followed by a sharp increase. After a certain ratio of CPAM2 and CMC, the optical density becomes constant. Combined with the observation in the microscope, it indicates that no PEC2s are made in the beginning of the CPAM addition. Then distinct spherical PEC2s start to be created after a certain addition. When the ratio goes to 5:40, spherical PEC2 stopped to be formed.

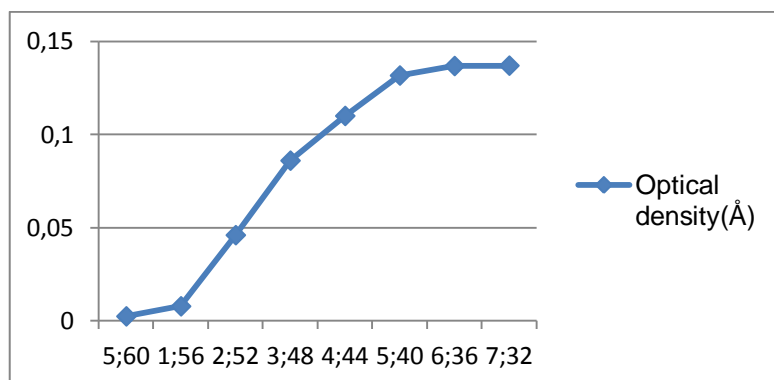


Figure 15. Optical density at different ratio of CPAM2 and CMC in PEC2s

#### 4.5 Viscosity measurements

Compared to the CPAM2, CPAM1 has a very low viscosity, close to the viscosity of water. That indicates that CPAM1 has a much lower Mw than the claimed value (500,000g/mol) (Figure 16). Both of the curves strive upwards at high shear rates due to turbulence.

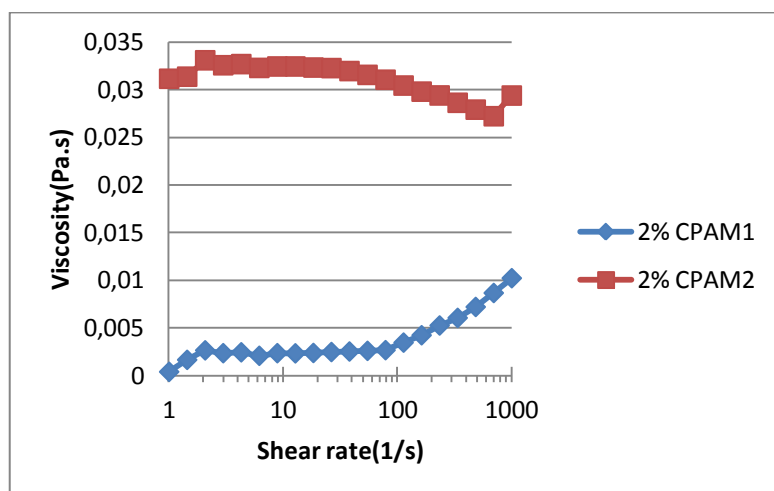


Figure 16. Viscosities of 2wt% CPAM1 and CPAM2

Figure 17 shows that the 60:60 PEC2 sample has a much higher viscosity than 0.5% CMC (these two samples have the same amount of CMC). It indicates that PEC particles combined with the network of “free” polymers enhance the viscosity of the samples. Moreover, the viscosity of the 40:80 PEC2 is higher than the one of the 60:60 PEC2 samples. It shows that the viscosity decreases with addition of CPAM2 into the solution. It is already known that at addition of CPAM2 after a certain ratio, no more PEC2 were created according to observation in the microscope. It indicates that at addition of CPAM2, it associates with CMC to become PEC2 particles or networks in the solution up to a certain ratio. After that, CPAM2 added will be free in solution which then merely dilutes the solution and thus reduces the total viscosity.

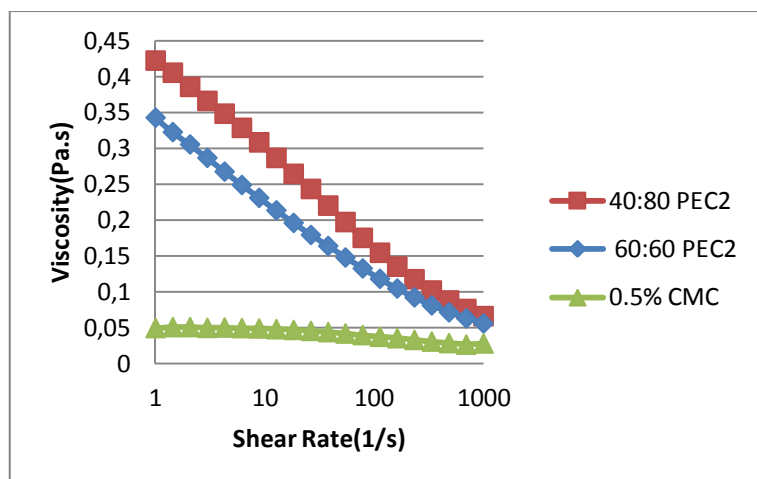


Figure 17. Viscosity of PEC2 solutions with different composition ratios (60:60, 40:80) and 0.5% CMC

