

# Effects of Chitosan, Poly-diallyldimethylammonium chloride, and Cationic Polyacrylamide on the Optical and Mechanical Properties of Paper from Chemi-mechanical Pulp

Ramin Vaysi,\* Majid Kiaei, and Hatef Heydari

The effects of chitosan, poly-DADMAC, and cationic polyacrylamide (cPAM) were evaluated relative to the optical and mechanical properties of paper from chemical-mechanical pulp (CMP) from Mazandaran Pulp and Paper Mill. Additives were applied at different concentrations: chitosan (0%, 1%, and 2%), poly(diallyldimethylammonium chloride) (poly-DADMAC): 0%, 0.3%, 0.5%, and 0.7%), and cPAM (0%, 0.25%, 0.5%, and 0.75%). Papers with a basis weight of 60 g/m<sup>2</sup> were prepared, and brightness, opacity, *a*\* factor, tensile strength, breaking length, tear strength, and burst strength were evaluated. Factorial analysis of variance showed that the effects of the three additives varied depending on the property evaluated. Chitosan positively affected brightness, breaking length, and tear strength; PAM showed a particularly strong effect on breaking length and tensile strength; and poly-DADMAC contributed to improvements in brightness, tensile strength, and the *a*\* factor. Scanning electron microscopy showed a relatively denser and more interconnected fiber network in treated papers, with fewer visibly open void spaces and greater apparent fiber contact. These morphological changes may be associated with improved inter-fiber interactions and the observed changes in paper properties. Among the tested formulations, the combination of 2% chitosan, 0.25% cPAM, and 0.7% poly-DADMAC provided favorable overall performance.

DOI: 10.15376/biores.21.4.10449-10465

*Keywords:* Poly DADMAC; Chitosan; Cationic polyacrylamide; CMP pulp; Optical and mechanical properties

*Contact information:* Department of Wood and Paper Science and Technology, Cha.C., Islamic Azad University, Chalus, Iran; \*Corresponding author: vaysi\_r452@iaui.ac.ir

## INTRODUCTION

In recent years, the global rise in population and the corresponding increase in demand for paper and cardboard, combined with the growing scarcity of raw materials, has driven the pulp and paper industry to focus on high-yield and mechanical pulps. These pulps offer a higher yield of over 85% and a lower proportion of dissolved wood substances compared to chemical and semi-chemical pulps. However, due to the presence of lignin, extractives, and metal ions, their use is generally restricted to short-term applications. Over time, they tend to face issues such as brightness reversion and photo-yellowing, which limit their performance in certain paper grades.

Chemical-mechanical pulp (CMP) is typically produced through a multi-stage process, achieving yields between 80% and 90%. The CMP process requires longer treatment times and higher temperatures compared to the CTMP (chemithermomechanical

pulp) process. Wood chips undergo pre-treatment at temperatures below 100 °C, followed by chemical treatment using sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) at temperatures above 100 °C. After cooking, the pulp is refined under atmospheric pressure in one or two stages, depending on the desired freeness (approximately CSF 300 to 400). The higher chemical content used in CMP production results in superior pulp quality compared to CTMP, which is why CMP is often preferred in paper mills where paper strength and printability are prioritized.

In Iran, CMP pulp is produced at the Mazandaran Pulp and Paper Mill using a mixture of 75% hornbeam and 25% poplar and beech wood. Future plans include gradually replacing beech wood with imported poplar. This mill produces approximately 52,000 tons of newsprint and 38,000 tons of printing and writing paper annually. To improve paper runnability during production and printing, about 15% of long fiber is imported, typically sourced from softwood kraft pulp. This reliance on imported materials leads to significant foreign currency expenditure, creating a dependency on external supplies (Vaysi and Ebadi 2021).

Although CMP pulps have lower mechanical strength, shorter fiber lengths, higher fines content, and reduced retention of fines and fillers compared to chemical pulps, they are still widely used in certain products, such as newsprint, printing papers, and cardboard, due to their higher yield and better printability. To improve the optical properties, printability, and reduce production costs, approximately 5 to 15% of non-fibrous additives (fillers) are added to the stock. Most of these additives are anionic and do not bind well to the fibers, making them prone to being washed away with white water during the paper formation process. Moreover, the fines, which arise from wood cell structures or are introduced after refining, also carry a negative charge. To enhance the retention of these anionic fines and fillers on the fibers, cationic (positively charged) additives are necessary.

The use of cationic additives, such as poly(diallyldimethylammonium chloride) (poly-DADMAC), chitosan, and cationic polyacrylamide (cPAM), has shown promising results in improving retention and enhancing the optical and mechanical properties of papers made from CMP pulps. Therefore, this study focused on the role of these additives in improving retention and the properties of CMP pulp-based paper.

Chitin, the second most abundant natural biopolymer after cellulose, has a structure similar to cellulose, with the key difference being the presence of acetyl amino ( $-\text{NHCOCH}_3$ ) groups at the C2 position of the carbon chain. The deacetylated derivative of chitin is known as chitosan. Chitosan is biodegradable, biocompatible, antibacterial, and antifungal. It is derived from renewable sources such as marine crustaceans. The structural similarities between chitosan and cellulose make it highly compatible with cellulose fibers in pulp. The primary distinction is that the hydroxyl group at C2 in cellulose is substituted with an amino group in chitosan, significantly enhancing its reactivity with cellulose fibers (Steckel and Mindermann-Nogly 2003; Rahmaninia *et al.* 2015). Previous studies have demonstrated that chitosan, as an amino polysaccharide, can form strong bonds with cellulose fibers, achieving up to 40% higher efficiency than starch. The positive charges of chitosan, combined with the negative charges on cellulose materials, help form stronger bonds, resulting in more durable paper (Pariser and Lombardi 1998; Vanerek *et al.* 2006).

Poly-DADMAC is another cationic polymer that is commonly used as an organic coagulant in wastewater treatment. It is synthesized through radical polymerization and is highly effective in neutralizing negatively charged colloidal particles, resulting in reduced sludge volumes. Poly-DADMAC is known for its strong ability to improve retention and paper strength properties when incorporated into papermaking systems.

Cationic polyacrylamide (cPAM), a widely used retention aid in papermaking, is a high-molecular-weight polymer with moderate cationic charge. It is produced from acrylamide monomers polymerized in a chain structure. cPAM exhibits excellent thermal stability and is highly soluble in water. Its applications in papermaking include improving dewatering efficiency through the bridging mechanism, reducing fines loss, and enhancing paper strength. The cPAM is extensively used not only in the paper industry but also in other industrial sectors, such as wastewater treatment, mining, and oil extraction.

In the paper industry, cPAM is commonly used to improve the dewatering of paper sheets, reducing the amount of polymer required when combined with other additives such as bentonite. The combination of cPAM with other cationic polymers has been shown to improve both retention and the overall quality of the paper produced. Additionally, by minimizing the loss of fibrous materials and non-fibrous additives, these additives can also reduce pollution from wastewater, thereby addressing environmental concerns and reducing raw material costs.

Recent studies have also highlighted the potential of chitosan in improving the strength and retention properties of paper. For example, Zhang *et al.* (2022) demonstrated that chitosan significantly enhanced the strength properties of paper made from mechanical pulp by improving the fiber bonding and reducing water retention issues. In addition, Heydari *et al.* (2024) reported that in all treatments, the best results were found at 1% chitosan and 0.5% cPAM due to favorable mechanical and optical properties.

