Preparation of Cationic CMP and Softwood Long Fibers as Strength-Enhancing Additive to CMP Pulp

Iman Rashidi Jouybari, a, * Mahdi Yoosefi, b and Mohammad Azadfallah a

Compared to chemical pulp, mechanical and chemi-mechanical pulps (CMP) are limited in regards to the manufacturing of high quality paper. Chemical additives are an effective way to enhance the properties of paper; however, the effectiveness depends on the additive type and dosage. The utilization of cationized natural polymers has been shown to offer a promising solution. In this study, softwood long fiber (SLF) and CMP were cationized by 3-chloro-2-hydroxypropyl-trimethylammonium-chloride (CHPTAC), and the effects of cationization on the properties of CMP pulp were studied. Cationization was characterized by FTIR and the nitrogen content, and its effect on the CMP properties was evaluated through mechanical tests and fines retention. Cationization at low and moderate levels and in higher mixing rates improved the mechanical properties of CMP. Compared to cationized CMP, the addition of cationized SLF (CLF) improved the strength and fines retention properties. The CLF application to CMP at a CHPTAC dosage of 5% increased the tensile, burst, and tear strengths by 66.4%, 100%, and 3.6%, respectively. The cationized SLF increased the fines retention by 12.7%.

Keywords: Softwood; CMP; Cationization; EPTMAC; FTIR; Nitrogen content; Mechanical properties; Fines retention

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INTRODUCTION

Compared to chemical pulp fibers, mechanical and chemi-mechanical pulp (CMP) fibers have encountered some limited applications in the production of high quality papers. This limitation in usage can be attributed to the high lignin content and the fact that the fibers tend to be shorter, less flexible, and weak, resulting in papers with weak properties. However, mechanical pulps are able to provide paper with favorable characteristics, including high opacity (due to the high content of fines) and high bulk (mainly due to less flexible fibers), in which they are used in printing papers or in carton boards. Chemical additives are usually used in the papermaking industry as an effective way to enhance the strength of paper. Due to the negative charge density of cellulose fibers, cationic agents are mainly used to decrease the repulsion force while increasing the attraction force between particles during the paper forming process (Montplaisir et al. 2006a). Cationic agents also improve interfiber bonding, drainage, fines retention, and the mechanical properties of paper (Carre 1992; Gruber et al. 1996; Cezar and Xiao 2005; Khosravani 2006). In the past, cationic poly vinyl alcohol, cationic acrylamides, etc., have been used as strength agents and retention aids for various paper grades (Tanaka et al. 1990; Fatehi and Xiao 2008; Fatehi et al. 2009; Oulanti et al. 2009; Fatehi et al. 2010; Liu et al. 2011).
Natural polymers, such as cellulose fibers, chitosan, starch, etc., have been modified by cationization and used as strength agents in papermaking to improve the specific bond strength or increase the bonding area (Wei et al. 2008; Ma et al. 2010). Montplaisir et al. (2006a,b) reported that the cationization of thermo-mechanical pulp fibers as softwood thermo-mechanical pulp (TMP) fibers grafted with a quaternary ammonium group improved the strength of papers and the adsorption of fines on fibers. In another study, Wei et al. (2008) investigated the application of cationized pulp fibers as a papermaking wet-end additive. They found that the tensile strength of papers was improved by 12% when 0.9% cationized softwood fiber was added to wheat straw soda pulp, and no noticeable effect was found on the stock drainage. In another work by Ma et al. (2010), it was found that cationization could improve the interfiber bonding, but cationized fibers had no positive effect on sheet density.

The addition of amine groups to fibers is a commonly used method in functionalizing cellulose fibers and cationization, which is obtained through a polymer precipitate onto the fiber. Generally, the cationic modification of cellulose is achieved through the etherification of 2,3-epoxypropyltrimethylammonium chloride (EPTAC). However, the EPTAC, is unstable, toxic, and cannot be safely applied in industrial applications (Prado and Matulewicz 2014). An alternative to EPTAC is the use of environmentally friendly and stable form of (trimethylammonium) propyl group as 3-chloro-2-hydroxypropyltrimethylammonium-chloride (CHPTAC). The CHPTAC has successfully been used for the cationization of cellulose (Hashem et al. 2003a,b; Song et al. 2008), textile fibers (Liu et al. 2007; Montazer et al. 2007; Khalil-Abadet et al. 2009), and other polysaccharides (Pal et al. 2009; Prado et al. 2011; Hashem et al. 2013; Rashidi Jouybari 2012, 2013, 2015). Cationization affects the anionic surface charge density, which can settle the issues related to the repulsion and thereby increase the reactivity of the components used in papermaking (Schempp et al. 1983; Gess et al. 1989; Montplaisir et al. 2006a).