#### 4.6 Static light Scattering

Static light scattering is usually used to characterize the size of particles or polymers in dispersion. Here, PEC1s and PEC2s with a ratio of 40:80 were studied. The solutions were filtered with a 3 $\mu$ m syringe filter and degassed by vacuum to remove other particles and air. Dilution was also performed with isotonic salt water until the obscuration value reached 15%. The refractive index was assumed as the average value of the ones of CPAM and CMC. It can be seen from Figure 18 that the peak of PEC1s is around 2 $\mu$ m while the one of PEC2s is around 1,5  $\mu$ m. Size distributions of both of them are narrow. The other peak around 1000  $\mu$ m in the PEC2s can be due to air bubbles still present in the solution.

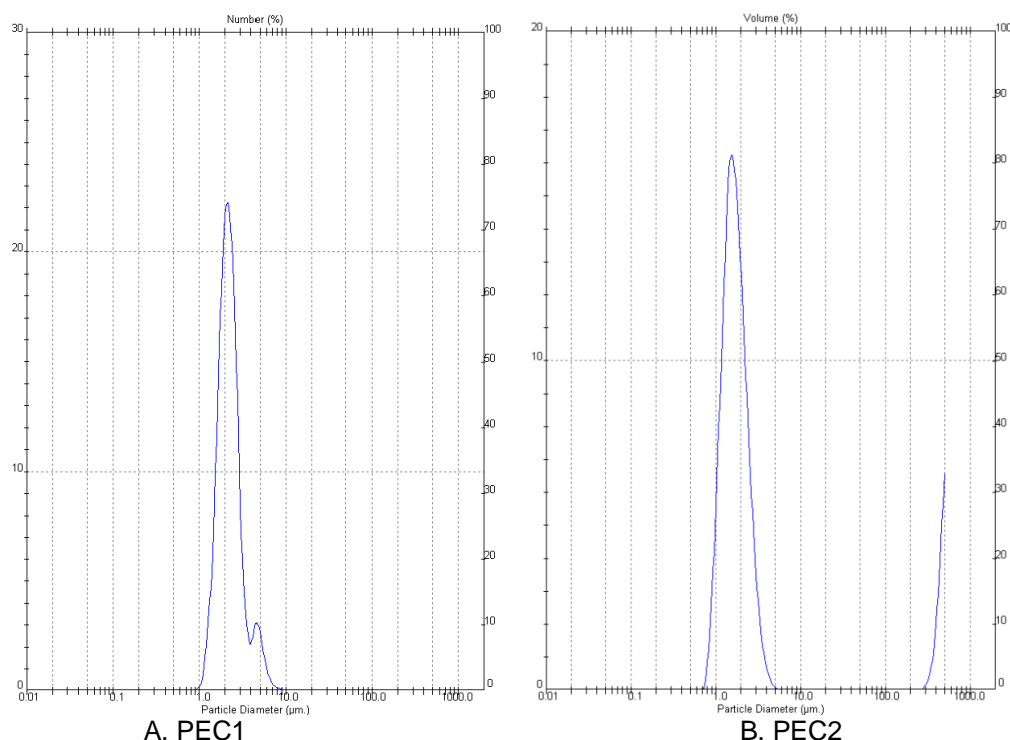


Figure 18. Static light scattering of A. PEC1 and B. PEC2

These results suggest a little bit bigger PECs than observed in the optical microscopy. This may be due to the assumption of refractive index. Possibly, a refractive index close to the one of water should be chosen because PEC particle contains a lot of water (see Section 4.2). Furthermore, the addition of CMC to PEC1 did not affect the size of PEC1 (still around 2  $\mu$ m).



#### 4.7 Flow Cytometry

Flow cytometry was used to try to estimate the size and number of PEC2s in the solution. Since the scattering intensity is proportional to the size of the particles, Figure 19 shows that the size distribution is very narrow which corresponds well to the static light scattering result. Compared to SLS on the Malvern instrument used in this diploma work, flow cytometry has an advantage in that it only needs a small amount of sample and each particle is observed once it passes through the light beam. However, in this project, the exact size of the PEC2s is hard to determine by this measurement due to the lack of calibration curve for PEC2 particles.