For instance, Ahmadi Lajimi *et al.* (2019) investigated the effect of a cationic stabilizer based on poly-DADMAC on the strength properties of old corrugated container (OCC) pulp, reporting significant improvements in tensile strength, burst strength, and other key mechanical properties.

In this context, this study aimed to investigate the use of chitosan, poly-DADMAC, and cPAM, both individually and in combination, to enhance the optical and mechanical properties of chemical-mechanical pulp (CMP). The goal of this investigation was to optimize the application of these additives to achieve superior paper properties while addressing environmental concerns associated with high-pollution effluents from paper mills.

## EXPERIMENTAL

### Materials

#### *Preparation of test samples*

For this study, CMP was sourced from the paper machine unit (Unit 600) at Mazandaran Wood and Paper Industries (MWPI). The pulp was bleached and refined to achieve a freeness of approximately 300 CSF. A portion of this pulp was designated as the control sample for comparison. At MWPI, the CMP is derived from a blend of 75% hornbeam (*Carpinus betulus*) and 25% poplar (*Populus* spp.) and beech (*Fagus* spp.) wood. Future production plans indicate that poplar and imported species will gradually replace beech wood (Vaysi and Ebadi 2021).

#### *Cationic polyacrylamide (cPAM)*

Cationic polyacrylamide (cPAM), commercially available under the brand name Farinret K325 (Degussa), was selected for this study. The cPAM used in this work was a high-molecular-weight polymer (about 10 mDa) with a moderate cationic electric charge

(about 15 % mol). It is commonly utilized as a retention aid and dewatering agent in papermaking. A 0.1% solution of cPAM was prepared and incorporated into the pulp slurry at concentrations of 0%, 0.25%, 0.5%, and 0.75%. This polymer is being evaluated for potential use at MWPI, where alum and cationic starch are currently employed as retention aids in the production of newspaper-grade paper (Tajik 2015; Li *et al.* 2022).

#### *Chitosan preparation*

Chitosan was purchased from (“Seafresh”, Thailand), which was prepared from exoskeletons of crustaceans. The material was described as nanochitosan, and the powder had an average diameter of 40 to 60 nm. The chitosan had a deacetylation degree of 93% and a molecular weight of 270 kDa. To preparation, the required amount of chitosan was dissolved in a 1% acetic acid, and mixture was stirred at room temperature for 2 h. Chitosan was loaded at 1 and 2% of the dry pulp weight (Table 1, Ashoori *et al.* 2005; Nicu *et al.* 2010; Rezazadeh *et al.* 2022).

#### *Poly-DADMAC*

Poly(diallyldimethylammonium chloride) (poly-DADMAC), a cationic polymer, was supplied by Chinafloc Fine Chemical Company, China. It was obtained as a colorless to pale-yellow aqueous solution, with a viscosity range of 200 to 1000 cP, a pH of 4 to 7, and a solids content of approximately 30%. The poly-DADMAC used in this study had a molecular weight ranging from 400,000 to 600,000 g/mol and was purchased from Sigma-Aldrich. This polymer was incorporated into the CMP pulp slurry at concentrations of 0%, 0.3%, 0.5%, and 0.7% (Zhao *et al.* 2023; Heydari *et al.* 2024).

**Table 1.** Variables Information in this Study

| Chitosan | cPAM | Poly-DADMAC | Number of Handsheets | N |
|----------|------|-------------|----------------------|---|
| 0        | 0    | 0           | 10                   | 3 |
| 1        | 0.25 | 0.3         | 10                   | 3 |
| 2        | 0.5  | 0.5         | 10                   | 3 |
| -        | 0.75 | 0.7         | 10                   | 3 |

Note: The combinations of treatment levels resulted in a total of 48 experimental treatments. For each treatment, 10 handsheets were prepared and each property was tested with three repetitions (N = 3)

#### **Optical and Mechanical Properties**

Handmade paper sheets were formed from the CMP pulp and the control pulp, adhering to Technical Association of Pulp and Paper Industry (TAPPI) standard method T205 om-88 (2009), with a basis weight of 60 g/m<sup>2</sup>. The optical properties, including brightness and opacity, were measured using a spectrophotometer calibrated according to the CIE (Commission Internationale de l'Éclairage) *L\*a\*b\** color system. Brightness and opacity were determined following TAPPI methods T452 om-98 (1996) and T425 om-96 (1996), respectively.

Mechanical properties of the handmade papers, namely the tear strength, burst strength and tensile strength, were evaluated using the following TAPPI standard methods: T414 om-98 (1998), T403 om-02 (2002), and T 494-om-96 (1996).

## Statistical Analysis

Statistical analysis of the data was conducted using SPSS software (version 21). A factorial experimental design was employed to evaluate the main and interaction effects of the variables. A multi-way analysis of variance (ANOVA) was performed to determine the significance of the treatments. Pairwise mean comparisons were made using Duncan's multiple range test to assess statistical differences between the groups.

## RESULTS

The statistical results illustrating the effects of additives (chitosan, poly-DADMAC, and cPAM) on the mechanical and optical properties of CMP are presented in Table 2. Due to the large number of treatment combinations (48 treatments), only representative treatments showing the most pronounced effects for each paper property are presented graphically, while the entire dataset was used for statistical analysis, and the best treatment for each property was selected.

**Table 2.** Multi-way Analysis of Variance for the Effects of Chitosan, Poly-DADMAC, and cPAM on CMP Paper Properties

| Properties      | Source        | Sum of Squares | df | Mean Squares | F       | Sig                 |
|-----------------|---------------|----------------|----|--------------|---------|---------------------|
| Brightness      | Chit (A)      | 3.288          | 2  | 1.644        | 5.305   | 0.007*              |
|                 | cPAM (B)      | 124.684        | 3  | 41.561       | 134.102 | 0.0001*             |
|                 | Poly-ADMAC(C) | 954.72         | 3  | 318.241      | 1026.84 | 0.0001*             |
|                 | A×B×C         | 252.14         | 18 | 14.008       | 45.197  | 0.0001*             |
| Opacity         | Chit (A)      | 111.89         | 2  | 55.94        | 81.32   | 0.0001*             |
|                 | cPAM (B)      | 224.17         | 3  | 74.72        | 108.62  | 0.0001*             |
|                 | Poly-ADMAC(C) | 3.105          | 3  | 1.035        | 1.504   | 0.218 <sup>ns</sup> |
|                 | A×B×C         | 170.174        | 18 | 9.45         | 13.74   | 0.0001*             |
| Tear            | Chit (A)      | 1038.9         | 2  | 519.47       | 5.91    | 0.004*              |
|                 | cPAM (B)      | 3261.8         | 3  | 1087.27      | 12.37   | 0.0001*             |
|                 | Poly-ADMAC(C) | 508.5          | 3  | 169.51       | 1.926   | 0.130 <sup>ns</sup> |
|                 | A×B×C         | 1465.9         | 18 | 81.441       | 0.927   | 0.549 <sup>ns</sup> |
| Breaking Length | Chit (A)      | 6.480          | 2  | 3.240        | 84.01   | 0.0001*             |
|                 | cPAM (B)      | 13.971         | 3  | 4.657        | 120.75  | 0.0001*             |
|                 | Poly-ADMAC(C) | 13.897         | 3  | 4.632        | 120.12  | 0.0001*             |
|                 | A×B×C         | 5.883          | 18 | 0.327        | 8.474   | 0.0001*             |
| Tensile         | Chit (A)      | 1.709          | 2  | 0.855        | 14.107  | 0.0001*             |
|                 | cPAM (B)      | 13.42          | 3  | 4.474        | 73.854  | 0.0001*             |
|                 | Poly-ADMAC(C) | 3.042          | 3  | 1.014        | 16.737  | 0.0001*             |
|                 | A×B×C         | 2.540          | 18 | 0.141        | 2.330   | 0.004*              |
| Bust            | Chit (A)      | 5762           | 2  | 2881         | 72.39   | 0.0001*             |
|                 | cPAM (B)      | 2060.354       | 3  | 686.78       | 17.256  | 0.0001*             |
|                 | Poly-ADMAC(C) | 99.299         | 3  | 33.1         | 0.832   | 0.480 <sup>ns</sup> |
|                 | A×B×C         | 70.056         | 18 | 3.862        | 0.098   | 1.000 <sup>ns</sup> |
| a* factor       | Chit (A)      | 0.847          | 2  | 0.424        | 10.29   | 0.0001*             |
|                 | cPAM (B)      | 28.77          | 3  | 9.59         | 233.19  | 0.0001*             |
|                 | Poly-ADMAC(C) | 87.73          | 3  | 29.24        | 710.99  | 0.0001*             |
|                 | A×B×C         | 23.678         | 18 | 1.315        | 31.98   | 0.0001*             |

