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Research Article

Retention-Drainage and Strength Performances of Carboxylated Cellulose-Synthetic Polymer Systems

Sinem ŞENTÜRK, Orçun KURTULUŞ*

Kastamonu University, Tosya Vocational School, Kastamonu, TÜRKİYE
*Corresponding Author: caglarkurtulus@hotmail.com

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Abstract

Aim of study: The main aim of the study was investigating of different cationic polymers' retention and drainage performances with pure (PC) and oxidized cellulose (OC1, OC2) by using precipitated calcium carbonate (PCC).

Material and method: Cationic polymers were added to the cellulose-PCC suspension at three dosage ratios (1 mg/g, 3 mg/g, and 5 mg/g). After mixing for 6 minutes., samples were withdrawn by using a syringe and a retention test was performed by colorimetric titration. Drainage time was determined by using the Schopper Riegler apparatus for drainage tests, and test papers were prepared by the Rapid Köthen Paper Machine.

Main results: Cationic polyacrylamide (CPAM) provided higher retention values than all polymeric substances for both modified cellulose and pure cellulose. Drainage performances were enhanced by the whole polymers, especially polyethyleneimine (PEI), with both PC and oxidized samples.

Research highlights: Cationic polymer addition to celluloses (pure and oxidized) clearly increased the retention of the system, and also drainage performances were affected positively. The wet strength of papers was significantly enhanced compared to the dry strength, and this situation is a result of the highly hydrophilic nature of the carboxyl groups introduced during the oxidation process.

Keywords: Papermaking, Retention, Drainage

Karboksillenmiş Selüloz-Sentetik Polimer Sistemlerinin Retansiyon, Drenaj ve Sağlamlık Performansları

Öz

Çalışmanın amacı: Bu çalışmanın temel amacı, farklı katyonik polimerlerin çöktürülmüş kalsiyum karbonat (ÇKK) kullanılarak saf selüloz ve okside selüloz ile retansiyon ve drenaj performanslarının belirlenmesidir.

Materyal ve yöntem: Katyonik polimerler selüloz-ÇKK süspansiyonuna üç miktarda (1 mg/g, 3 mg/g, and 5 mg/g) ilave edilmiştir. 6 dakika karıştırma işlemi sonrası, süspansiyondan şırınga ile örnek alınmış ve retansiyon testi kolorimetrik titrasyon ile gerçekleştirilmiştir. Drenaj testleri için drenaj süresi Schopper Riegler cihazı kullanılarak, test kağıtlarının üretimi ise Rapid Köthen Kağıt Makinesi kullanılarak gerçekleştirilmiştir.

Temel sonuçlar: Katyonik poliakrilamit hem saf selüloz hemde modifiye selülozlar için tüm katyonik polimerlerden daha yüksek retansiyon sağlamıştır. Drenaj performansları, başta Polietilenimin olmak üzere tüm polimeler ile hem saf selüloz hemde okside selülozlarda artış göstermiştir.

Araştırma vurguları: Selüloza (saf ve okside) katyonik polimer ilavesi sistem retansiyonunu net bir şekilde arttırmış, drenaj performanları da pozitif yönde etkilenmiştir. Kağıtların ıslak sağlamlığı, kuru sağlamlık ile kıyaslandığında ciddi oranda artış göstermiş olup bu durum, oksidasyon prosesi sırasında oluşan yüksek oranda hidrofilik özelliğe sahip karboksil gruplarından kaynaklanmaktadır.

Anahtar kelimeler: Kağıt Üretimi, Retansiyon, Drenaj

Introduction

The wet end process and wet end chemistry are the most important parts of the whole papermaking process, which directly affect the end production of paper or paperboard. Paper pulps are differented mainly as short fiber and long fiber (Eroğlu & Usta, 2004; İstek et al., 2008) and recently the most common chemical pulp production method is Kraft cooking process which provides higher strength properties to paper (Vaaler et al. 2002; Santos et al., 2011;

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Gülsoy, 2012). However, a combination of these two fibers can be used for increasing the specifical characters of the end product of paper. Different chemical precursors are being used for different purposes in papermaking process, such as increasing drainage, retention, dry strength, wet strength, and diminishing foaming during pulp production. Raw materials and different chemical agents used in the process comprise a huge amount of the production cost, and the retention of these materials on the wire is the most important issue for producing and obtaining a highly qualified end product of paper. Low level of retention resulted with these negative results such as; low speed of paper machine, increased white water pollution, higher production and additive chemicals cost, and higher level of sewer with much more pollution, poor wet mat and paper formation, low amount drying energy (Simola, 2008; Bajpai, 2015) For this reason, different retention systems are being used during the paper and paperboard processes, which basically depends on the coagulation of pulp components via different process such as brinding mechanism, patching or charge neutrolization. As a result, retention aids bind cellulosic fibers with fillers and also act as a bridge between fines and fiber-filler flocs, which also increases the drainage performance of the papermaking system (Cadotte et al., 2007; Chi et al., 2007). However, addition to different retention systems and synthesis of new papermaking agents, modification of cellulose such as carboxymethylation and using cellulose based precursors such as nanofibrillated celluloseare also attractive routes for improving paper quality (Lourenço et al., 2019). Fillers and fines may be retained through deposition on fibers that are either immobilized in the forming sheet or freely suspended in the papermaking suspension, or they may be retained through mechanical entrapment of fines and filler aggregates inside the sheet (Van De Ven, 2005). For obtaining proper retention, it is not enough of deposition of filler onto cellulose. Addition to deposition of fillers, this situation should be kept stable during the process. Shear forces occurring during mixing the suspension with different angles and directions can disrupt the flocs occurred by interaction between fiber and PCC. Additionally, floc size and bonds between flocs' components are also responsible factors that caused the dispersion of floc stabilization. Retention aids increase the bond strength and prevent disrupting the floc by creating bridges between fibers and PCC.

The most common type of the combine retention processes can be explained by dual component systems, microparticle retention systems (starch/polymer with silica microparticle), microparticle systems (polymer with bentonite) (Thorn & Au, 2009). General routine in these process based on the filler's and fines' bonding effect on the fibers during the wet end and resulting lower degree of white water contamination (Unbehend, 1992). As a result of the increasing retention with efficient drainage performance, high yield, high end production qulity and lower production costs are obtained.

