Improving the Properties of Soda Bagasse Pulp by Using Cellulose Nanofibers in the Presence of Cationic Polyacrylamide

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Cellulose nanofiber (CNF) was used to improve the optical and strength properties of soda bagasse pulp (500 CSF) in the presence of cationic polyacrylamide (CPAM). Cationic polyacrylamide was added at 0.05, 0.1, and 0.15%, and cellulose nanofiber was added at 0.1, 0.5, 1, and 2% based on pulp O.D. Laboratory handsheets were prepared (60 g/m^2), and optical and strength properties were measured according to TAPPI standards. Scanning electron microscopy and atomic force microscopy images showed that empty spaces between fibers decreased under CPAM/CNF treatments. The effect of the additives and their addition level on all the measured paper properties was significant at the 99% confidence level. The light scattering coefficient, brightness, and whiteness increased with the addition of cellulose nanofibers, but the light absorption coefficient, yellowness, and opacity decreased. At the highest levels of the additives (2% CNF and 0.15% CPAM), the tensile and burst strengths of handsheets increased by 33% and 15%, respectively. Generally, cellulose nanofibers/cationic polyacrylamide complexes improved the optical and strength properties of bagasse pulp.

Keywords: Nanofiber; Cationic polyacrylamide; Freeness; Bagasse Pulp

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INTRODUCTION

Annually in Iran, a huge amount of agricultural residual materials including bagasse is burned due to the lack of suitable and available processing plants. Pulp and paper mills have much experience in making value-added products from wastes. However, paper made from bagasse is weaker than when using fibers derived from wood, especially those made from long pulp fibers; several attempts have been made to enhance the final properties and applications of bagasse. Paper strength properties depend considerably on hydrogen bonding between cellulosic fibers (Bledzki and Gassan 1999). Organic and inorganic nanoparticles have potential to improve product quality in the pulp and paper industry. Nanotechnology uses materials with nanometer dimensions (Gonzalez *et al.* 2012; Tajik *et al.* 2014b; Habibi *et al.* 2010). Cellulose nanofiber has great potential for industrial development because it is a renewable raw material that is easily accessible, relatively inexpensive, and environmentally friendly; thus, cellulose nanofibers have been developed in different industries (Aulin *et al.* 2009; Tajik *et al.* 2014a).

Due to their much smaller dimensions than the diameter of mesh used in paper-making and its negative charge similar to cellulose, cellulose nanofibers are not retained or uniformly distributed on a paper machine forming wire; hence, cellulose nanofiber is usually combined with a cationic polymer, which acts as a retention aid (Habibi 2014). For high-density cationic acrylamide copolymers, polyelectrolytes conform to the fiber surfaces due to strong electrostatic attraction between the cationic charges of the polymer and anionic charge of the fiber, resulting in less bridging of the pulp ingredients (Hubbe *et al.* 2009; Niskanen 1998). Cationic polyacrylamide is used in the paper-making industry as a drainage and retention aid. When a cellulose fiber suspension is drained during paper-making, the colloidal contact between fibers initiates hydrogen bonding, leading to the formation of paper (Retulainen *et al.* 1998). Cellulose nanofibers have high specific surface area and uniform distribution in the paper network and placement in empty spaces that increase the bonds between fibers in suspension and, therefore, increase the mechanical properties of the paper (Gregory 1989). Soluble polymers also can provide bonding. For instance, sheets formed from glass microfibers were found to have almost zero tensile strength in the absence of a polymer, but a paper-like dry-strength was achieved when the fiber suspensions are treated with a combination of a cationic polyelectrolyte and an anionic polyelectrolyte before sheet formation (Hubbe 2007).