\* Significant at 5%; ns: not significant

## Brightness

Statistical analysis using multi-way analysis of variance (ANOVA) indicated that the independent effect of chitosan on brightness was statistically significant ( $F = 5.305$ ,  $p = 0.007$ ). Similarly, the independent effects of cPAM ( $F = 134.102$ ,  $p < 0.001$ ) and poly-DADMAC ( $F = 1026.84$ ,  $p < 0.001$ ) were significant. Moreover, the three-way interaction effect of chitosan, cPAM, and poly-DADMAC on brightness was also significant ( $F = 45.197$ ,  $p < 0.001$ ), highlighting the importance of the combined application of these additives in affecting the optical properties of the paper.

The results revealed that the incorporation of chitosan, along with cPAM and poly-DADMAC, into CMP pulp resulted in 48 distinct treatment combinations. Compared to the control sample, which was prepared without any additives and had a brightness of 66.3%, ten treatments showed a decrease in brightness, while 37 treatments exhibited a significant increase. The lowest brightness (60.8%) was observed in paper produced from the treatment containing 1% chitosan, 0.75% cPAM, and 0% poly-DADMAC. In contrast, the highest brightness (75.4%) was obtained in the treatment with 2% chitosan, 0.5% cPAM, and 0.7% poly-DADMAC, while a brightness of 75% was also recorded for the treatment containing 2% chitosan, 0.75% cPAM, and 0.7% poly-DADMAC.

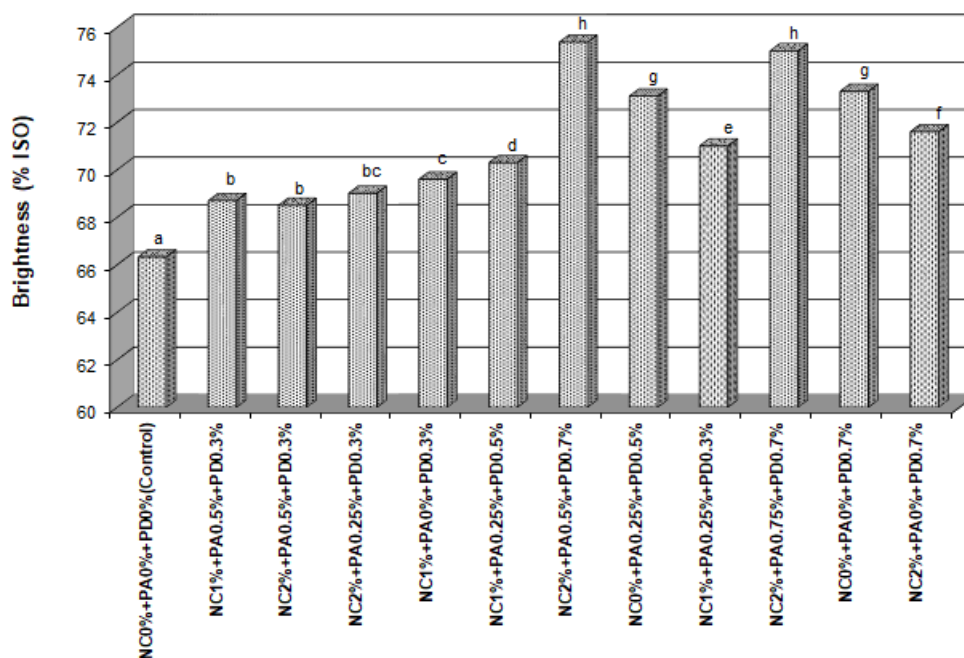


**Fig. 1.** Comparing brightness in the paper made by adding cPAM, poly-DADMAC and chitosan to CMP

## Opacity

Statistical analysis (Table 2) indicated that the main effects of chitosan and cPAM on paper opacity were significant at the 1% level, whereas the main effect of poly-DADMAC was not significant. Moreover, the three-way interaction effect of chitosan, cPAM, and poly-DADMAC was significant ( $F = 13.74$ ,  $p < 0.001$ ), indicating that the effect of these additives on the opacity of CMP paper depended on their combined application.

Qualitative results showed that the incorporation of chitosan along with cPAM and poly-DADMAC into CMP pulp resulted in 48 distinct treatment combinations. Compared

to the control sample (0% chitosan, 0% cPAM, and 0% poly-DADMAC) with an opacity of 80.8%, two treatments exhibited lower opacity.

The lowest opacity (80.2%) was observed in the paper produced with 2% chitosan, 0% cPAM, and 0% poly-DADMAC. In contrast, 45 treatment combinations caused a significant increase in opacity. The highest opacity (89.0%) was recorded in the treatment with 2% chitosan, 0.25% cPAM, and 0% poly-DADMAC, while an opacity of 88.8% was observed in the paper produced from the treatment with 2% chitosan, 0.75% cPAM, and 0.7% poly-DADMAC.