Materials and Methods

Materials

Raw material of cellulose was choosen as softwood bleached kraft pulp and obtained form Lila Paper Ind. (Türkiye). Cationic synthetic polymers of PEI (Mw:600-800) and polydadmac (PDADMAC) (Mw: 20000-100000) were purchased from Sigma Aldrich, and CPAM (Fennopol K3400 R, Mw: 6-7x10^6 g/mol, charge density: 1 meq/g) was purchased from Kemira Oyj. (Finland). PCC was obtained from Minerals Technologies-USA. NH_3, NaBr, TEMPO, NaClO, NaOH, HCl and ethyl alcohol were also purchased from Sigma Aldrich and retention test chemical of Eriochrom Black T and Titriplex III (EDTA) were purchased form Merck Millipore Chemical Company (USA). Deionized water was used during the all experiments except wet strength tests.

Methods

Oxidation of cellulose (TEMPO Process)

Oxidation process of cellulose was carried out by the method of Saito et. al. (2006). TEMPO (0.1 mol/g) and 0.1 mol/g NaBr was prepared in 50 ml deinized water and pH of the solution was adjusted to 10 before adding to cellulose suspension. After adding TEMPO-NaBr mixture to cellulose slurry, the whole ingredients were mixed at 500 rpm for 10 min. and NaClO was added as 1 mmol and 3 mmol per g based cellulose after preparing pH at 10. Reaction was proceeded at mixing rate of 500 rpm until the obtaining pH stabilization at pH 10. Oxidation was stopped by adding 50 ml ethyl alcohol to slurry and oxidized pulps were washed with excess of deionized water.

Determining carboxyl and aldehyde amounts

Carboxyl fraction of oxidized celluloses was determined according to method proposed by Saito and Isogai (2007). 50 mg cellulose was added into 250 ml deionized water and 15 ml (0.01 M) HCl added into this system. Whole mixture was titrated by using 0.01 M NaOH after mixing 10 minutes of the slurry and fractions were determined by using formula below (Eq. 1).

$$\text{Carboxyl-Aldehyde Amo. (mmol/g)} = \frac{V x\, N}{W} \qquad (1)$$

Where; V, consumed NaOH amount during titration (ml); N, NaOH Normality (mol/L); W, dry weight of cellulose sample (g).

By using the same formula above, aldehyde amount of the celluloses was determined by using Sirvio et al. (2011)' s study. Cellulose suspension's (0.1 g/30ml water) pH was adjusted to 4.5 and hydroxyl amine hydrochloride ($NH_2OH.HCl$) (0.43 g/20 ml-pH 4.5) was added into mixture and mixed for 24 hours. Titration was completed by using base and fraction was calculated from the formula above.

PCC retention and drainage test

Retention performance of PCC with the addition of the cationic polymers with different amounts were performed by withdrawing white water of the suspension using a syringe equipped with a 200-mesh wire. For this, 1 g cellulose was suspended in 500 ml of deionized water, and 0.3 g of PCC was added to the suspension. After completing the total volume of the suspension to 1000 ml, cationic polymers added three different amounts (1 mg/g, 3 mg/g, and 6 mg/g) and the suspension stirred at 500 rpm with mechanical stirrer. White water of the suspension was withdrawn by a syringe equipped with 200 mesh wire. For colorimetric titration, 1 ml 0.6 M HCl added and PCC converting to Ca^{2+} ions. pH was adjusted by adding 3 ml of ammonia solution (pH 10.5) and 5-6 drops of Eriochrom Black T to ease color change monitoring during colorimetric titration. Titration was performed and stopped when the color of the solution turned from purple to violet by adding standardized Titriplex III. Retention value of the PCC was calculated according to obtained free PCC amount presented in the solution.

Addition to retention test, dewatering efficicency of the system was performed by measuring drainage time of the suspension. The same amounted cellulose-PCC-cationic polymer suspensions were mixed for 6 min and at the end of the sitrring, suspension was passed through the Schopper–Riegler Beating Freeness test equipment and release of the water from the wire was measured as a dewatering time.

Preparing test papers and performing strength tests

Test papers (60 g/m^2) for determining the both dry and wet strength values were prepared by using laboratory type Rapid Köthen Paper Machine (Singapore) according to standart TAPPI T 205. Pulp suspensions before papermaking were prepared with the same amount used in PCC retention tests and wet sheets were dried at 93 °C for 10 min using pressure of 90 kPA. Dry and wet strength values of papers were measured by using TAPPI 404-om-87 standard with the equipment of Karl-Frank-800 Pendulum (Germany) type tensile test analyzer. Wet strength tests were performed even after dipping the test rips into tap water for 30 second and removing of the excess water from the surface by filter paper. 5 tests were performed for each composition.

FTIR analysis

Chemical interactions between cellulose-PCC and cationic polymers were investigated by the FTIR diagrams. High amount of PCC retention systems were choosen as a model and FTIR experiments were performed between 400-4000 cm^{-1} spectrum with a resolution of 2 cm^{-1} by device of Bruker Alpha (USA).

SEM (Scanning Electron Microscopy) views

SEM images of the systems were obtained from the high performed PCC retention systems. Morphological views of the papers having high level of PCC retention were cut into small pieces and coated with gold-palladium before measurments and different images were taken from the surface with different magnifications by using device of FEI Quanta FEG 450 (USA).

Results and Discussion

Carboxyl-Aldehyde Amounts of Oxidized Cellulose

TEMPO oxidation is one of the modifying method for different carbohydrate compounds with the main of producing carboxyl fractions on the glucose chain with selectively oxidizing primer OH groups means that C6. Table 1 clearly shows the TEMPO oxidation results with carboxyl and aldehyde amounts of the cellulose. It can be seen that oxidation carried out on the surface of the cellulose and both carboxyl and aldehyde fractions of cellulose clearly increased after addition of NaClO oxidant in higher amount. Differ from carboxyl groups, aldehyde fraction of the PC could not be determined due to the low level of aldehyde amount of the PC which also increasing in low level with higher amount of oxidant. Although it mainly depends on the reaction conditions, the amounts of carboxyl and aldehyde groups have been determined similarly by different researchers. Wang et al. (2024) determined carboxyl fraction of cellulose 0.5 mmol/g and 1 mmol/g, for adding oxidant of NaClO as 2 mmol/g and 4 mmol/g. These results show similarity with our findings and 0.3326 mmol/g and 0.5109 mmol/g carboxyl amounts were found for oxidant used as 1 mmol/g and 3 mmol/g, respectively. Addition to changing both aldehyde and carboxyl fractions parallel to added oxidant amount of the reaction, FTIR results also clearly show that TEMPO oxidation carried out successfully on the surface of cellulosic fibers existing the main oxidation peaks on both the diagram of the OC1 and OC2 as a band of 1634-1635 cm^{-1}.