Because cationized long fiber (CLF) is an advantageous papermaking additive, if the technique of cationization could be improved, then the cost of papermaking would likely be decreased. Thus, it might replace synthetic cationic aids. The objective of this work was to develop a cationic biopolymer via grafting quaternary ammonium (CHPTAC) on softwood long fiber (SLF) as CLF, and its application as an additive to CMP pulp fiber in 5 different fractions. Furthermore, the CMP pulp fibers were cationized, and handsheets of cationized CMP fiber were made. The cationized fiber was characterized using Fourier transform infrared spectroscopy (FTIR), and nitrogen content; then the application performance of CMP cationization and CLF as an additive in CMP pulp fibers was evaluated by measuring the fines retention and the mechanical properties of handsheets.

EXPERIMENTAL

Materials

Bleached softwood kraft pulp (spruce) in the form of dried sheet was purchased from U-ilimsk Mill, Russia. The CMP prepared from native hardwoods was found north of Iran, and included Carpinus, Betulus, Populus, and Fagus in a ratio of 56:26:18 (without any additive, CSF 320) and a consistency of 5% was obtained from a pulp and paper mill in Mazandaran, Iran. The cationic ester quaternary ammonium salt was an aqueous solution

of 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC) at 60% (w/w), and the NaOH pellets were purchased from Sigma Aldrich.

**Methods**

**Cationization**

The CHPTAC was alkali-treated to obtain the more reactive form EPTAC. Scheme 1[a] presents the mechanism of synthesis of EPTAC. As a fast reaction, the chlorohydrin CHPTAC is converted to the epoxide EPTAC using alkali (Moral et al. 2015). Likewise, in each experiment (Table 1), the CMP and SLF were alkalized at an alkaline solution concentration of 20% (on the basis of oven-dry pulp mass), at 23 °C and kneaded well for 20 min. The treatment took place by the addition of an aqueous NaOH solution in a plastic bag containing pulp fiber. Subsequently, a hydroxyl group of the cellulose was converted into an alkoxide by reacting with an alkali (NaOH).

![Scheme 1](image)

**Scheme. 1.** [a] Alkali treatment of CHPTAC to produce EPTAC, [b] alkali treatment of cellulose to form alkoxide, and [c] cationization of alkali-treated cellulose with EPTAC according to Song et al. (2008)

After 20 min of kneading by hand, the bag that contained pulp fiber and the aqueous NaOH solution at room temperature, the EPTAC (alkalized CHPTAC) was added to the mixture and the container bag was sealed and placed in a water bath for 90 min at 50 °C. Meanwhile, the plastic bag was kneaded every 30 min to facilitate the cationisation reaction between the alkoxide on the cellulose and the EPTAC. Finally, the alkoxide from cellulose reacted with the EPTAC, resulting in cationized cellulose. During cationization, the degree of substitution is highly influenced by the quantity of NaOH. However, this addition is vital not only to generate EPTAC from CHPTAC, but also to weaken the hydrogen bonds between molecules, making the cellulose more accessible (Montazer et al. 2007). Therefore, it can be used as a pretreatment, taking into account the fact that an excess of NaOH causes polysaccharide hydrolysis and epoxide degradation towards the diol compound.

After the reaction time, the mixture was washed and neutralized to pH of 6.8 to 7.1 with acetic acid to hinder further reactions. The acidified long fiber suspension was then filtered and thoroughly washed by distilled water. The resulting suspension of cationized
CMP (denoted as CCMP) and SLF (denoted as CLF) with a consistency of 10% was stored in a refrigerator for further experiments.

**Table 1. Conditions of the Quaternization of CMP and SLF with CHPTAC in NaOH Aqueous Solution**

<table>
<thead>
<tr>
<th></th>
<th>NaOH (%) *</th>
<th>CHPTAC (%) *</th>
<th>Time (Minutes)</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CMP</strong></td>
<td>20</td>
<td>5</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>10</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td><strong>SLF</strong></td>
<td>20</td>
<td>5</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>10</td>
<td>90</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>15</td>
<td>90</td>
<td>50</td>
</tr>
</tbody>
</table>

* Based on fiber oven-dry weight

**Pulp blending and handsheets**

According to Table 2, 12 different scenarios were determined for the mixture trials and preparing of the handsheets.