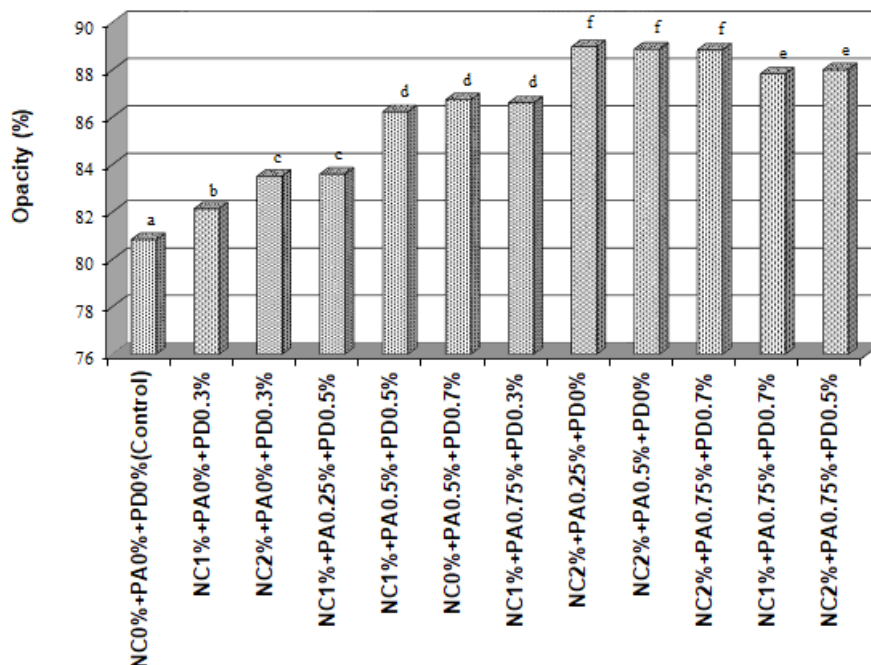


**Fig. 2.** Comparing opacity in the paper made by adding cPAM, poly-DADMAC, and chitosan to CMP

### ***a*\* Coefficient**

In the CIE  $L^*a^*b^*$  color system, the  $a^*$  factor indicates the color range from green to red in paper. In newsprint and printing paper, the degree of greenness is particularly important.

The results showed that the addition of chitosan, along with cPAM and poly-DADMAC, to CMP pulp resulted in 48 distinct treatment combinations. Statistical analysis of the data (Table 2) indicated that the main effects of chitosan ( $F = 10.29$ ,  $p < 0.001$ ), cPAM ( $F = 233.19$ ,  $p < 0.001$ ), and poly-DADMAC ( $F = 710.99$ ,  $p < 0.001$ ) on the  $a^*$  factor were statistically significant. Moreover, the three-way interaction effect of chitosan, cPAM, and poly-DADMAC was also significant ( $F = 31.98$ ,  $p < 0.001$ ), indicating that the effect of these additives on the  $a^*$  factor depended on their combined application.

Compared to the control sample, which was produced by simultaneously adding chitosan, poly-DADMAC, and cPAM at 0%, with an  $a^*$  coefficient of 0.2, three treatments exhibited a lower  $a^*$  value and a higher degree of greenness. The lowest  $a^*$  value (-0.5) was observed in the paper produced from the treatment with 0% chitosan, 0.25% cPAM, and 0% poly-DADMAC.

In contrast to the control, 44 treatments showed a significant increase in the  $a^*$  value, indicating a reduction in greenness. The highest  $a^*$  value (5.5) was recorded in the treatment containing 0% chitosan, 0.5% cPAM, and 0.7% poly-DADMAC. Similarly, the paper produced from the treatment involving 2% chitosan, 0.5% cPAM, and 0.7% poly-DADMAC also exhibited a notable  $a^*$  value of 4.6.

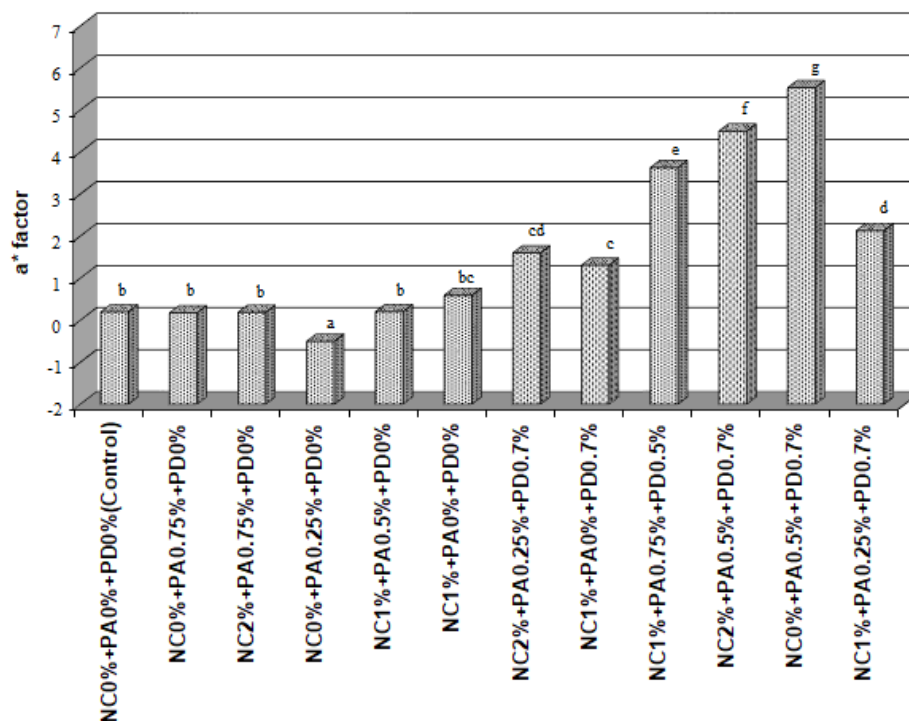


**Fig. 3.** Comparing  $a^*$  value in the paper made by adding cPAM, poly-DADMAC, and chitosan to CMP

### Breaking Length

The ANOVA revealed that all three main factors chitosan (A), cPAM (B), and poly-DADMAC (C) had statistically significant effects on the breaking length of the treated pulp samples ( $p < 0.01$ ). The main effects of chitosan ( $F = 84.01$ ,  $p < 0.001$ ), cPAM ( $F = 120.75$ ,  $p < 0.001$ ), and poly-DADMAC ( $F = 120.12$ ,  $p < 0.001$ ) were all highly significant, indicating that variations in the dosage levels of each additive independently influenced breaking length. Among these factors, cPAM and poly-DADMAC exhibited the highest F-values, suggesting stronger effects on breaking length compared with chitosan. In addition, the three-way interaction effect ( $A \times B \times C$ ) was also statistically significant ( $F = 8.474$ ,  $p < 0.001$ ), indicating that the effect of each additive on breaking length depended on the levels of the other two additives when applied in combination.

The results revealed that the addition of chitosan, in combination with cPAM and poly-DADMAC, to CMP pulp resulted in 48 distinct treatment formulations. In comparison with the control sample, which was obtained by simultaneously adding chitosan, poly-DADMAC, and cPAM at 0% (with a breaking length of 3.88 km), 11 treatments exhibited lower breaking length values. The lowest breaking length (3.23 km) was observed in the paper produced from the treatment containing 1% chitosan, 0.5% cPAM, and 0% poly-DADMAC. In contrast, 36 treatment formulations showed a noticeable increase in breaking length compared to the control. The highest breaking length

(5.73 km) was recorded in the treatment containing 0% chitosan, 0.75% cPAM, and 0.7% poly-DADMAC. Additionally, the paper produced from the treatment with 1% chitosan, 0.25% cPAM, and 0.7% poly-DADMAC exhibited a breaking length of 4.54 km. Statistical analysis of the data indicated that the interaction effects of chitosan, cPAM, and poly-DADMAC on breaking length were statistically significant at the 1% level.