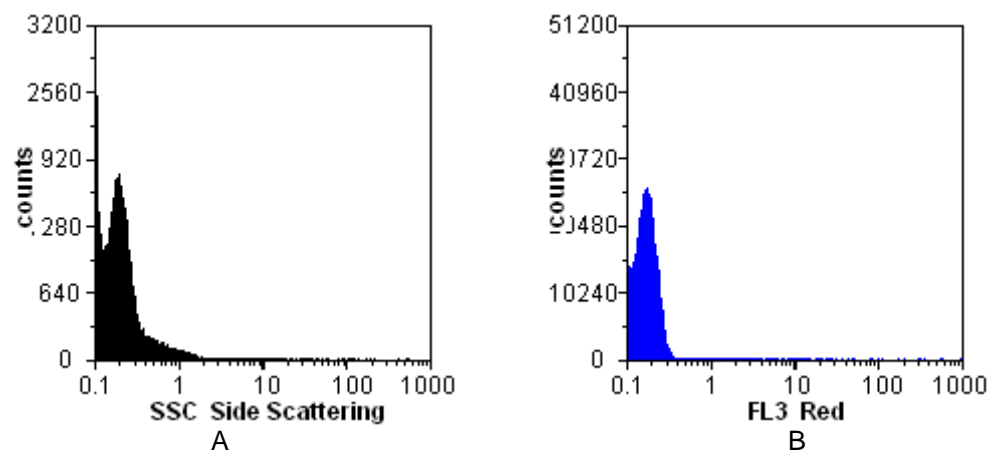


Figure 19. Flow cytometry study performed on 1ml 40:80 PEC2 solution with 0.02ml propidium iodide. A. numbers of PEC2 particles with different intensity of side scatterings; B. numbers of PEC2 particles with different intensity of red fluorescents

In order to distinguish PEC2 particles from other kinds of particles and estimate the number of PEC2 particles, various dyes were tried and finally propidium iodide was found to be a suitable dye which associated with PEC2 particles, probably predominantly by interaction with the CMC.

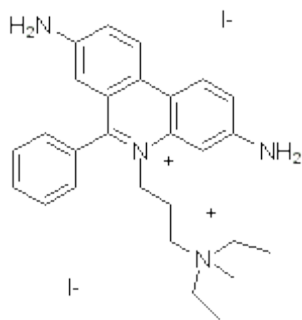


Figure 20. Chemical structure of Propidium Iodide (Marker Gene Technologies, Inc, 2011)

Experiments were made to try to measure the number of PEC2 particles, but inexplicably, the number of particles measured did not change at different dilutions of the solution. Probably, this was due to that at all concentrations tested here, the concentration was too high, which made the PEC2 particles overlap in the detection.

#### 4.8 Nuclear magnetic resonance (NMR)

In this project, NMR spectroscopy was used to try to estimate the amount of free polymers around PEC2s. Compared to the low mobility of PEC particles in the solution, the chains of free polymers have a higher mobility which gives an NMR signal. Moreover, the amount of free polymers should be possible to calculate by integrating the peak area and compare it to the pure polymer solution. The concentration of pure polymer solution can theoretically be determined by relating it to a reference compound (e.g. 1mM 4, 4-dimethyl-4-silapentane-1-sulfonic acid (DSS)). This reference chemical will not interact with CMC and CPAM2, which

makes the comparison possible.

The spectrum of the reference compound is as follows (Figure 21). The peaks at 3.1ppm, 1.9, 0.8 and 0 came from DSS and the peak at 4.8ppm was from water.

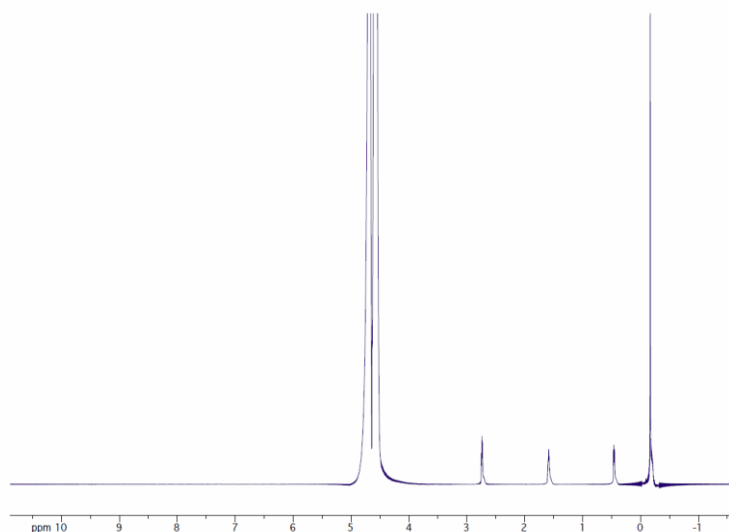


Figure 21. NMR spectrum of 1mM DSS in H<sub>2</sub>O

It is clear that in the CMC spectrum, there is a broad range of peaks between 3ppm and 4.5ppm (see Figure 22). The carboxymethyl group contributes with the sharpest peak in this area because it is not on the backbone of the polymer and thus is more flexible compared to the other parts.