Table 1. Carboxyl and aldehyde amounts of PC, OC1 and OC2

Sample	Carboxyl Amo. (mmol/g)	Aldehyde Amo. (mmol/g)
PC	0.2328	-
OC1	0.3326	0.1358
OC2	0.5109	0.2003

PCC Retention and Drainage Performances

PCC retention is one of the important issue during the wet end system for improving system's efficiency which directly affect the end product specifications. Retention results of PC, OC1 and OC2 based celluloses with PCC and cationic subtances are shown in Figure 1-3. In Figure 1 (a-c), non modified PC component's PCC retention results are seen with the addition amount of 1 mg/g (a), 3 mg/g (b) and 6 mg/g (c) cationic polymer. It can be seen from the all figures that the maximum PCC retention performance was obtained by CPAM for each addition amounts. The maximum value was determined as 236.24 mg/g for 3 mg/g CPAM addition and 219 mg/g for 1 mg/g and 231 mg/g for addition amount of 6 mg/g.

Except PEI, all cationic polymers showed decreasing trend with increasing time of the retention test. This negative result being thought as a fast chemical interaction between cellulose and cationic polymers even after the 1st min. Decreasing of the charge amount which was firstly diminished by the fast interaction probably caused the decreasing of the retention amounts with increasing time. Having high amout of charge density and solubility in water, PEI is a commonly used fixative agent in papermaking processes for old years (Kobayashi et al., 1990; Wang et al., 2016). The main mechanism of PEI as a retention polymer in papermaking process is charge neutralization and patching (Shetty et al., 1994). For this reason, in retention studies with PC, first the increased retention in the 1st minute was detected at a higher rate (208.48 mg/g) in the 3rd minute, and then, with the effect of mixing speed, the formation of the weakly retention PEI-PC-PCC patch was probably weakened. It showed low dispersibility and a slight decrease in retention (202.49 mg/g). As a result of PC-PCC-CP (cationic polymer) retention system, all cationic polymers provided the increasing trend for PCC retention from 18 mg/g for PC to the maximum value of 236 mg/g for adding amount of 3 mg/g CPAM for 1st min. Anionic sites of cellulosic compound clearly interacted with the cationic sites of polymers easily and PC-PCC-CP flocs occurred. The OC1-based system's PCC retention values with different polymer dosages are shown in Figure 2 a-c. It can be seen from the figures that higher retention values were determined by the addition of CPAM for different dosages (1 mg/g, 3 mg/g, and 6 mg/g), 272 mg/g, and 271 mg/g PCC retentions were determined for 3 mg/g and 6 mg/g polymer dosages, respectively. PEI and PDADMAC polymers had better retention characteristics even after CPAM. When investigated of the relative retention values of CPAM for each celluloses, the highest PCC retention values (262 mg/g and 264 mg/g) were observed by OC1-PCC system with addition amount of CPAM as 3 mg/g and 6 mg/g means that 87.33% and 88% of PCC vas retained on the system. It is worth noting nonetheless, that the lowest retention values were obtained with the largest dosage of PDADMAC polymer, even to a smaller extent than OC1 without polymer addition, and that the lowest retention value was the lowest degree throughout the entire research retention performances. However, increasing amount of carboxyl fraction (OC2) caused low degree of diminishing for relative retention value as 257 mg/g for 6 mg/g means 85.66% of PCC retention. This phenomena can be explained by the sitociometric balance of oxidized cellulose' s charged groups and CP'-NH2 groups. After reaching polymeric charge blockage between fiber and polymer, CPAM could not provide enough tails for PCC to binding and probably free and small flocs between anionic PCC and cationic polymer with occured and retention values decreased. One of other explanation about decresing trend with higher carboxyl fraction of cellulose is the effect of mixing conditions. During the experiment, all suspensions mixed with 500 rpm mixing rate by using mechanical stirrer. However, after first passing retention of PCC, mixing of the slurry was kept stable and mechanical forces in the suspension probably caused the delamination of polymeric line from the weak bonding point between fiber and PCC as shown in Figure 3 a-b. High level of PCC retention with CPAM can be correlated with different studies. Saito and Isogai (2007), performed CPAM retention with TEMPO oxidized cellulose and according to results, 80% of CPAM was deposited onto oxidized cellulose and this situation means that CPAM can easily react with negative charges of oxidized cellulose. Addition to this study, Ondaral et al. (2011) also proposed that increasing carboxyl fraction on cellulose by carboxymethyl cellulose modification clearly increased the adsorption level of CPAM and this situation depends on the carboxyl moities on the cellulose. According to these data, increasing PCC retention on higher level is almost expected results due to increasing negative charge and increasing saturation point as a result of 1:1 sitochiometry. In Figure 4 a-c, the highest amounted carboxy and aldehyde fractionated cellulose's PCC retention performances are seen. When compared to different cationic polymers' efficiency on OC2-PCC system, it is seen that different retention performances occurred with the addition amount of polymer and time. According to Figure 4, it is seen that higher PCC retention values were performed by CPAM for 1 mg/g addition amount of polymer as 214 mg/g, PEI, 235 mg/g for dosage of 3 mg/g and 266 mg/g for addition amount of 6 mg/g CPAM. However, pure OC2 based system's PCC retention was determined approximately 191 mg/g. As dedicated above, polymeric substances performed different retention values according to both dosage and test time. In general, increasing amount of polymer dosage resulted with higher PCC retention. PEI based system showed increasing trend with also increasing time. This situation clearly shows that higher amount of carboxyl fraction presented on OC2 cellulose need much more charged to be blocked and this situation probably caused higher contact and bonding points between fiber and PCC (Figure 3-b) which was resulted higher retention performances. This situation shows that increasing reactive carboxyl fraction fastly reacted with cationic polymer and acted as a strong bridge between cellulose and PCC. As a study by Satio and Isogai (2007), retention of PEI onto TEMPO oxidized cellulose reached approximately to 90% by addition amount 0.3% according to cellulose. Increasing PCC retention with higher level for PEI can be thought as a parallel trend with this study. When compared to other polymers, PDADMAC showed lower degree of retention but higher than pure celluloses (PC, OC1, OC2). Results showed that addition amount of PDADMAC clearly increased the PCC retention with higher level. This situation can be thought as higher level of polymer react much more anionic charges of both cellulose and PCC resulted with higher bonding area with strong bonds and as a result of this issue PCC deposition onto OC2 increased. This behavior of PDADMAC can be seen in a study by Ondaral and Usta (2010). According to results, increasing amount of PDADMAC caused retention value until reaching addition amount of 1.8 mg for 0.4 g cellulose mixture of 70% bleached softwood kraft pulp and 30% stone ground mechanical pulp. Compared to our results of retention, they added PDADMAC two fold of our addition amount and PCC retention reached 88.5% and 70%, for their study and our results, respectively. In a brief, compared to two studies' results, when they reached PCC retention as 74% with the addition of PDADMAC as amount of 9 mg/g cellulose, our results showed 73% PCCretention with the addition of PDADMAC as 6 mg/g. Almost the same amount of PCC retention values can be probably results of highly anionic charged cellulose in our study provided by TEMPO oxidation compared to other study's cellulose mixture composed of non-modified celluloses.