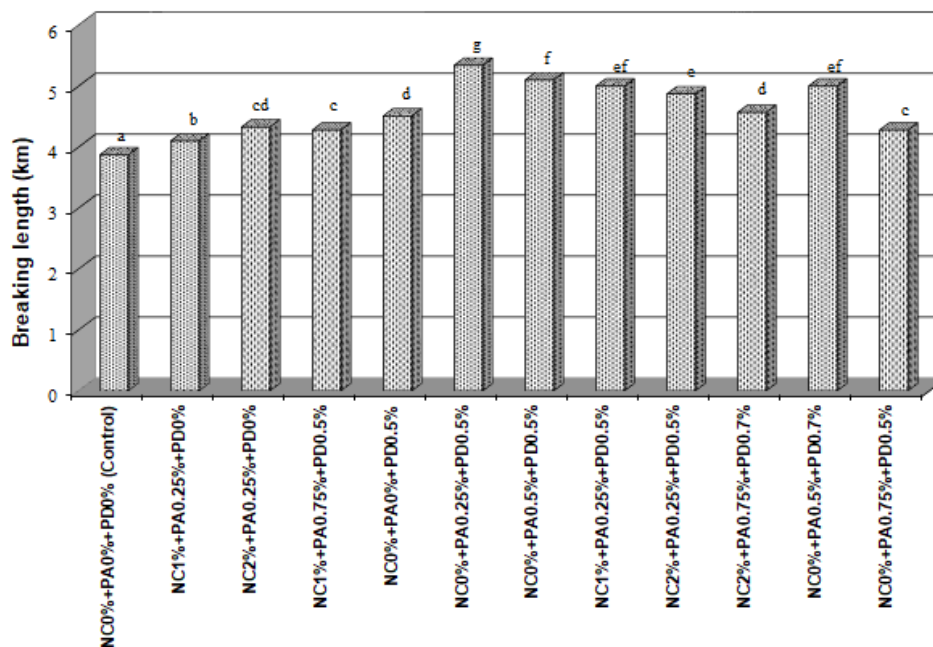


**Fig. 4.** Comparing breaking length in the paper made by adding cPAM, poly-DADMAC, and chitosan to CMP

### Tensile Strength

All main factors showed statistically significant effects on tensile strength ( $p < 0.001$ ), with cPAM exhibiting the largest F-value (73.854), followed by poly-DADMAC (16.737) and chitosan (14.107), indicating that cPAM had the strongest individual effect on tensile strength.

The three-way interaction ( $A \times B \times C$ ) was also significant ( $F = 2.330$ ,  $p = 0.004$ ), although its effect was considerably weaker than those of the individual main factors. This indicates that tensile strength was primarily governed by the individual effects of the additives, particularly cPAM, while the combined application of chitosan, cPAM, and poly-DADMAC also produced a statistically significant interaction effect.

The results demonstrated that the incorporation of chitosan, in combination with cPAM and poly-DADMAC, into CMP pulp led to the creation of 48 distinct treatment combinations.

Compared to the control sample, which was produced by simultaneously adding 0% chitosan, poly-DADMAC, and cPAM (with a tensile strength of 2.41 N/g, 6 treatments exhibited lower tensile strength values. The lowest tensile strength (1.64 N/g) was observed in the paper produced from the treatment with 1% chitosan, 0% cPAM, and 0.5% poly-DADMAC.

In contrast, 41 treatment formulations showed a significant increase in tensile strength. The highest tensile strength (3.53 N/g) was recorded in the treatment containing 0% chitosan, 0.5% cPAM, and 0.5% poly-DADMAC. Additionally, the paper produced

from the treatment with 1% chitosan, 0.25% cPAM, and 0.5% poly-DADMAC also exhibited a tensile strength of 3.53 N/g.

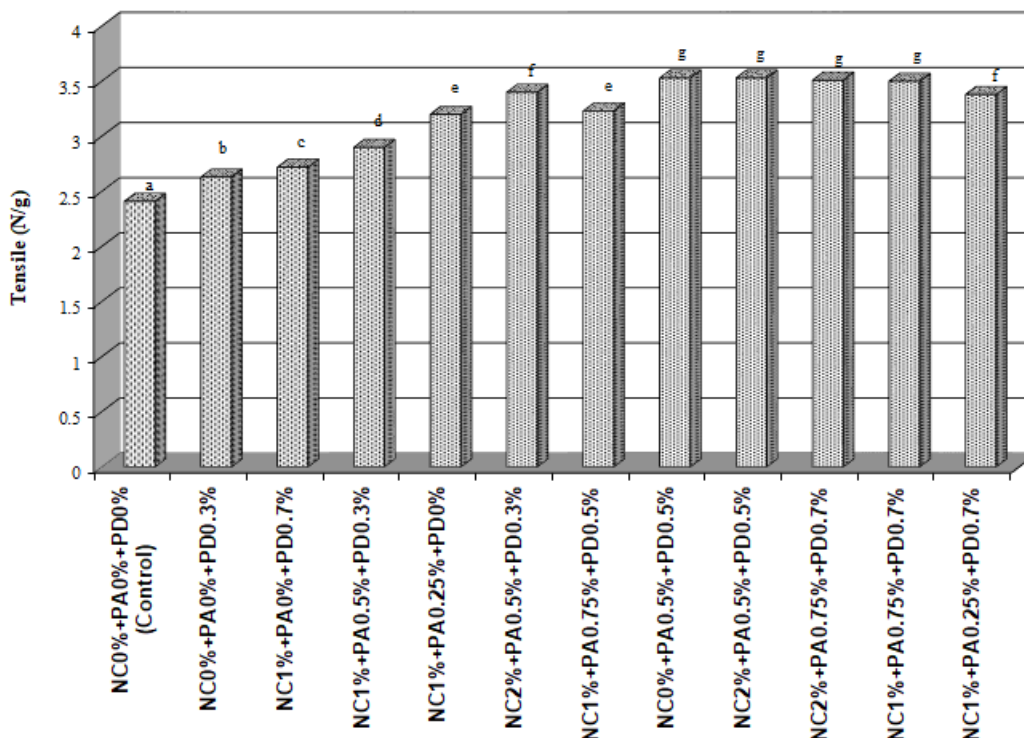


**Fig. 5.** Comparing tensile strength in the paper made by adding cPAM, poly-DADMAC, and chitosan to CMP

## Tear Strength

The ANOVA revealed that the main factors had different effects on tear strength. Both chitosan (A) and cPAM (B) showed statistically significant effects ( $F = 5.91$ ,  $p = 0.004$  and  $F = 12.37$ ,  $p = 0.0001$ , respectively), indicating that variations in the dosage levels of these additives significantly affected tear strength. In contrast, poly-DADMAC (C) did not exhibit a significant effect ( $F = 1.926$ ,  $p = 0.130$ ), suggesting that its individual effect on tear strength was not statistically significant.

The three-way interaction ( $A \times B \times C$ ) was also not statistically significant ( $F = 0.927$ ,  $p = 0.549$ ), indicating that the combined interaction among chitosan, cPAM, and poly-DADMAC did not significantly affect tear strength. Overall, the results indicate that tear strength was primarily affected by the individual effects of chitosan and cPAM, whereas poly-DADMAC and the three-way interaction did not have statistically significant effects.