Hassan *et al.* (2015) studied the effects of cellulose nanofiber (MFC) and cellulose nanofiber treated with Tempo (TMFC) from palm stem on the properties of bagasse pulp and long fiber softwood pulp. Cellulose nanofiber was used at four loading levels: 2.5, 5, 10, and 20%. While strength properties increased up to 20%, air permeability was reduced. Also, the MFC and TMFC increased the resistance of paper made from bagasse and long-fiber softwood pulp, with this effect being greater in the bagasse pulp. Su *et al.* (2013) found that the addition of microfibrillated cellulose (MFC) to pulp fibers combined with polyamideamine-epichlorohydrin (PAE) increases the dry strength and wet strength of cellulosic materials by an order of magnitude. They also found that air permeability of the composites decreased by up to four orders of magnitude with MFC addition.

HassanJanzadeh *et al.* (2014) investigated the effect of cellulose nanofiber and cationic starch on the properties of soda-anthraquinone pulp of rice stem; by adding 10% cellulose nanofiber and 1.5% cationic starch, the tensile strength index and burst resistance index were increased by 21.59% and 18.33%, respectively. Syverud and Stenius (2009) prepared films made of cellulose nanofibers to create a surface layer on paper by using polyamide filters. Films made of cellulose nanofibers had high tensile strength, density, and length changes. Paper coated with cellulose nanofibers with a grammage of 35 g/m^2 resulted in a tensile index of 146 (N.M/g) and elongation of 8.6%. In another study, the use of cellulose nanofibers as a surface layer (8% based on a dry weight) increased paper strength and reduced air permeability significantly. Jalali Torshizi *et al.* (2014) studied the effect of cationic polyacrylamide-nanobentonite on the retention, drainage, and paper characteristics of old corrugated container board. They reported that the addition of cationic polyacrylamide and nanobentonite increased the tensile, burst, and tear strengths. Cationic polyacrylamide also improved drainage and enhanced retention up to 98.7%.

In this study, the influence of cellulose nanofiber combined with cationic polyacrylamide on optical and strength properties of soda bagasse pulp was investigated.

EXPERIMENTAL

Materials and Methods

Bleached soda bagasse pulp was collected from Pars pulp and paper mill (Ahvaz, Iran) and had a freeness of 500 CSF. Cellulose nanofiber was purchased from Nano Novin Polymer Co. (Sari, Iran); it was prepared from softwood alpha cellulose pulp Synthesize mechanical method with an average fiber diameter of 32 nm (Fig 1). Cellulose nanofiber was loaded at 0.1, 0.5, 1, or 2% of the dry pulp weight. High molecular weight cationic polyacrylamide was purchased from Kimia San (Turkey) and was added to 0.05, 0.1, or 0.15% of the pulp dry weight.