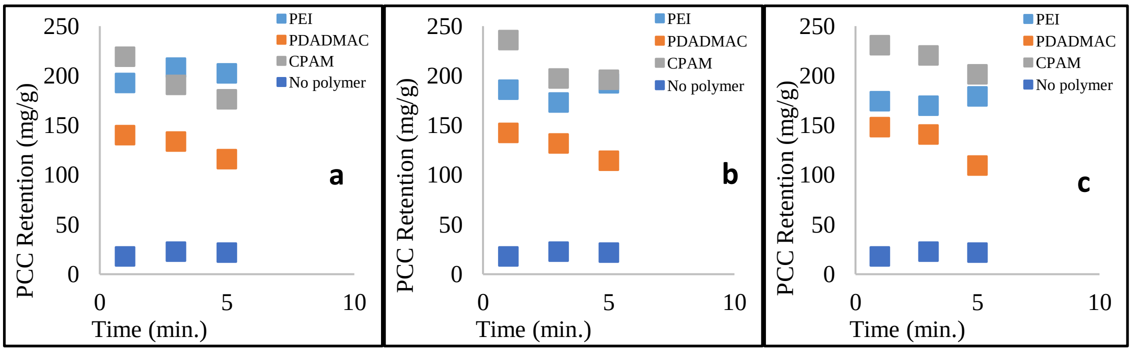

Figure 1. PC-PCC retention (a: 1mg/g, b:3 mg/g, c:6 mg/g) values for different polymer dosages

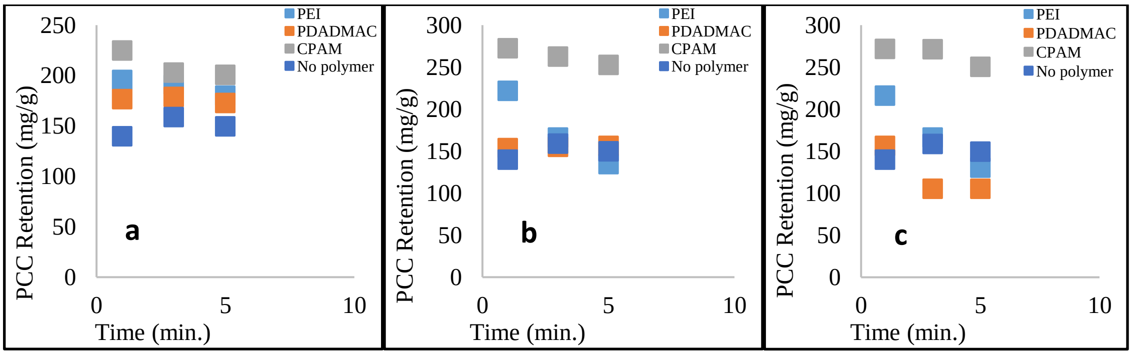

Figure 2. OC1-PCC retention (a: 1mg/g, b: 3 mg/g, c:6 mg/g) values for different poylmer dosages

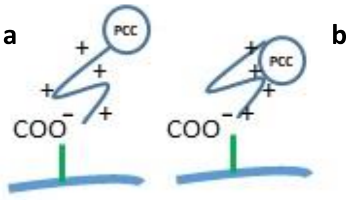

Figure 3. Weak (a) and strong (b) bonding of PCC onto cellulose via CPAM

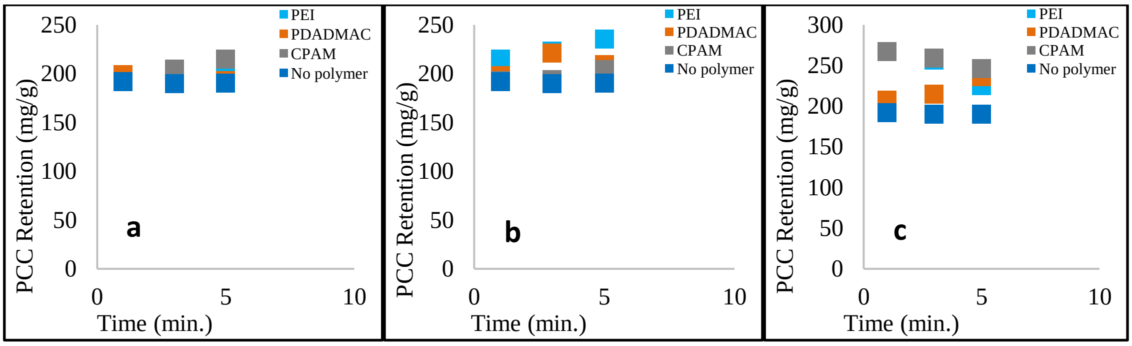

Figure 4. OC2-PCC retention (a: 1mg/g, b: 3 mg/g, c:6 mg/g) values for different polymer dosage