The results demonstrated that the incorporation of chitosan, in combination with cPAM and poly-DADMAC, into CMP pulp led to the creation of 48 distinct treatment combinations. Compared to the control sample, which was produced by simultaneously adding 0% chitosan, poly-DADMAC, and cPAM (with a tear strength of 285 mN, 5 treatments exhibited lower tear strength values. The lowest tear strength (272 mN) was observed in the paper produced from the treatment with 1% chitosan, 0% cPAM, and 0.7% poly-DADMAC.

In contrast, 42 treatment formulations showed a significant increase in tear strength. The highest tensile strength (316 mN) was recorded in the treatment containing 1% chitosan, 0.25% cPAM, and 0.7% poly-DADMAC. Additionally, the paper produced from the treatment with 1% chitosan, 0.25% cPAM, and 0.5% poly-DADMAC also exhibited a tear strength of 315 mN.

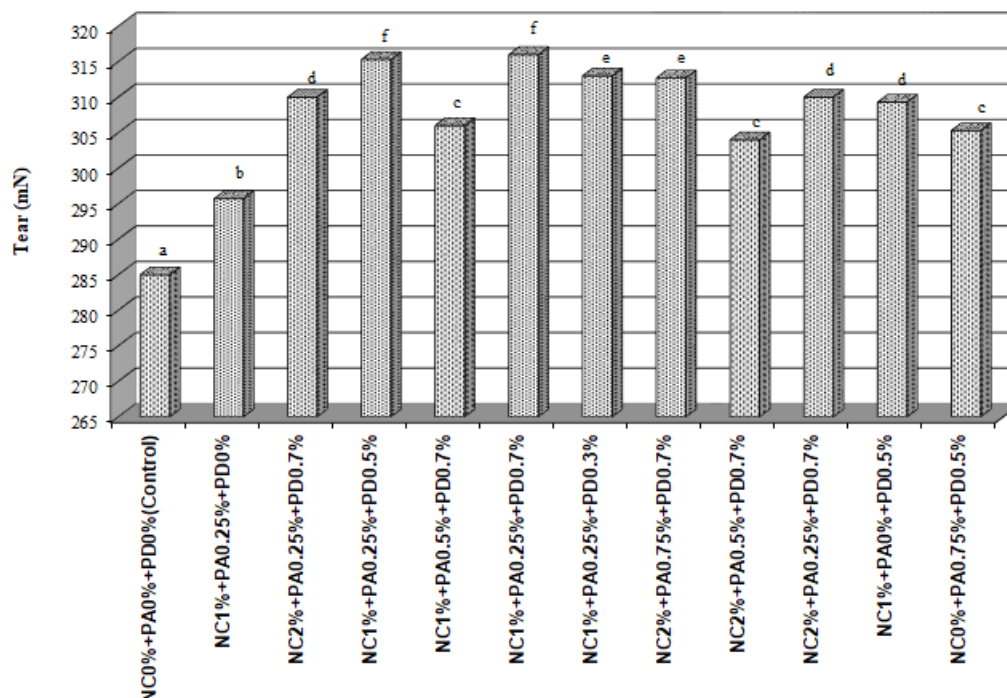


**Fig. 6.** Comparing tear resistance in the paper made by adding cPAM, poly-DADMAC, and chitosan to CMP

### Surface Morphology

The SEM images were used to compare the morphology of the untreated control and the CMP paper treated with chitosan, Poly-DADMAC, and cPAM (Fig. 7). Compared with the control, the treated paper exhibited a relatively denser and more interconnected fiber network, with fewer visibly open void spaces between the fibers. In addition, fine materials or aggregated structures were observed in some of the inter-fiber regions and on the fiber surfaces of the treated sample. These morphological features may be associated with the retention and deposition of fines and additive-associated materials within the fiber network.

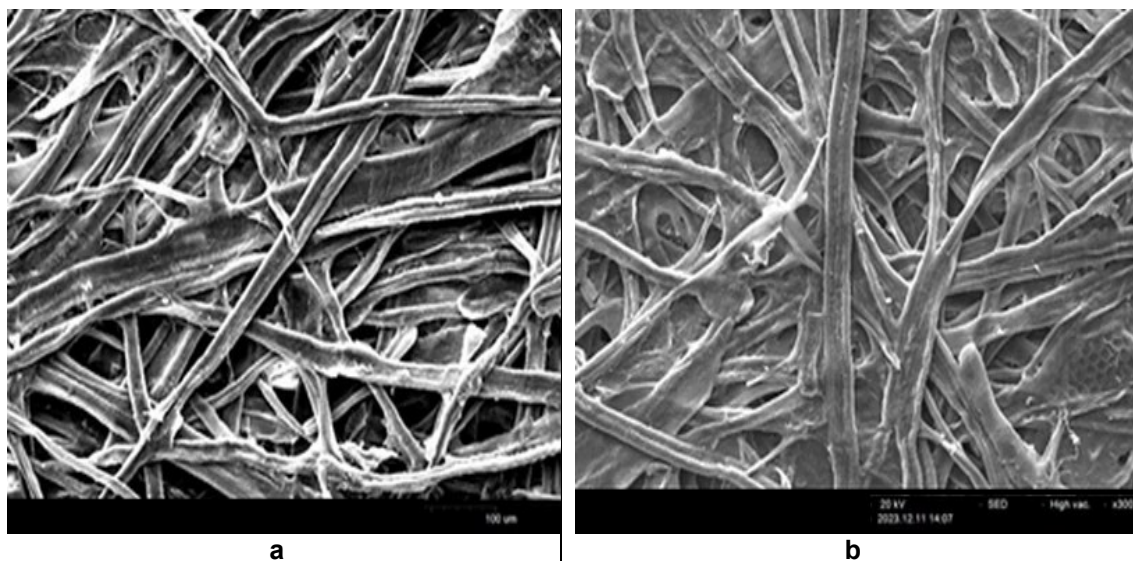


**Fig. 7.** SEM images of CMP paper: (a) paper treated with chitosan, Poly-DADMAC, and cPAM, and (b) untreated control. The scale bar represents 100  $\mu\text{m}$ .

The greater apparent compactness of the treated fiber network may increase the effective contact area between fibers and facilitate interfiber bonding, which could partly contribute to the improved tensile and other strength properties observed for the treated papers. However, the SEM images alone cannot determine the chemical identity of the materials observed between the fibers. Therefore, these structures should not be conclusively assigned to chitosan, polymer flocs, or fines without complementary analytical evidence such as SEM-EDS. Similarly, the SEM observations provide morphological evidence of changes in the fiber network but do not by themselves demonstrate covalent bonding or confirm the occurrence of charge neutralization or charge reversal.

## DISCUSSION

Enhancing the mechanical and optical properties of chemical-mechanical pulp (CMP) paper is essential for improving its industrial applicability and expanding the utilization of mechanical pulp-based products. In the present study, the effects of chitosan, poly-DADMAC, and cPAM on CMP paper properties were investigated through 48 different additive combinations. The results demonstrated that the application of these cationic additives, individually and in combination, significantly influenced paper strength and optical characteristics; however, the magnitude of improvement depended strongly on additive dosage and the balance between polymer adsorption and fiber interaction. The observed improvements can be attributed to the ability of these additives to modify fiber surfaces, enhance interactions among fibers, and improve the formation of the fiber network.