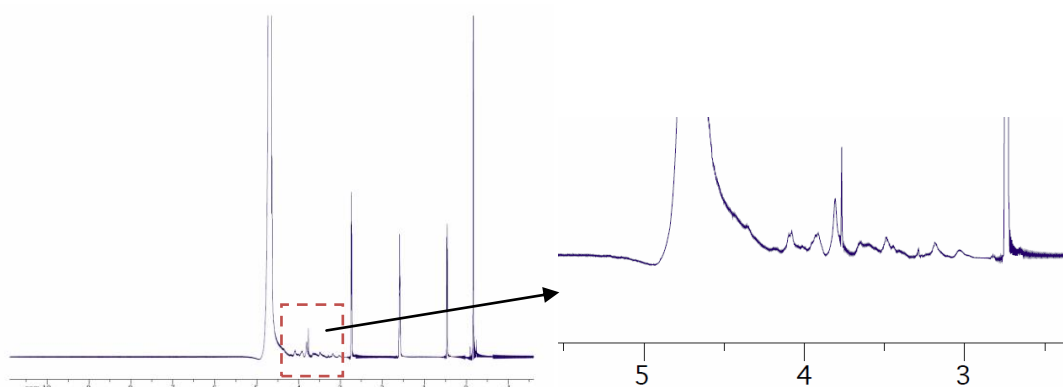


Figure 22. NMR spectrum of 1% CMC with DSS reference

2% CPAM2 was filtered using a 30K MWCO (molecular weight cut off) filter tube by centrifugation to distinguish polymer peaks from monomer and reaction by-product peaks. Monomers and by-products can pass through the filter but not the polymers. From this experiment, monomer peaks were determined around 5.5ppm to 6ppm and 3.5ppm to 3.8ppm (Figure 23). Except for the DSS reference peaks, the rest comes from CPAM2 polymers. Compared to the CMC spectrum, the CPAM2 peaks are sharper due to the higher mobility of the polymer chains.

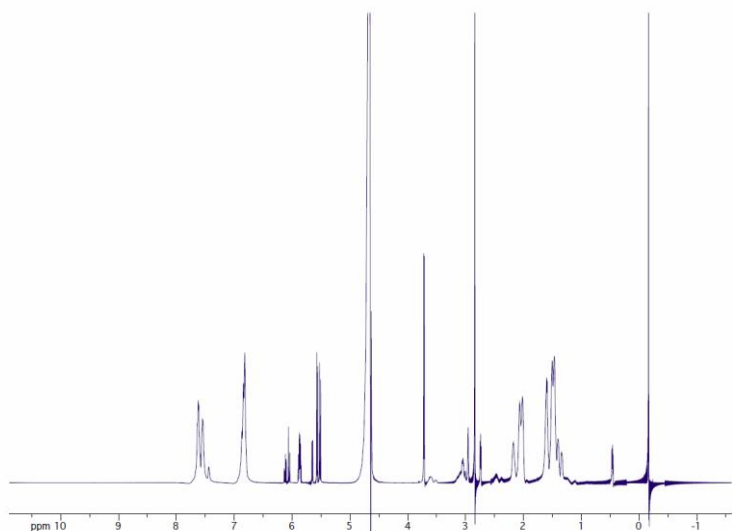


Figure 23. NMR spectrum of 2% CPAM2

PEC2s with different ratios (2:118, 10:110, and 20: 100) were also measured by NMR. All PEC2 spectra indicate that both flexible CPAM2 and CMC are presenting fairly mobile in the solution. Even though polymers do not form PEC2 particles, part of them shall associate with each other to become networks in the solution and the spectra of PEC2 solution shall be significantly lower. One possible explanation is that CPAM2 and CMC interact in a way that they still appear as free polymers in NMR. That agrees with the observation in the microscopy and centrifugation that after a certain addition of CPAM2 into CMC, no more PEC2s were formed and also after centrifugation, very little turbid phase sediment to the bottom of the bottle.