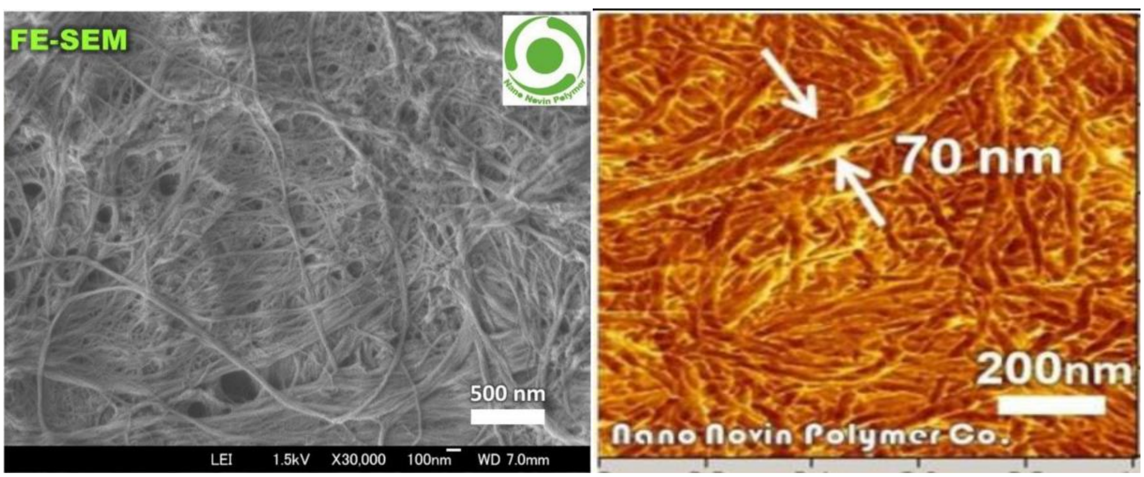

Fig. 1. (FE-SEM) and (AFM) cellulose nanofiber

Bagasse paper laboratory handsheets were made according to the TAPPI standard with a basis weight of 60 g/m^2. First, CPAM was added to the suspension and it was mixed mechanically for 2 min. Then, flocs were broken by increasing the rotation speed. At the same time, cellulose nanofibers were added to the suspension, which was mixed by mixer for another 2 min.

Paper testing was carried out at a temperature of 23 °C and 50% relative humidity. All experiments and tests were based on the following standards: freeness, TAPPI T 227 om-99 (1999); preparing handmade paper, TAPPI T 205 sp-95 (1995); thickness measurement, TAPPI T 411 om-97 (1997); bulk measurement, TAPPI T 500 cm-98 (1998); air permeability resistance, TAPPI T 460 om-96 (1996); mechanical test preparation, TAPPI T 220 sp-96 (1996); tensile resistance, TAPPI T 494 om-96 (1996); burst resistance, TAPPI T 403 om-97 (1997); tear resistance, TAPPI T 496 sp-99 (1999); opacity, absorption, and scattering coefficient, TAPPI T 1214 sp-98 (1998); and brightness, whiteness, and yellowness, TAPPI T 1216 sp-98 (1998).

Scanning Electron Microscopy (SEM)

Micrographs of the paper samples were taken to evaluate the bonding and distribution of cellulose nanofibers in the paper network. The samples were first coated with gold and imaged with a voltage of 10 kV and 100,000× magnification on a Hitachi scanning electron microscope (model SU3500, Tokyo, Japan).

Atomic Force Microscopy (AFM)

Atomic force microscopy was used to take topographical images of the paper samples. AFM provides details on the uniformity and non-uniformity in the third dimension. The samples were imaged with an Ara Pajoohesh AFM (model 0101/A, Tehran, Iran).

Data Analysis

Data analysis was performed using SPSS software (IBM, Armonk, USA) and one-way ANOVA ($p < 0.01$). Significant differences among the average values of the samples were determined using Duncan's multiple range tests. The error indexes were also calculated for the average values of each test.

RESULTS AND DISCUSSION

Statistical analysis showed cellulose nanofibers and cationic polyacrylamide had significant effects on all paper properties at the 99% confidence level. SEM showed empty spaces between fibers. Fines in the paper network were decreased compared with the blank, and the fibers had close contact together and were well flocculated (Fig. 1a, b). With 2% cellulose nanofibers and 0.15% cationic polyacrylamide, the fiber fines and cellulose nanofibers were deposited in the fiber intervals, resulting in more contact surface area between fibers and stronger bonds. The fibers were closer to each other, forming a more compact network (Fig. 2c, d).