Chitosan has attracted considerable attention as a bio-based additive due to its abundant amino groups and affinity toward cellulose fibers. The improvement in mechanical properties after chitosan addition can mainly be explained by electrostatic interactions and hydrogen bonding between dissolved chitosan and cellulose fibers. These interactions improve fiber contact efficiency and contribute to the development of a

stronger inter-fiber bonding network. Although chemical interactions between chitosan and cellulose have been reported under specific reaction conditions, the nature of the bonds was not directly verified in the present study because complementary analyses such as FTIR were not performed. Therefore, the enhancement observed here is mainly attributed to physical and intermolecular interactions between dissolved chitosan and cellulose fibers (Nada *et al.* 2005).

Cationic polyacrylamide and poly-DADMAC also play important roles in modifying the colloidal behavior of CMP suspensions. Poly-DADMAC, as a highly cationic polymer, can neutralize negatively charged substances present on fiber surfaces and fines, facilitating their retention within the paper structure. The cPAM further promotes floc formation and improves fines retention through polymer bridging mechanisms, which can increase fiber-fiber bonding and paper strength. The combined application of these additives may therefore provide a synergistic effect by improving the distribution of fines and increasing the bonding efficiency within the fiber network (Li *et al.* 2004; Wagberg *et al.* 2002).

However, the interaction among several cationic additives requires careful consideration because excessive polymer addition may disturb the charge balance of the pulp suspension. Charge reversal or excessive flocculation may occur when the amount of cationic additives exceeds the optimum level, resulting in poor fiber formation and reduced mechanical properties. In the present study, some treatments exhibited lower strength values compared with the control sample. This reduction may be related to non-optimal polymer dosage, excessive aggregation of fibers and fines, or reduced uniformity of the paper structure caused by over-flocculation. Therefore, achieving the optimum additive concentration is essential to improve paper properties without negatively affecting sheet formation.

The optical properties of CMP paper were also influenced by the addition of chitosan and polymer additives. The improvement in brightness and optical quality observed in treated samples may be associated with changes in fiber surface morphology and improved distribution of fine materials within the sheet structure. Previous studies have reported that chitosan-based systems can improve paper optical properties due to their ability to modify fiber interfaces and increase light scattering efficiency (Abdallah *et al.* 2023; Rezazadeh *et al.* 2022).

The addition of chitosan also affected the CIE  $L^*a^*b^*$  color parameters, particularly the  $a^*$  factor. Previous research has indicated that the incorporation of chitosan-based additives can influence the color coordinates of paper by modifying surface interactions and optical responses (Wang *et al.* 2023). Higher  $a^*$  values imply a reduced green component, indicating a shift toward a more reddish hue. This change suggests that additive incorporation not only influenced strength properties but also modified the visual characteristics of CMP paper.

SEM observations provided additional information regarding structural changes caused by additive application. The SEM images indicated a more compact fiber network, reduced visible void spaces, and improved contact among fibers after additive treatment. These morphological changes are consistent with enhanced bonding between fiber surfaces. However, the exact composition of materials observed within fiber voids cannot be confirmed based only on SEM images. The deposited structures may include retained fines, polymer complexes, or chitosan-based aggregates. Additional analyses such as SEM-EDS, FTIR, zeta potential measurement, or retention analysis would be required for definitive identification.

The observed improvement in mechanical properties is also consistent with previous studies showing that increased fiber surface area, improved flexibility, and enhanced fibrillation contribute to stronger hydrogen bonding and greater inter-fiber contact. These mechanisms subsequently improve tensile strength, tear resistance, and other mechanical properties of paper products (Vaysi and Kord 2013). Similar improvements following the use of nano-additives and polymer systems have been reported in CMP and other mechanical pulp systems (Yosefi and Vaysi 2020; Zhang *et al.* 2022).

From an industrial perspective, the use of chitosan should consider both performance improvement and economic feasibility. Although chitosan provides significant improvements in paper properties, its commercial application requires optimization of dosage, production cost, and compatibility with existing retention and strength-enhancement systems. A combination of chitosan with conventional cationic additives may provide a more economically feasible approach compared with using chitosan alone.

Overall, the results demonstrate that the combined use of chitosan, poly-DADMAC, and cPAM can effectively modify CMP paper properties by improving fiber interactions and sheet structure, with potential benefits for fines retention. Nevertheless, the optimum balance between additive concentration, charge interactions, and fiber network formation is critical because excessive cationic polymer addition may adversely affect paper formation. The findings provide useful information for further optimization of bio-based and polymer-assisted additive systems for improving the optical and mechanical properties of CMP paper.

## CONCLUSIONS

The results of this study provide a comprehensive understanding of the effects of chitosan, poly(diallyldimethylammonium chloride) (poly-DADMAC), and cPAM on the optical and mechanical performance of CMP-based paper.

1. This study demonstrated that chitosan, poly-DADMAC, and cPAM significantly influenced the optical and mechanical properties of CMP paper, both individually and through their combined application. The factorial ANOVA results confirmed that most main effects and interaction effects were statistically significant, highlighting the potential effectiveness of these cationic additives in CMP-based papermaking systems.
2. Chitosan showed positive effects on several key properties, including brightness, breaking length, and tear strength. These improvements may be associated with the cationic nature of chitosan, as well as the presence of amino functional groups that can promote electrostatic interactions and hydrogen bonding with negatively charged cellulose fibers, thereby potentially contributing to enhanced inter-fiber bonding.
3. The cPAM played an important role in improving mechanical properties, particularly breaking length and tensile strength, as reflected by its relatively high F-values in the ANOVA results. Its effectiveness may be related to its high molecular weight and polymer-bridging behavior, which can contribute to

strengthening the fiber network and improving stress distribution within the paper structure.

4. Poly-DADMAC significantly affected brightness, tensile strength, and the  $a^*$  color coordinate. Its effects may be related to interactions with negatively charged fines and colloidal materials and associated changes in the charge environment of the pulp suspension. However, because charge demand, zeta potential, and fines retention were not directly measured in the present study, the specific contribution of charge neutralization and retention mechanisms cannot be experimentally confirmed.
5. Significant three-way interaction effects among chitosan, cPAM, and poly-DADMAC were observed for several optical and mechanical properties, indicating that the response to the additives depended on their combined application. The optimal treatment combinations varied depending on the target property; for example, the highest brightness was obtained using 2% chitosan, 0.5% cPAM, and 0.7% poly-DADMAC, whereas the maximum tensile strength was achieved in formulations containing cPAM and poly-DADMAC without chitosan.
6. Scanning electron micrograph (SEM) observations provided representative morphological evidence of differences in the fiber network under selected treatment conditions. The observed morphological features, including apparent changes in the fiber–fiber contact and material deposition within the network, may be associated with the observed changes in paper properties. However, because SEM analysis was performed on selected samples only, these observations should not be generalized to all 48 treatment combinations, and the specific chemical composition of the observed deposits could not be confirmed in the absence of SEM-EDS analysis.
7. Overall, the controlled application of chitosan, cPAM, and poly-DADMAC, either individually or in optimized combinations, provides a promising strategy for improving CMP paper quality. The observed improvements in strength and optical properties demonstrate the potential of these additives for CMP-based papermaking. Further studies incorporating FT-IR, zeta potential, charge-demand, retention, and drainage measurements are recommended to directly verify the proposed molecular interactions, charge behavior, fines retention, and dewatering mechanisms.