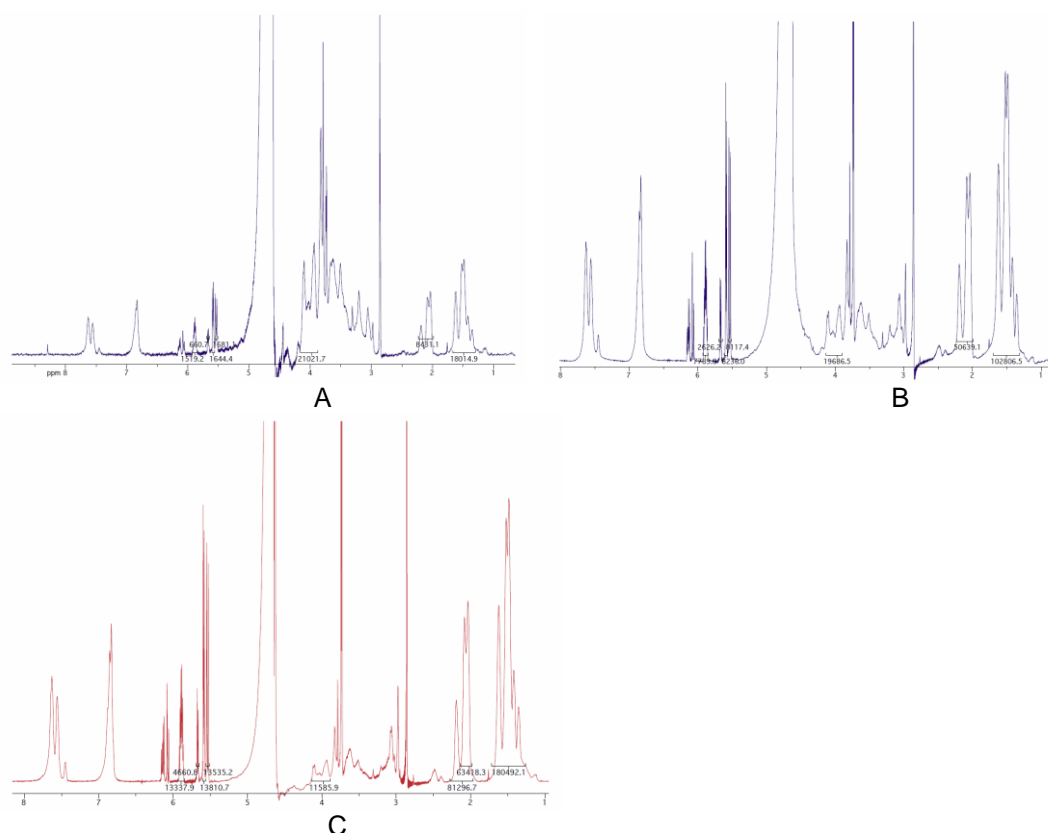


Figure 24. NMR Spectra of PECs with different ratios of CPAM: CMC (A. 2:118, B. 10:110, C.20:100)

Figure 24 shows that by increasing the addition of CPAM2 in the PEC2 solution, the amount of free CMC gradually decreases. PEC2s with ratio 60:60 has the least amount of free CMC compared to the others.

In the microscopy result discussed above, the order of addition influenced whether visible PEC2s could be formed. Therefore, the NMR spectra of 40:80 PEC2 solutions with different order (CPAM2 pumped into CMC or CMC pumped into CPAM2) were also studied to see the difference of the PEC2 formation.

The spectra of these two solutions are almost the same. It suggests that other kinds of structures of polyelectrolyte complexes instead of the visible spherical PEC2s are made by reversed pumping order (CMC pumped into CPAM2). The compositions of these two types of PEC2s are the same.

In order to know the exact amount of free CPAM2 and CMC in the solution, the areas of polymer peaks were integrated and compared with the DSS reference. However, the signals from both CMC and CPAM2 were much lower than they were supposed to be. One explanation could be that CMC peaks (3-4.5ppm) are too close to H<sub>2</sub>O peak (4.5 ppm) which will influence the spectra of the CMC hydrogens. Nevertheless, it is still hard to explain why the polymers signals are much lower than they are supposed to be.

#### 4.9 Centrifugation

PEC2 particles settled to the bottom after approximately one week. The PEC2 particles with some free polymers will form a turbid phase at the bottom of the bottles. The volume percentage of turbid phase in the 40:80, 30:90, and 20:100 PEC2 solutions are around 20%, 15% and 10%, respectively.

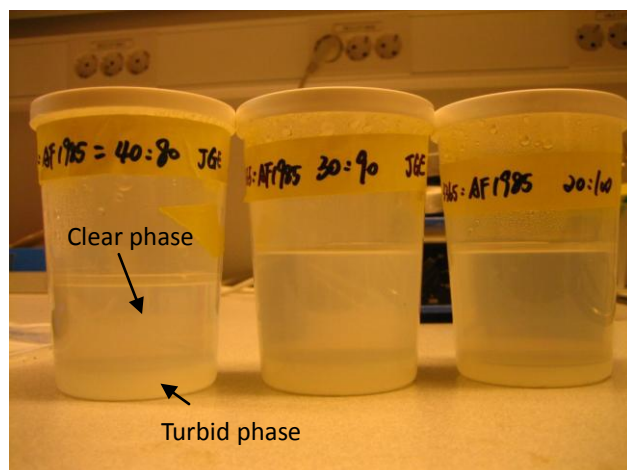


Figure 25. Phase separation of PEC2s with different ratios

Since it could prove advantageous for the paper strengthening effect to be able to increase the yield of PEC2 particles in the solution, it was considered to be of interest to try to prepare pure PEC2 samples (without “free” polymer) from the PEC2 stock solution. Thus, centrifugation was used aiming to accelerate the speed of sedimentation to obtain a pure PEC2. Non-diluted PEC2 solution did not, however, exhibit sedimentation even at 5800rpm for 60 minutes. It may be because with time, slight aggregation of PEC2 particles causes larger structure of PEC2 particles to sediment to the bottom of bottle. Therefore, PEC2s were instead diluted by isotonic salt solution followed by centrifugation. Polymers that did not form PEC2s stayed in the clear upper phase and were removed later. After centrifugation, PEC2s were redispersible into individual PECs to be used in the filler slurry preparation.

Different speeds and times of centrifugation along with various dilutions were tested using PEC2s at different ratios (40:80; 10:110; 2:118). 40:80 PEC2s were redispersible even after two times centrifugation while 2:118 solutions had almost no visible turbid phase. Although 10:110 PEC2s did have a turbid phase after the first centrifugation, these PECs could not be dispersed again (irreversible aggregation). Therefore, it was tested to add 10µl of 0.1M NaOH

into 10g 10 times diluted 10:110 PEC2s solution to change the pH prior to centrifugation. The addition of NaOH did improve the redispersibility of 10:110 PEC2s, but not enough to produce pure, dispersed PECs (without free polymer).