Drainage performances of all celluloses with PCC are illustrated in Fig. 5-7 (a-c) for PC-PCC, OC1-PCC, and OC2-PCC, respectively. Non-modified celluloses' drainage performances with different amount of cationic polymer dosages are seen in Fig. 5 (a-c) and it is clear that addition of polymers decreased drainage time from 8.96 second to approximately 7 second firstly by PEI. Although all polymers contributed the positive effect on dewatering process the maximum performances provided by PEI, PDADMAC, and CPAM, respectively. Increasing trend for drainage of PC-PCC system can be thought with parallel to retention behaviours. Occuring fiber-PCC flocs during retention mechanism provided micro gaps between the fibers in the paper mat and as a result of this phenomena, better drainage performances obtained by all polymers with different dosages. Fig 6 a-c shows OC1-PCC drainage system and almost different behaviours for drainage can be clearly seen. Fast drainage times were determined for pure OC1 as 3.9 s and the fastest drainage performance provided by PEI, with dosage 1 mg/g and draine performance was determined as 3.28 s which is the fastest drainage performance through the whole drainage tests in this study. This behaviour of CPAM probably caused by almost high molecular weight (6-7x10^6 g/mol) and charge density (1 meq/g) of polymer caused creating much bigger flocs by fiber and PCC by means of binding on the longer fraction on cellulose and PCC and as a result of this, bigger flocs inhibited draining of water through the mat. Additionally, higher amount of 6 mg/g dosage CPAM showed better performance than other two dosages due to non sitociometric balance resulted with also adsorption onto smaller sized PCC particles and cellulosic fines resulted the filling micro gaps. Figure 7 shows OC2-PCC system's drainage performances. Compared to the PC and OC1 systems, a low level of higher drain performance was provided by the addition of different amounts of cationic polymers, and the highest drainage time was performed by 6 mg/g CPAM at 3.4 s, whereas non-polymer-added OC2 showed 3.62 s. The high level of drain performance for OC2-PCC system is almost expected due to the higher retention of each polymer system, which probably created bigger flocs and micro-gaps in the fiber mats, which clearly provide removing excess water easily and faster drainage.

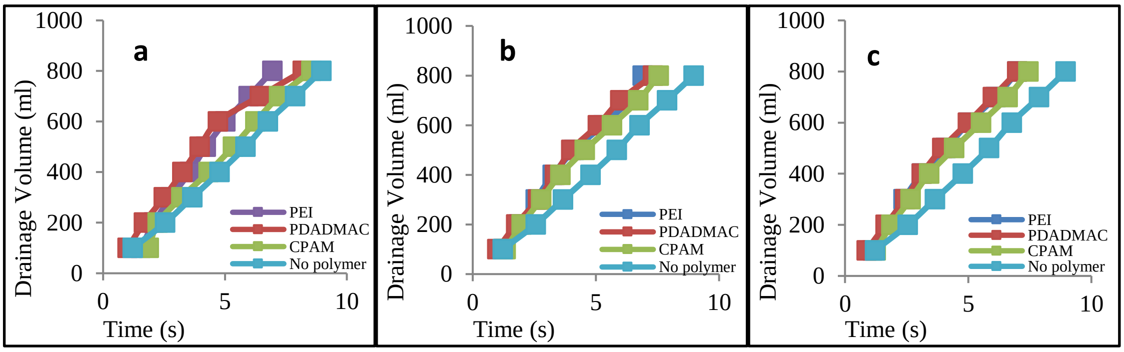

Figure 5. PC-PCC drainage (a: 1mg/g, b:3 mg/g, c:6 mg/g) values for different polymer dosages

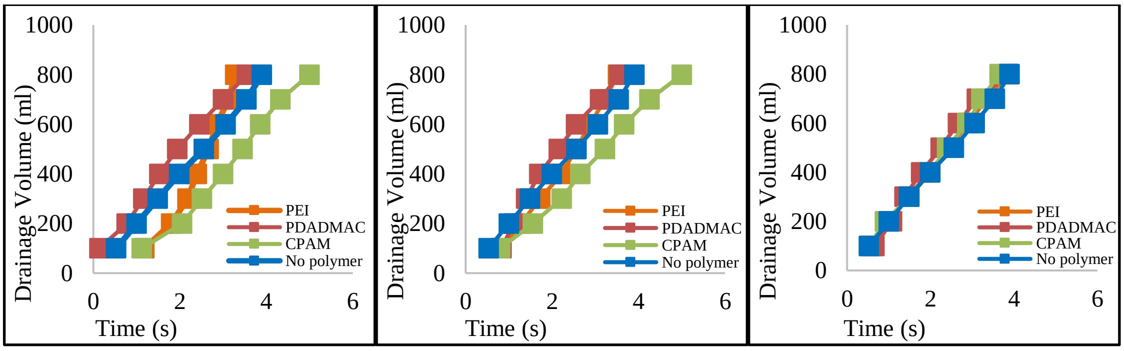

Figure 6. OC1-PCC drainage (a: 1mg/g, b:3 mg/g, c:6 mg/g) values for different polymer dosages

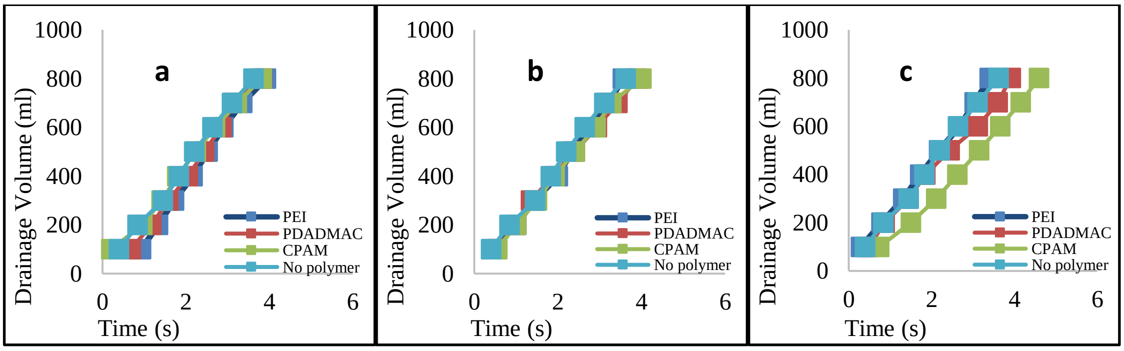

Figure 7. OC2-PCC drainage (a: 1mg/g, b:3 mg/g, c:6 mg/g) values for different polymer dosages

FTIR Diagrams

Chemical changes of components as a result of the TEMPO oxidation process were determined by FTIR diagrams (Figure 8 (a-c)). Figure 8-a, shows the characteristic FTIR diagram of PC and the peaks at 3297 cm^{-1}, 1634 cm^{-1}, 1547 cm^{-1}, 1450 cm^{-1}, 1405 cm^{-1}, 1057 cm^{-1} can be clearly seen. In general, peak band between 2800-3600 cm^{-1} attributed to C-H tension based upon alcholic groups and also OH tension of water presented in the material (Ibrahim et al., 2011; Fan et al., 2012). As a result of oxidation, characteristic peak of carboxyl fraction is generally seen at peak around 1600 cm^{-1} and except the PC, this peak clearly seen in both OC1 and OC2 between the 1634 cm^{-1}-1635 cm^{-1}. The peak of 1634 cm^{-1} moved to 1635 cm^{-1} for OC1 and OC2 compared to PC, and peak behaviour changed with higher intenstiy and sharper line. In addition the main reason of seeing carboxyl groups at higher bands at 1634 cm^{-1}-1635 cm^{-1} is probably presence of low amount of water in test samples after drying of paper sheets decreased the the efficiency of carboxyl groups. However, presence of carboxyl fractions in different peak intensities clearly shows that TEMPO oxidation process carried out by featly. Addition to oxidation, PCC's characteristic peaks can also be seen at 1450 cm^{-1} and 1405 cm^{-1} which are attributed to assymetric tension peak and titration peak of CO_3^- ions, respectively (Rodriguez-Blanco et al., 2011).