**Table 2. Scenarios for Handsheet Mixtures (Based on the Oven-dry Weight of Handsheet Mass)**

<table>
<thead>
<tr>
<th>Experiments</th>
<th>CMP (%)</th>
<th>CCMP (%)</th>
<th>SLF (%) *</th>
<th>CLF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMP</td>
<td>100</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CCMP</td>
<td>0</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SLF 1</td>
<td>99</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>SLF 3</td>
<td>97</td>
<td>-</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>SLF 5</td>
<td>95</td>
<td>-</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>SLF 10</td>
<td>90</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>SLF 15</td>
<td>85</td>
<td>-</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>CLF 1</td>
<td>99</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>CLF 3</td>
<td>97</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>CLF 5</td>
<td>95</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>CLF 10</td>
<td>90</td>
<td>-</td>
<td>-</td>
<td>10</td>
</tr>
<tr>
<td>CLF 15</td>
<td>85</td>
<td>-</td>
<td>-</td>
<td>15</td>
</tr>
</tbody>
</table>

*Untreated Softwood long fiber (SLF) + CMP = "Control"

**Characterization of cationized fiber-FTIR**

The FTIR spectrum of the cationized sample was performed with a Nicolet 170SX Fourier transform infrared spectrometer. Samples of 0.5 g of pulp were prepared and analyzed via the KBr-disk method.

**Nitrogen content and degree of substitution (DS)**

The cationization levels on the treated fibers could be quantified by measuring the nitrogen content (Liu et al. 2007; Song et al. 2008). The nitrogen contents of CLF were measured with an elemental analyzer (CHN-O-Rapid, Foss Hera us GmbH, Hanau, Germany). The DS value estimated the average number of substituent cationic groups per anhydro-glucose unit of cellulosic fiber. The DS value of CLF was determined by the nitrogen content and calculated according to Eq. 1,
where $N\%$ denotes the percentage of dry elemental nitrogen, 14 is the atomic weight of nitrogen, and 151.5 is the molecular weight of the epoxypropyl trimethyl ammonium chloride (EPTMAC) group that was added.

**Measurement of the physical strength properties**

The handsheets were prepared according to TAPPI T-205-sp-95 (2002) using a FORMAX Standard Sheet Mold (Queensbury, USA). The grammage of the handsheets was targeted at 60 g/m². For every experiment, 10 handsheets were made for the different levels of mixing of CLF (Table 2) as an additive with the CMP pulp fibers and CMP. The handsheets conditioned at 23 °C ± 1 °C and used for further analyzing.

To investigate the effect of cationization on mechanical properties of CMP pulp fibers, the tensile, burst, and tear strength tests were measured on handsheets according to ISO-1924-2 (2008), TAPPI T-403 om-97 (1997), and TAPPI T 414 om-04 (2004) standards, respectively.

**Fines retention**

The effect of the cationized fiber on the retention of fines of CMP pulp fibers was evaluated by a Dynamic Drainage Jar (DDJ) equipped with a 100-mesh wire. The well-mixed pulp (CMP and CMP + CLF) was made at a 0.8% consistency (similar to headbox consistency) and a rotational speed at 1200 rpm filtered through the DDJ. The measurement was performed at CHPTAC dosages of 5% and 10% and in six different levels of mixture (as required by the experiment scenarios), as shown by Gruber et al. (1998).

**RESULTS AND DISCUSSION**

**Characterization of Cationization**

**FTIR spectroscopy**

To determine the existence of the cationic agent on the surface of CLF, a Fourier transform infrared spectroscopic (FTIR) analysis was used. Figure 1 shows the FTIR spectra of the CMP and the cationized fiber sample as CLF.
The CMP pulp fiber showed a broadband at around 3400 cm$^{-1}$, assigned to the stretching vibration modes of the O-H groups. The bands at 1062 cm$^{-1}$, 1375 cm$^{-1}$, and 2900 cm$^{-1}$ were attributed to the stretching vibration of the -CH$_2$- groups in CMP pulp. Compared to the spectrum of CMP, an additional absorption band was observed around 1734 cm$^{-1}$ in the spectrum of CLF and was assigned to the ester carbonyl group of the cationic agent. The most striking difference between the native cellulose and the CLF spectra were the peaks at 1482 cm$^{-1}$, which correspond to the methyl groups of ammonium (Loubaki et al. 1991) and the peak region around 1414 cm$^{-1}$, which was referenced as the C-N stretching vibration according to Pal et al. (2005). The FTIR spectra have proven the existence of the quaternary ammonium on the cationized softwood long fibers.