#### 4.10 Total organic carbon (TOC)

The carbon content of the PEC2 samples was measured by TOC. According to the polymer structures, the carbon content in the CMC is 51.6wt% and in the CPAM2 it is 40wt%. PEC2 particles were assumed to have the same polymer composition as the total polymer content in bulk solution.

In order to remove as much as possible of the free polymers in the solution and then estimate the composition of the PEC2 samples ("free" and PEC polymer), a 40:80 PEC2 solution was first diluted with isotonic salt solution for 5 times and centrifuged at 4000rpm for 60 minutes to spin down the PEC2 particles. The turbid phase was regarded as PEC2 particles with some free polymer and the clear phase as free polymer solution. Then the clear phase was removed and turbid PEC2 solution was diluted 10 times again. Then this solution was centrifuged at 2000 rpm for 60mins again in order to minimize the amount of free polymers surrounding the PEC2 particles. Finally, very little turbid phase was left and this 2nd centrifuged turbid phase was collected for TOC measurement.

The range of measurable TOC values was between 30mg/L to 300mg/L, so the centrifuged turbid phase was diluted 50 times for TOC measurement. From the calculations made in the TOC, around 14% of the total amount of polymers could be estimated to form PEC2 particles. TOC shows that the polymer content of the pure PEC solutions is very low (<0.6%), but in the microscope, it can be observed that the PEC particles are packed close to each other. Therefore, it strongly suggests that a large fraction of the PEC2 particles is water (>90%)

#### 4.11 Paper strength evaluation

Paper strength evaluations such as tensile strength index and internal bond strength determination were used to characterize the final paper properties. Several reference samples were used to compare with the slurries containing PEC2s. The general idea for this experiment was to see the effects of the different filler preparations on the paper strength. The "Ref" was a filler slurry only consisting of PCC filler without any fixation agent and binder. All the other slurries contained cationic fixation agents to help the CMC or PEC2s to bind to the filler. "CMC Ref" was a technical quality CMC with a weight average molecular weight of ~600,000 g/mol, while "CMC" was the CMC used to make the PECs.

Two PEC2-containing slurries with different ratios of CPAM2 and CMC (40:80 and 5:55) were compared. Moreover, "40:80 PEC2 clear phase" came from the preparation of "40:80 PEC2" but was the clear phase obtained upon sedimentation of the PEC2s to the bottom of the sample upon standing for a long time. Apart from the pure PEC2 samples, the different slurries have the same amount of total polymer in the filler slurry (10kg/ton).

In order to know the influence of pure PECs on the paper properties, 40:80 PEC2 solutions were diluted and centrifuged to get the pure PECs without free polymers. Different amounts of the pure PEC2 solutions (17.8kg/ton, 8.9kg/ton, and 1.06kg/ton) were added to the filler slurry to evaluate their influence on the paper strength.

#### 4.12 Tensile strength

Figure 26 shows that with increasing filler content, tensile strengths gradually decrease in all samples. "Ref" has the lowest tensile strength compared to the others.

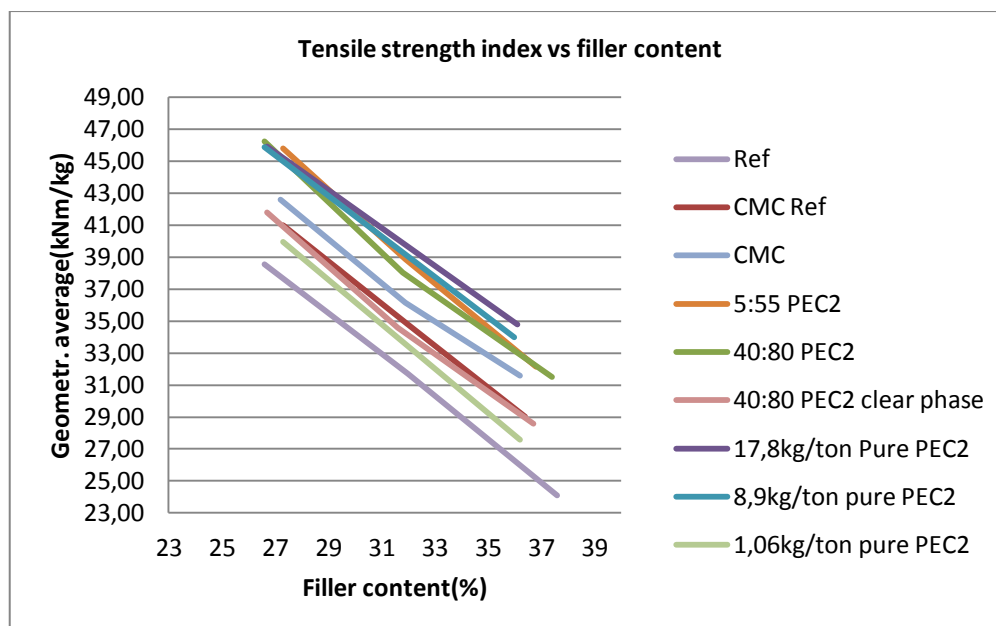


Figure 26. Tensile strength index vs. filler content

The “CMC” sample has a higher strength value than the “CMC Ref” sample, which may be due to its higher purity. It is obvious that all the PEC samples but the “1,06 kg/ton pure PEC2” have a significantly higher tensile strength than the pure CMC samples which shows that PEC particles have a big influence on the tensile strength.