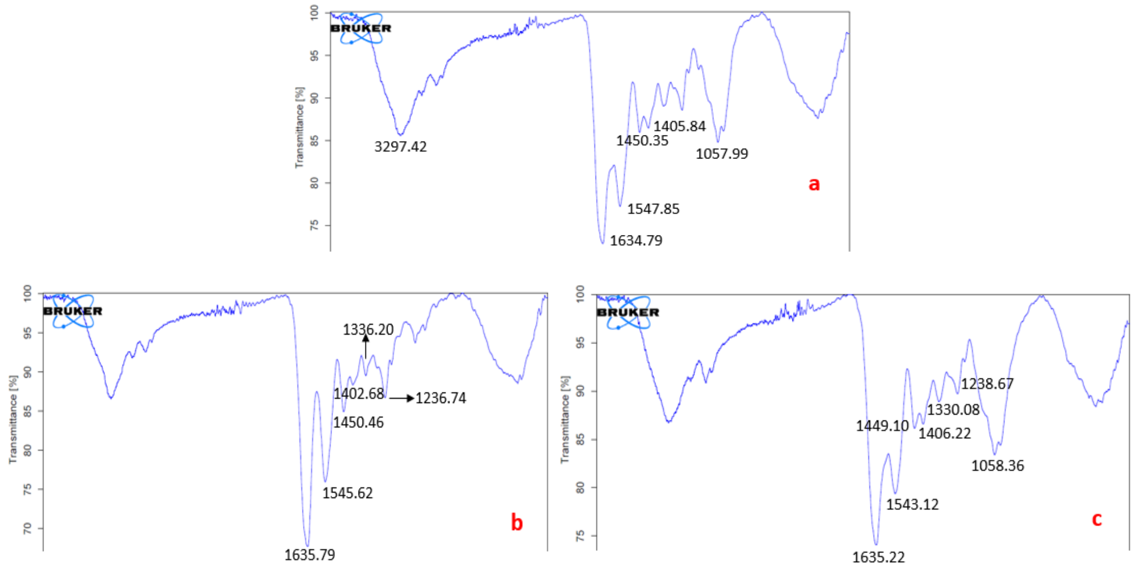

Figure 8. FTIR diagrams of all celluloses. a) PC, b) OC-1, c) OC-2

Addition to cellulosic components, high level of retention performances' FTIR diagrams were also determined and illustrated in Figure 9 (a-c). In figure 9-a, PC-PCC-CPAM (3mg/g) FTIR diagram is seen and comapred to PC, small differences can be seen in diagrams. Addition of CPAM into suspension caused the moving carboxyl fraction peak of 1634 cm^{-1} to 1635 cm^{-1} with higher and sharper intensity of peak line probably caused by interaction of CPAM both with carboxyl fraction of PC1 and also with anionic sites of PCC resulted of non reacted free carboxyl groups presence in the cellulose suspension.

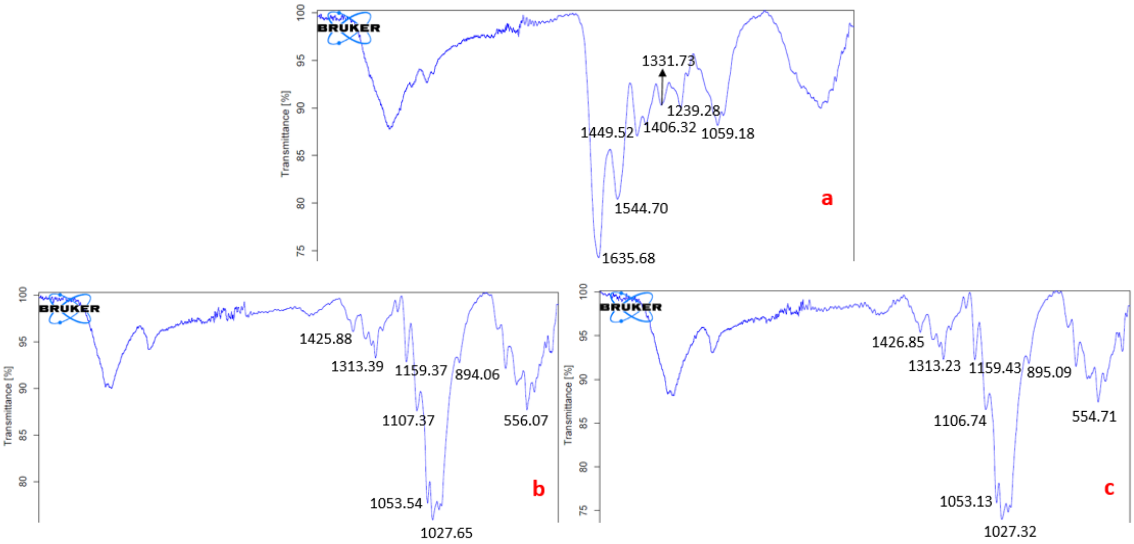

Figure 9. FTIR diagrams of different cellulose-PCC-CPAM compositions. a) PC-PCC-CPAM (3 mg/g), b) OC1-PCC-CPAM (6 mg/g), c) OC2-PCC-CPAM (6 mg/g)