**Nitrogen Content and Degree of Substitution (DS)**

The nitrogen content of cationized softwood long fibers was listed as an indicator of the amount of CHPTAC that reacted with the fibers in Table 3. Nitrogen content and DS increased with an increase in the CHPTAC concentration; this implied that by increasing the concentration of CHPTAC, more quaternary ammonium groups were attached to the fibers. This may have been because the reactivity of the cellulosic fibers was improved after treatment due to the increased accessibility of the primary and secondary hydroxyl groups (Montazer et al. 2007; Pönni et al. 2014; Rashidi Jouybari 2013, 2015). In comparison with SLF, the nitrogen content and DS increased for the modified fibers, which was assigned to the grafting of the quaternary ammonium on the fibers.

**Table 3. Nitrogen Content and DS**

<table>
<thead>
<tr>
<th>CHPAC/fiber Ratio (wt.%)</th>
<th>Nitrogen Content (%)</th>
<th>DS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLF 5%</td>
<td>1.7</td>
<td>0.241</td>
</tr>
<tr>
<td>CLF 10%</td>
<td>2.18</td>
<td>0.33</td>
</tr>
<tr>
<td>CLF 15%</td>
<td>2.43</td>
<td>0.386</td>
</tr>
</tbody>
</table>

**Handsheat Density**

As seen in Fig. 2, the cationization of fibers, for both CCMP and CLF, increased the handsheet density.
As a result, when the CLF was blended with the CMP, the sheet density was augmented with increased CHPTAC dosage. The sheet density for CMP was approximately 0.31 g/cm$^3$; however, the cationization of CMP at the CHPTAC dosage of 15% reached the highest value of 0.42 g/cm$^3$, an improvement of approximately 35%. The SLF was insignificantly changed in the different pulp blendings. However, the addition of cationized SLF, increased the sheet density up to 30%. It could be found that the handsheets of cationized CMP increased the sheet density more remarkably compared to the addition of CLF.

The alkali treatment and cationization increased the fiber flexibility, which improved the sheet density. The augments in the CHPTAC dosage and fiber flexibility led to substantial improvement in interfiber bonding, as a result of improved fiber conformability.

**Measurement of the Physical Strength Properties**

To investigate the effect of cationization on the mechanical properties of CMP paper, the tests including tensile, burst, and tear strengths were applied. Alkali treatment appears to form an ether group, which then is available to form ion-dipole interaction with the cationic quaternary amine group of the cationized additive attached to the fiber and introduce an ether bond of the ion-dipole between fibers. However, the main bond in paper, is of Van der Waals (induced dipole interactions) with binding energy of 2 kJ/mol to 8 kJ/mol and hydrogen bonds with the bond energy around 8 kJ/mol to 32 kJ/mol. The cationization of CHPTAC induced ion-dipole with a binding energy of 65 kJ/mol to 72 kJ/mol, which implied that it could greatly increase the paper strengths (Gullichsen et al. 2000).

**Tensile strength**

The tensile strength is certainly the property that responds most to interfiber bonding. As in the case of sheet density, the tensile index of the handsheets increased as the CHPTAC dosage was augmented. According to Fig. 3, the cationization of CMP (denoted as CCMP), improved the strength up to 45.8% at the 15% CHPTAC dosage, while the sheet density was increased by approximately 35%. Furthermore, the addition of
untreated SLF as a reinforcing fiber to CMP increased the tensile strength by approximately 1.3% to 28.5%, but grafting increased the tensile strength by approximately 40% to 66.4%. As seen in Fig. 3, the tensile index increased with increased CLF portions. The long fiber treatment in a 10% CHPTAC dosage had a noticeable effect. However, further cationization decreased the tensile index noticeably when the cationic dosage was higher than 10%. At a low level of pulp mixture up to 5%, a CHPTAC dosage of 10% was the best treatment, but in CLF 10 and CLF 15, a 5% CHPTAC dosage had the best effect on the tensile index. The highest increase in the tensile strength index (51 Nm/g) was achieved by a 5% CHPTAC dosage and a 15% portion of mixture. According to the result, it was found that the addition of CLF compared to the cationization of CMP, was more effective in improving the tensile strength. In other work conducted by Fatehi and Xiao (2008), the effect of charge density and molecular weight of cationic poly (vinyl alcohol) on paper properties was investigated. They reported that cationic polyvinyl alcohol increased the tensile strength from 35.4 N.m/g for control to 45.6 N.m/g (i.e., a maximum improvement of 28.8%) was achieved.