In the microscopy observation, 5:55 and 40:80 PEC2 samples have the same amount of PEC particles and in this figure (Figure 26), these two samples show a similar value. Moreover, compared to “40:80 PEC2”, “40:80 PEC2 clear phase” (which only contains the “free” polymers from the PEC preparation) exhibits a drastically lower tensile strength, even lower than the pure CMCs. It further proves that PEC particles considerably improve the tensile strength of the paper. Compared to pure CMC, the lower value of “40:80 PEC2 clear phase” suggests that some free CMC interact with free CPAM2 in the clear phase, and thus do not contribute as much as binders. All of these observations taken together indicate that most of the tensile strength is contributed by PEC particles instead of free polymers.

Although pure PECs with 17,8kg/ton in the filler slurry have twice as many PEC particles than the one with 8,9kg/ton, they have the same tensile strength. Moreover, pure PECs with 1.06kg/ton displays a noticeable increase in comparison with “Ref” (pure PCC). Judging from these results, it seems that pure PEC particles positively affect tensile strength up to a certain level at a certain dosage. Beyond that dosage, the PEC particles do not contribute so much to the tensile strength. From these results, it is however impossible to tell what dosage between 1.06 and 8,9 kg/ton that is sufficient for maximum tensile strength.

#### 4.13 Internal bond strength

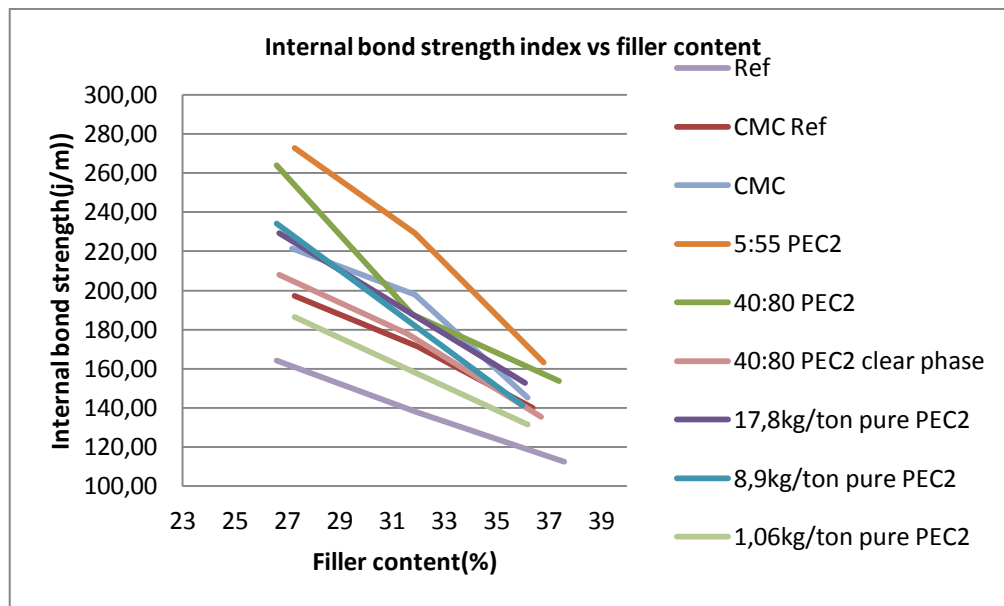


Figure 27. Internal bond strength index vs. filler content

Due to the high variance of the test results, the results of the internal bond strength measurements are not as reliable as the tensile strength index. These results exhibit some differences compared to the tensile strength index. All the PEC samples (except “1.06kg/ton pure PEC2”) still have the highest values among all these 9 samples, but “5:55 PEC2” now has the highest values which may be due to higher amount of CMC. Pure PECs with 17.8kg/ton and 8.9 kg/ton have roughly the same values as “CMC” in contrast to the tensile strength results. The rest of the results are similar to the tensile strength. In order to obtain a more accurate value of the internal bond strength, more than 5 samples should probably have been tested.