Dry and Wet Strength Performances

Dry and wet strength performances of all components were performed to investigate of polymer dosage efficiency and all results are illustrated in Figure 10-12. Figure 10 shows dry and wet strength values of PC-PCC and polymer based system. When compared of dry strength results, all polymers with different dosages provided higher performance than PC (0.1 kNm/g). The highest dry strength value was observed by the addition amount of CPAM as 6 mg/g as 0.17 kNm/g. In general, strength of papers were determined between 0.12-0.16 kNm/g. Increasing dosage of CPAM clearly increased the dry strength values, however, 3 mg/g PEI addition caused decreasing of strength and 6 mg/g addition increased the value in positive range again. This behaviour of 3 mg/g PEI addition is expected result due to the performed with same behaviour seen in retention test and this issue was explained as inadequate time of mixing with PEI and suspension components in which charge neutralization could not be completed as a sitochiometric balance. However, the same issue of PEI can also be seen in wet strength test. Higher performance of both CPAM and PEI were seen in wet strength development. Although PDADMAC showed similar values with PC, all amount of dosages with CPAM and 6 mg/g PEI dosage clearly improved the wet strenght values.Wet strenght of PC was determined as 0.0044 kNm/g and the highest performance was belong to 6 mg/g CPAM addition calculated as 0.0274 kNm/g means that increasing of 6.22 fold. CPAM is one the most common used retention chemical in papermaking industry due to having highly capability of floccing cellulose and suspension components in high activity (Horn & Linhart, 1996; Mosse et al., 2012). Increasing of paper properties with the addition of CPAM was investigated by different researhers. According to Charani and Moradian (2019), breaking lenght of hardwood cellulose with the addition of 0.03% and 0.05% CPAM clearly increased.

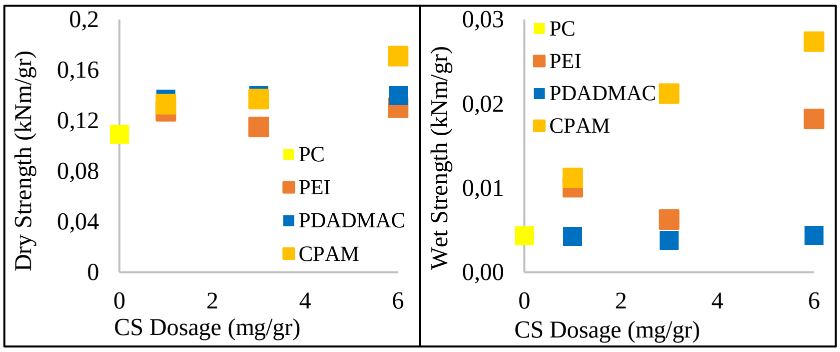

Figure 10. Dry-Wet strength performances of PC-PCC-polymer system

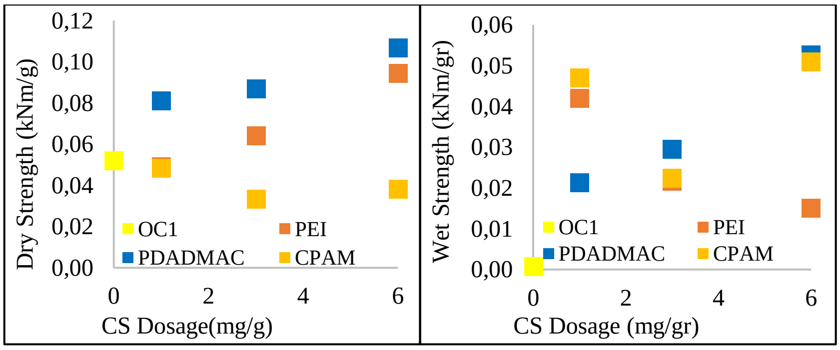

Figure 11. Dry-Wet strength performances of OC1-PCC-polymer system

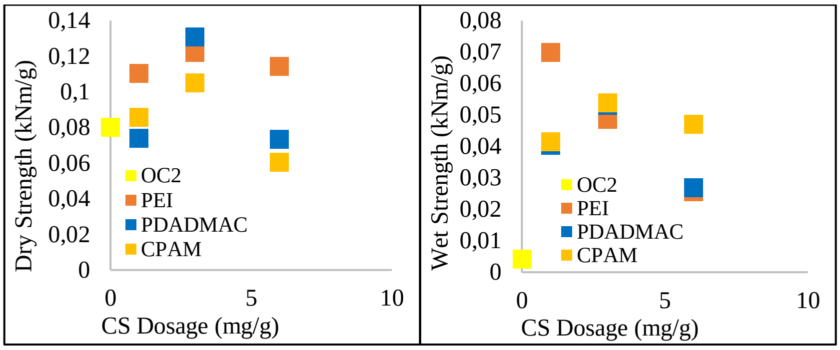

Figure 12. Dry-Wet strength performances of OC2-PCC-polymer system

When compared to PC-PCC-CP based systems, OC1 and OC2 based systems' dry and wet strength performances were measured at a low level. Pure OC1 and OC2's dry strength values were observed as 0.05 kNm/g and 0.079 kNm/g, respectively; however, this value is 0.10 kNm/g for PC. The wet strength value of PC was 0.004 kNm/g, and this value was calculated for OC2 as 0.0042 kNm/g. Contrastily, OC1 showed an almost low degree for this performance, calculated as 0.007 kNm/g. This situation is probabyl caused by a low level of carboxyl fraction with a low amount of aldehyde fraction. However, a higher level of carboxyl fraction in OC2 provided a higher level of water uptake due to the hydrophilic nature of carboxyl groups. It is clearly shown in the figures that wet strength performances were performed at a at a higher level than PC. As stated before, interaction between anionic sites of cellulose and PCC by means of cationic polymers provided higher contact points and contact area, resulting in a higher amount of wet strength, which is basically proven by high carboxyl groups. When examined the cationic polymers' behavior for wet strength, PEI addition caused decresing trend for both OC1 and OC2 based system. However, high amount of CPAM and PDADMAC addition clearly increased the wet strenght values. As stated before in part of the retention, low amount of mixing time between polymer and cellulose resulted weak bonds which could be easily disrupted. Water molecules could diffused into cellulose mat and as a result of this issue wet strength values decreased for PEI. According to Saito and Isogai (2007), retained approximately 6 mg/g PEI in TEMPO oxidized cellulosic mat cellulosic mat wet strength value was determined 0.01 kNm/g, however, in recent stud wet strenght values for determined as 0.015 kNm/g and 0.026 kNm/g for OC1-PCC-PEI and OC2-PCC-PEI for 6 mg/g PEI addition. Decreasing strength performance of PEI was also dedicated by Trout that PEI creates ionic bonds between cellulose's carboxyl fraction in which can be also thought as response of low strength (Trout, 1951; Roberts, 1996).