**Fig. 3.** Effect of CCMP and CLF as additive to CMP pulp fiber in different portions on the tensile strength index

Pelton (2004) demonstrated that fiber bonding can be developed if fibers get closer to each other within a distance scale of 10 nm. In other words, a cationic additive could increase the fiber bonding if its size is greater than 10 nm, which would be sufficient to bridge the fibers. Therefore, the first factor that could improve the fiber bonding is the size of polymers, in which the cationized fiber meets this condition and cationization can improve the interfiber bonding (Ma et al. 2010). This explanation could have been the reason for the improving of the tensile strength of the CHPTAC-treated paper. The second factor influencing the fiber bonding enhancement through additive application could be the configuration of cationic agent on the fiber surface (Tanaka et al. 1990). The third factor affecting fiber bonding could be the effective interaction between the cationic agent and the anionic groups on the fiber surfaces that strengthens the bridges among neighboring fibers (Fatehi and Xiao 2008). On the contrary, the bonding capacity drops off with increasing cationic charge density (Ma et al. 2010).

**Burst strength**
The burst index also responded to the inter-fiber bonding. This is consistent with the multidimensional aspect of this method, but the relative effect was greater than the in the case of tensile strength. The result achieved by the burst strength test is illustrated in Fig. 4. The data corresponded to those achieved by the tensile strength.

The burst strength for CCMP increased to 73% at 15% CHPTAC dosage, compared to CMP. The addition of the untreated SLF as a reinforcing fiber to CMP increased the burst strength by approximately 23%, to 55.2%, and cationization grafting as CLF further increased by 46 to 44.8%. In other words, further cationization was not applicable to increase the strength in paper. This was possibly due to the alkali hydrolysis and unwanted side reaction of the cationic agent with the alkali and increasing repulsive force between the fibers, in which the bonding capacity dropped off with increased cationic charges (Ma et al. 2010).

Compared to CMP, the highest strength improvement was approximately 100% for CLF 15 at the 5% CHPTAC dosage. According to the results, it could be found that the CLF was more effective in improving paper strength compared to CCMP. According to Fatehi and Xiao (2008), cationic poly vinyl alcohol (C-PVA) improved the burst strength from 2.7 kPa.m²/g for control to 3.4 kPa.m²/g, a maximum improvement of 25.9% was obtained.

Compared to CMP, the highest strength improvement was approximately 100% for CLF 15 at the 5% CHPTAC dosage. According to the results, it could be found that the CLF was more effective in improving paper strength compared to CCMP. According to Fatehi and Xiao (2008), cationic poly vinyl alcohol (C-PVA) improved the burst strength from 2.7 kPa.m²/g for control to 3.4 kPa.m²/g, a maximum improvement of 25.9% was obtained.

**Tear strength**

The higher sheet density and interfiber bonding rate causes less mobility of the fibers within the sheet, which results in a reduction of the tear strength, but this change is highly dependent on the intrinsic fiber strength, according to Gullichsen et al. (2000). The result achieved for the tear strength is shown in Fig. 5. Generally, the tear strength index is a good indication of the treatment effects on the intrinsic fiber strength. The result confirmed the observations achieved by the tensile and burst data. The tear index for CMP paper was approximately 4.11 N.m²/kg and it increased to 4.14 N.m²/kg for CCMP at the 15% CHPTAC dosage.

By the addition of 1% untreated SLF to 99% of the CMP mixture (based on the handsheet oven dry weight), the index increased to 4.13 N.m²/kg, and by 1% CLF reached 4.14 Nm²/kg at 10% CHPTAC. The CHPTAC dosage of 10% was sufficiently strong to increase the tear index for the experiments CLF 1 to CLF 10; however, in CLF 15 the
CHPTAC dosage of 5% had reached the peak. The maximum amount of tear strength was approximately 4.26 Nm^2/kg for experiment CLF 15 and the 5% CHPTAC dosage. In addition, the maximum strength gain rate was approximately 3.6% for CLF 15. Compared to the tensile and burst strength, the lower increase in tear was somewhat attributed to the repulsive force between the cationic groups. The addition of the long fiber enhanced the tear strength and the densification obtained by the addition of cationized fibers did not affect the tear strength.