#### 4.14 Bulk development

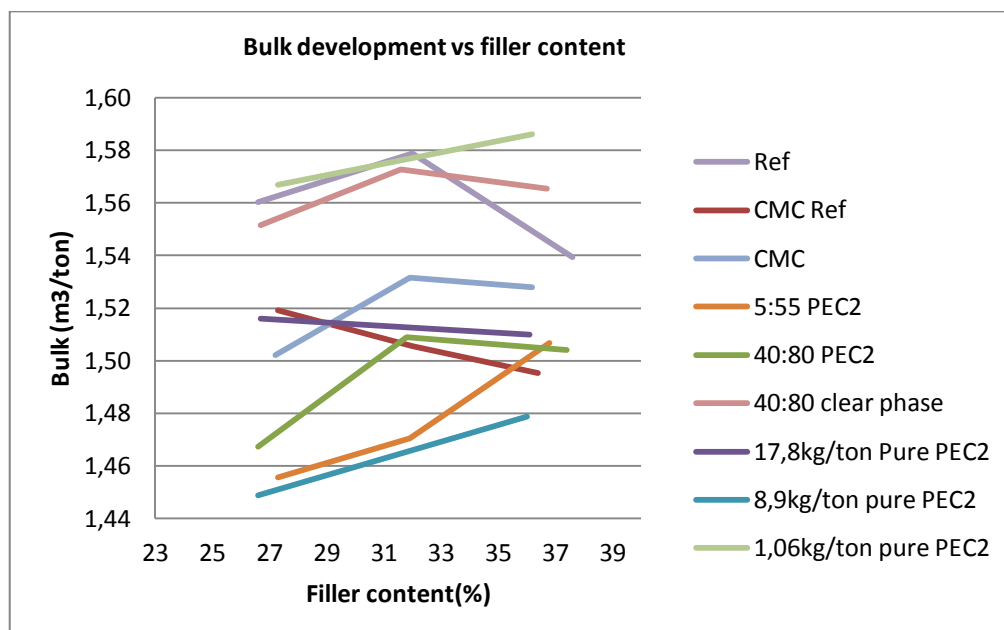


Figure 28. Bulk development vs. filler content

The bulk of the paper will influence the paper properties such as optical properties, stiffness and bending properties. Although it is hard to avoid the loss of bulk upon filler pretreatment in paper preparation, it is preferred to control it and lose as little as possible. These results show there is a general decrease of bulk content by introducing binders. Moreover, 5:55, 40:80 and 8,9kg/ton pure PEC samples have comparably lower bulk values which may be one of the reasons why they have higher strengths.



## 5. Conclusion

Unfortunately, the mechanism of the PEC2 formation is still unknown but it is known that by adding CPAM2 to CMC, more and more PEC2s are made until a certain ratio has been achieved, but after that ratio, PEC2s stop to be formed and CPAM and CMC become associated or free polymers around the PEC2s. The stability of the PEC system seems to be dependent on the charge of the PEC2 particles and also on the free polymers around them.

From Cryo-TEM pictures, it was observed that the PEC2 structure is very loose. Furthermore, there is a network structure made by CPAM2 and CMC spanning the solution around the PEC2 particles.

The PEC2 particles are only possible to make by pumping CPAM2 into CMC and not the other way around. From optical microscopy, the size of the PEC2 particles was judged to be around 600nm to 1µm and the size distribution of these PEC particles is rather narrow. The size of the PEC particles can be varied by changing the pumping speed of CPAM into CMC. Moreover, in accordance with the cryo-TEM observations, TOC indicates that a lot of water (>90%) is present in this kind of PEC particles.

From NMR observation, by increasing the addition of CPAM2 in the PEC2 solution, the amount of free CMC gradually decreases and the one of free CPAM2 increases. Although the order of addition influences whether visible PEC2s could be formed, the compositions of these two types of PEC2s with different polymer addition order are the same and somewhat surprisingly, these two samples have the same NMR spectra.

Among stock solutions, PEC2 particles settled to the bottom after approximately one week but not by heavy centrifugation. It may be because with time, slight aggregation of PEC2 particles causes larger structure of PEC2 particles to sediment to the bottom of bottle. However, several dilution and centrifugation cycles can be used to make pure PEC2 solution without “free” polymers.

From the final paper characterization, it is obvious that PEC2 particles have a big influence on the paper strength up to a certain amount added. A low dosage (8.9kg/ton) of pure PEC2s can achieve the same paper strength as the double dosage and even a very low dosage (1,06kg/ton) of pure PEC2s provides a comparably high strength. Furthermore, PEC2 solutions with “free” polymers present also give a big positive effect on the paper strength.

## 6. Future work

Despite the problems of PEC stability with the CPAM1 solution and CMC, relatively stable PEC2 solution could be made by the CPAM2 and CMC and the final results are good. A large amount of characterization methods have been tried to study the PECs such as PCD, microscopy, viscosity measurement, static light scattering, zeta potential, optical density, NMR, TOC, flow cytometry, etc. However, the mechanism of PEC formation is still illusive, and is left for future work.

NMR is a potential way to estimate the amount of free polymers around PEC2s. D<sub>2</sub>O can be used instead of H<sub>2</sub>O in order to remove the water peak to possibly enable estimations of the amount of free CMC and CPAM.

It is observed that PEC particles are only formed up to a certain ratio of CPAM and CMC. Although lots of experiments have been made trying to overcome this, the results were not satisfactory. Therefore, a more efficient way to make PEC particles should be further sought such as adding salt into the CMC and CPAM solution to make PEC particles.

In the strength evaluation, it was found that already a small amount of pure PECs influenced the paper strength a lot. Therefore, a new experiment would be very interesting where pure PECs at dosages in the range between the ones used here could be added into the filler slurry to study the strength effects.

Moreover, different polymers and pump rates used in PEC formation can be studied

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