SEM Views

SEM views of different types of celluloses (PC, OC2) with PCC and CPAM are shown in Figure 13 (a–f). PC-PCC without a polymer system's fiber morphology is seen. The presence of PCC particles can be seen in both different magnitudes. Fiber contacts with different sized fibers can also be clearly seen. In addition, the PC-PCC-CPAM-based system (with the addition of 3 mg/g CPAM) also shows similar morphological views; however, bigger PCC block retention on fibers can be clearly seen, which means that CPAM acts as a binder for PCC onto cellulose fibers. The OC2-PCC-CPAM (6 mg/g) mixture-based paper's SEM views are shown in Figure 13 (e-f). Compared to other images, OC2 based system showed a different micromorphological view. Contact points between fibers and a higher amount of PCC presence can be clearly seen, and this situation also shows the high retention performance of adding 6 mg/g of OC2 cellulose, which has a high level of carboxyl fraction. It is also seen that the addition of a higher amount of CPAM reacts not only with cellulose’s carboxyl groups but also with PCC’s CO_3^{2-} groups, which have proven to be PCC flocs in the paper mat.

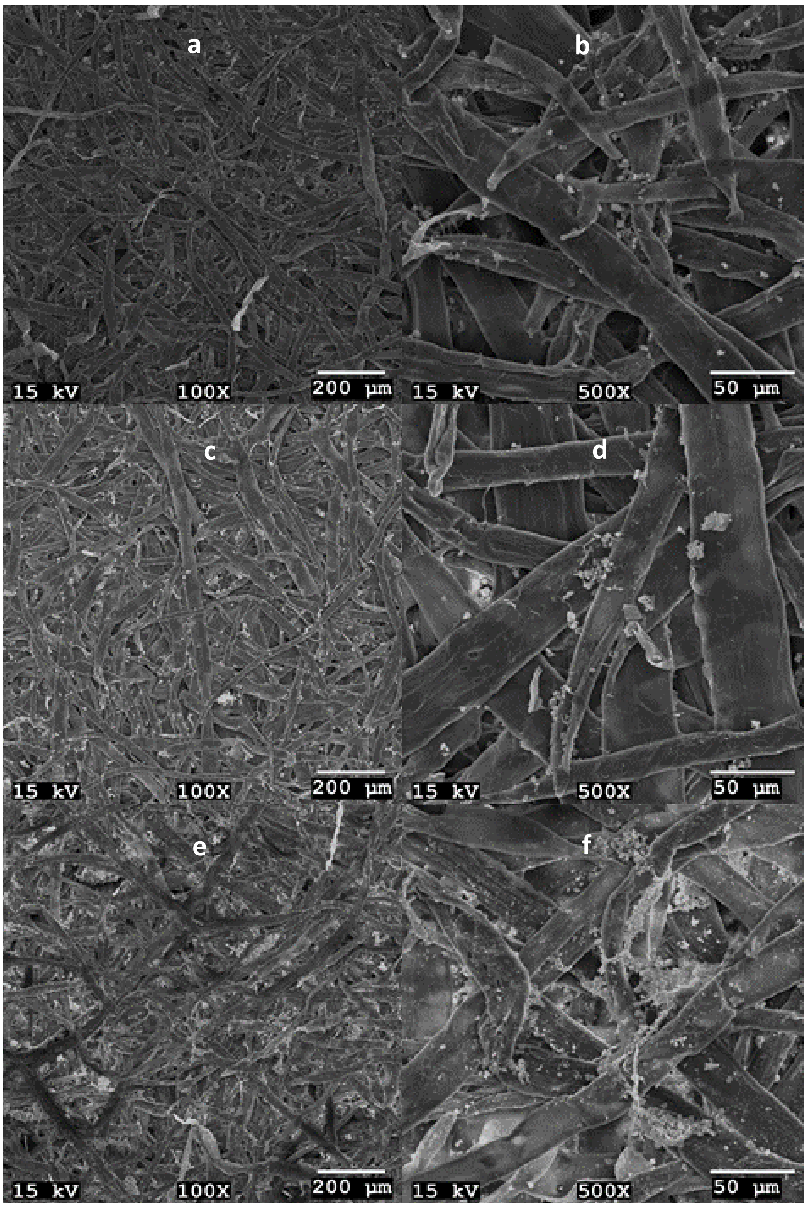

Figure 13. SEM views of different cellulose-PCC component. a-b) PC-PCC, c-d) PC-PCC-CPAM (3 mg/g), e-f) OC2-PCC-CPAM (6 mg/g)

Conclusion

Retention and drainage performances of cationic subtances of PEI, PDADMAC, and CPAM were investigated with PCC by using raw materials of TEMPO oxidated celluloses. Results showed that CPAM provided higher retention values across all polymeric precursors depending on the dosage ratio and time for PC-PCC, OC1-PCC, and OC2-PCC systems ranged between 176,35 mg/g-236,24 mg/g, 200,53 mg/g-272,36 mg/g, and 190,37 mg/g-266,83 mg/g, respectively. In addition to retention, drainage performances were enhanced by the whole polymers, especially with the addition of PEI with both PC and oxidized cellulose samples. Drainage performances were affected positively and dropped from 8.96 s to 6.95 s for the PC-PCC system. The oxidizing process of cellulose provided much more effective drainage time for OC1 and OC2-based systems, and the dewatering process was carried out near 4 s, which raised the paper machine to be worked faster. Due to the very hydrophilic character of the carboxyl groups found in oxidized celluloses, dry strength values often exhibited a downward trend with oxidizing celluloses. Parallel to this phenomenon, wet strength performances increased with the oxidition of cellulose, as expected. Wet tensile strength values increased from 0.0044 kNm/g to 0.0274 kNm/g for PC-PCC, 0.05 kNm/g for OC1-PCC system, and 0.06 kNm/g for OC2-PCC system. As a result, cationic polymers increased the retention performances of PCC and drainage performances in parallel to wet strength performances, which is an important issue in wet end systems to make papermaking systems faster.

Ethics Committee Approval

N/A

Peer-review

Externally peer-reviewed.

Author Contributions

Conceptualization: S.Ş., O.Ç.K.; Investigation: S.Ş., O.Ç.K.; Material and Methodology: S.Ş., O.Ç.K.; Visualization: S.Ş., O.Ç.K.; Writing-Original Draft: S.Ş., O.Ç.K.; Writing-review & Editing: S.Ş., O.Ç.K. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors declare that they have no conflict of interest.

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