With the increase in interfiber bonding and decrease in intrinsic fiber strength due to alkalization and cationization, it was understandable that the tear strength of the cationic fibers increased slightly as the cationic charge augmented (Fatehi et al. 2008; Ma et al. 2010). The decrease in the tear index of papers, while the tensile and burst indices were increased, has been attributed to the increase of fiber breakage, which needed less force than the pulling-out of fiber in the tear test (Fatehi and Xiao 2008).

**Fig. 5.** Effect of CCMP and CLF as an additive to CMP pulp fiber in different portions on the tear strength index

**Fines retention**

According to Fig. 6, the effect of cationization on CMP pulp fines in CHPTAC dosages of 5% and 10% is illustrated. There was a linear trend in the CHPTAC dosage and fines retention. The fines retention for CMP was approximately 15.9% (based on oven dry pulp mass); however, the cationization of CMP at the CHPTAC dosage of 10% increased the fines retention up to 8.7%. Furthermore, the addition of CLF at the CHPTAC dosages of 5% and 10% increased the fines retention to 16.3 and 17.0, respectively, in the mixing rate of 1%. Compared to the CHPTAC dosage of 5%, the 10% CHPTAC dosage had a better effect and improved the retention to 28.6%, a 12.7% retention gain. The maximum improvement at the CHPTAC dosage of 10% was 12.7% for CLF 15. This result corresponded with those achieved by mechanical strengths.
Fig. 6. Effect of CCMP and CLF as an additive to CMP pulp fiber in different portions on the fines retention

*Tensile strength as a function of density*

Figure 7 presents the tensile strength as a function of density. For untreated fibers, the tensile strength increased with further addition of the softwood long fiber to CMP, and both the tensile strength and sheet density were increased. The cationization at dosage rate of 15% had efficiently increased the tensile strength and sheet density. It could probably be attributed to the introduction of more bonding area and fines retention. By a cationization at 15% and a softwood long fiber content of 5%, the maximum values for tensile strength and sheet density were achieved approximately 48.24 Nm/g and 0.43 g/cm$^3$, respectively. It was clear that cationization was the main reason for strength increase, and sheet density was the second reason for increased tensile strength.

Fig. 7. Effect of CCMP and CLF as an additive to CMP pulp fiber in different portions on tensile strength as a function of density
Tear strength as a function of tensile strength

As Fig. 8 illustrates, the tear strength as a function of tensile strength, and the addition of cationized softwood long fiber significantly increased the tensile strength while the tear strength was slightly higher.

![Graph showing tear strength as a function of tensile strength](image)

**Fig. 8.** Effect of CCMP and CLF as an additive to CMP pulp fiber in different portions on tear strength as a function of tensile strength

Generally, increased tensile strength would lead to decreased tear strength, while the result confirmed that both properties have been increased. The correlation between the tear and tensile strength confirmed that cationization was the key factor in developed tensile strength.

**CONCLUSIONS**

1. The CMP pulp fiber and softwood long fibers were successfully cationized by CHPTAC in NaOH aqueous solution.
2. The FTIR spectra and nitrogen content confirmed the cationization of CHPTAC on softwood long fibers.
3. The proportion of nitrogen in cationized fibers increased with increased dosage of CHPTAC.
4. Cationic grafting was efficient in enhancing the overall paper strengths through increasing the inter-fiber bonding potential via introducing more bonded area under alkali pre-treatment, improving the bond strength and possibly the fines retention.
5. Cationization of both the CMP and the addition of CLF to CMP increased the sheet density and paper strength remarkably. However, compared to CCMP, the CLF presented less of an effect on the sheet density; it most increased the strength properties. The augments in the CHPTAC dosage and fiber flexibility led to significant improvement in the interfiber bonding, as a result of improved fiber conformability.
Consequently, the tensile and burst indices of the handsheets were considerably enhanced.

6. The promising results were achieved at a CHPTAC dosage of 5% and CLF mixing rate of 15%, which led to the tensile strength of 66.4%, a burst strength of 100, and tear strength of 3.6%. The result also showed promise, as 12.7% retention of fines was achieved for CLF 15 under the CHPTAC dosage of 10%.

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