## REFERENCES CITED

- Abdallah, A. F., Jawaid, M., Mohamed, A. Z., Tahir, P. M., and Abdullah, U. H. (2023). “Performance of nanofibrillated cellulose with chitosan as a wet-end additive for paper applications,” *Industrial Crops and Products* 203, article 117219. <https://doi.org/10.1016/j.indcrop.2023.117219>
- Ahmadi Lajimi, A., Azadfallah, M., Hamzeh, Y., and Rahmaninia, M. (2020). “Effect of cationic poly-DADMAC based fixing agent on strength properties of OCC pulp,” *Iranian Journal of Wood and Paper Industries* 10(4), 605-616.

- Ashoori, A., Harun, J., Raverty, J. D., Zin, W. M., and Nor, M. (2005). "Effect of chitosan addition on the surface properties of kenaf (*Hibiscus cannabinus*) paper," *Iranian Polymer Journal* 14(9), 807-814.
- Heydari, H., Vaysi, R., Hossenzadeh, A., Bakhshi, A., and Kiaei, M. (2024). "Effect of nano-chitosan and polyacrylamide on optical and mechanical properties of chemi-mechanical pulps," *BioResources* 19(2), 1901-1915. <https://doi.org/10.15376/biores.19.2.1901-1915>
- Li, Z., Wang, S., Zhang, H., and Peng, X. (2022). "Synergistic effects of poly-DADMAC and polyacrylamide on fiber bonding and optical properties of mechanical pulp paper," *Nordic Pulp & Paper Research Journal* 37(2), 243-252. <https://doi.org/10.1015/npprj-2021-0058>
- Nada, A. M. A., El-Sakhawy, M., Kamel, S., and Eid, M. A. M. (2005). "Effect of chitosan and its derivatives on the mechanical and electrical properties of paper sheets," *Egyptian Journal of Solids* 28(2), 202-208. <https://doi.org/10.1021608/ejs.2005.149335>
- Nicu, R., Bobu, E., and Desbrieres, J. (2010). "Chitosan as cationic polyelectrolyte in wet-end papermaking system," *Cellulose Chemistry and Technology* 10(1-2), 102-108.
- Pariser, E. R., and Lombardi, D. P. (1988). "*Chitin Sourcebook: A Guide to the Research Literature*, Plenum Press, New York, NY, USA.
- Rahmaninia, M., Rohi, M., Ramezani, O., and Zabihzadeh, S. M. (2015). "The effect of pulp suspension pH on the performance of chitosan-nanobentonite as a dry strength additive in hardwood CMP pulp," *Journal of Forest and Wood Products* 68(2), 347-357. <https://doi.org/10.22059/JFWP.2015.54836>
- Rezazadeh, E., Vaysi, R., Ebadi, S.E., Soltani, M., and Najafi, A. (2022). "Comparison of the internal functionalization and surface modification methods of chemi-mechanical pulp handsheets using cellulose-chitosan nano-biopolymers and DTPA," *BioResources* 17(2), 2810-2826. <https://doi.org/10.15376/biores.17.2.2810-2826>
- Steckel, H., and Mindermann-Nogly, F. (2003). "Production of chitosan pellets by extrusion/ spheronization," *European Journal of Pharmaceutics and Biopharmaceutics* 57(1), 107-114. DOI: 10.1016/S0939-6411(03)00156-5
- Tajik, M. (2015). *Using of Nano-Cellulose, Polyacrylamide, and Cationic Starch in Internal H-Bond Reinforced of Bagasse Printing Paper*, M.S. Thesis, Shahid Beheshti University, Zirab, Iran.
- TAPPI (2009). "TAPPI Standards, Technical Information Papers, and Useful Methods," TAPPI Press, Atlanta, GA, USA.
- TAPPI T403 om-02 (2002). "Bursting strength of paper," TAPPI Press, Atlanta, GA.
- TAPPI, T414 om-98 (1998). "Internal tearing resistance of paper (Elmendorf-type method)," TAPPI Press, Atlanta, GA.
- TAPPI T425 om-96 (1996). "Diffuse opacity of paper (d/0 paper backing)," TAPPI Press, Atlanta, GA, USA.
- TAPPI T441 om-04 (2004). "Water absorptiveness of sized (non-bibulous) paperboard, and corrugated fiberboard (Cobb test)," TAPPI Press, Atlanta, USA.
- TAPPI T452 om-98 (1996). "Brightness of pulp, paper, and paperboard (directional reflectance at 457 mm)," TAPPI Press, Atlanta, GA, USA.
- TAPPI T527 om-02 (2007). "Color of pulp, paper, and paperboard (d/0, c/2)," TAPPI Press, Atlanta, GA, USA.

- TAPPI T 494-om-96 (1996). "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)," TAPPI Press, Atlanta, GA, USA.
- TAPPI T 460 om-02 (2002). "Air resistance of paper (Gurley method)," TAPPI Press, Atlanta, GA, USA.
- TAPPI T1215 sp-03 (2007). "The determination of instrumental color differences," TAPPI Press, Atlanta, GA, USA.
- Vanerek, A., Alince, B., and Van de Ven, T. G. M. (2006). "Bentonite delamination induced by pulp fibers under high shear monitored by calcium carbonate deposition," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 280(1-3), 1-8. <https://doi.org/10.1016/j.colsurfa.2006.01.014>
- Vaysi, R., and Ebadi, S. E. (2021). "Thermal yellowing of hornbeam chemi-mechanical pulps bleached with hydrogen peroxide and sodium dithionite," *BioResources* 16(4), 7635-7647. <https://doi.org/10.15376/biores.16.4.7635-7647>
- Vaysi, R., and Kord, B. (2013). "The effects of H<sub>2</sub>O<sub>2</sub> bleaching and DTPA spraying on the brightness stability of hornbeam CMP pulp following accelerated irradiation aging," *BioResources* 8(2), 1909-1917. <https://doi.org/10.15376/biores.8.2.1909-1917>
- Wågberg, L., Forsberg, S., Johansson, A., and Juntti, P. (2002). "Engineering of fiber surface properties by application of polyelectrolyte multilayer concept, Part 1. Modification of paper strength," *Journal of Pulp and Paper Science* 28(7), 222-228.
- Wang, Y., Zhao, H., and Lin, Q. (2023). "Influence of nano-additives on the color properties of paper in the CIE Lab color system: A study on the greenness and redness factors," *Journal of Pulp and Paper Science* 49(1), 28-35. <https://doi.org/10.1002/jps.12345>
- Zhang, X., Chen, J., and Li, F. (2022). "Enhancement of paper strength properties by nano-chitosan in mechanical pulp-based papermaking systems," *Carbohydrate Polymers* 273, article 118625. <https://doi.org/10.1016/j.carbpol.2021.118625>
- Zhao, X., Chen, Z., and Liu, S. (2023). "Synergistic effects of poly-DADMAC and nano-chitosan on the mechanical properties of CMP-based paper," *Industrial Crops and Products* 188, article 115474. <https://doi.org/10.1016/j.indcrop.2023.115474>

Article submitted: January 5, 2026; Peer review completed: June 27, 2026; Revised version received and accepted: August 19, 2026; Published: September 8, 2026.  
DOI: 10.15376/biores.21.4.10449-10465