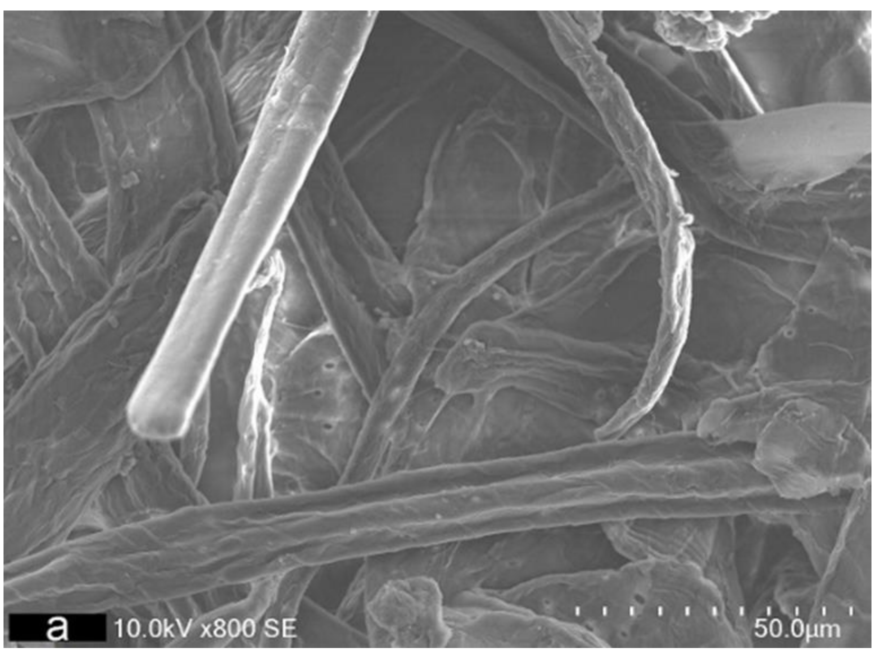

Fig. 2(a). Scanning electron micrographs of the bagasse paper (a, b) and bagasse paper with cellulose nanofibers and cationic polyacrylamide (c, d)

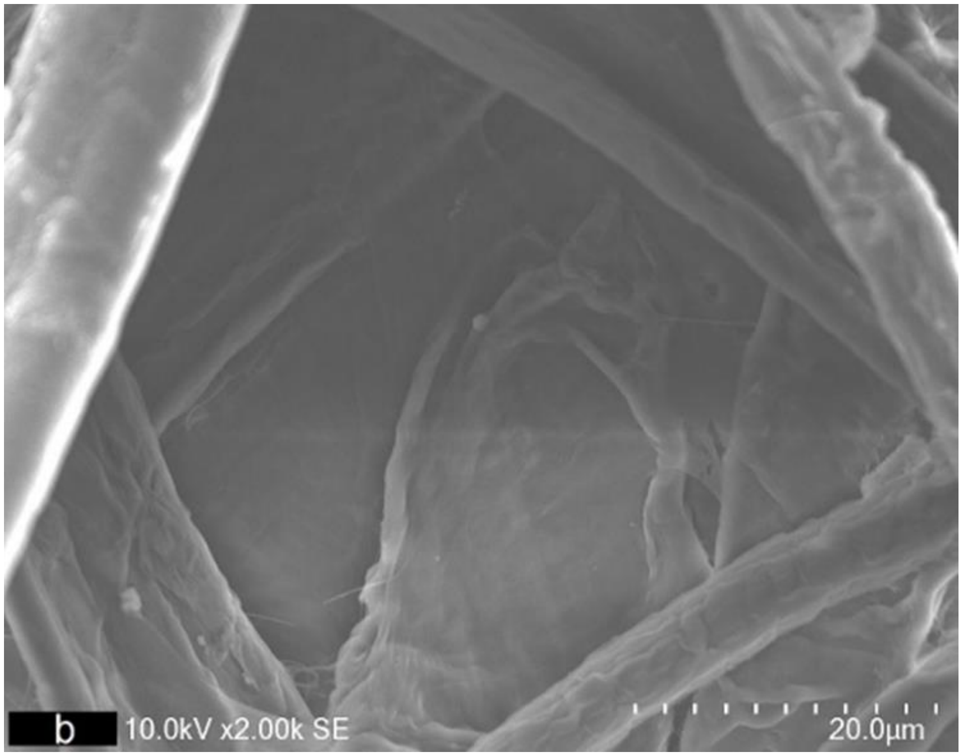

Fig. 2(b). Scanning electron micrographs of the bagasse paper (a, b) and bagasse paper with cellulose nanofibers and cationic polyacrylamide (c, d)

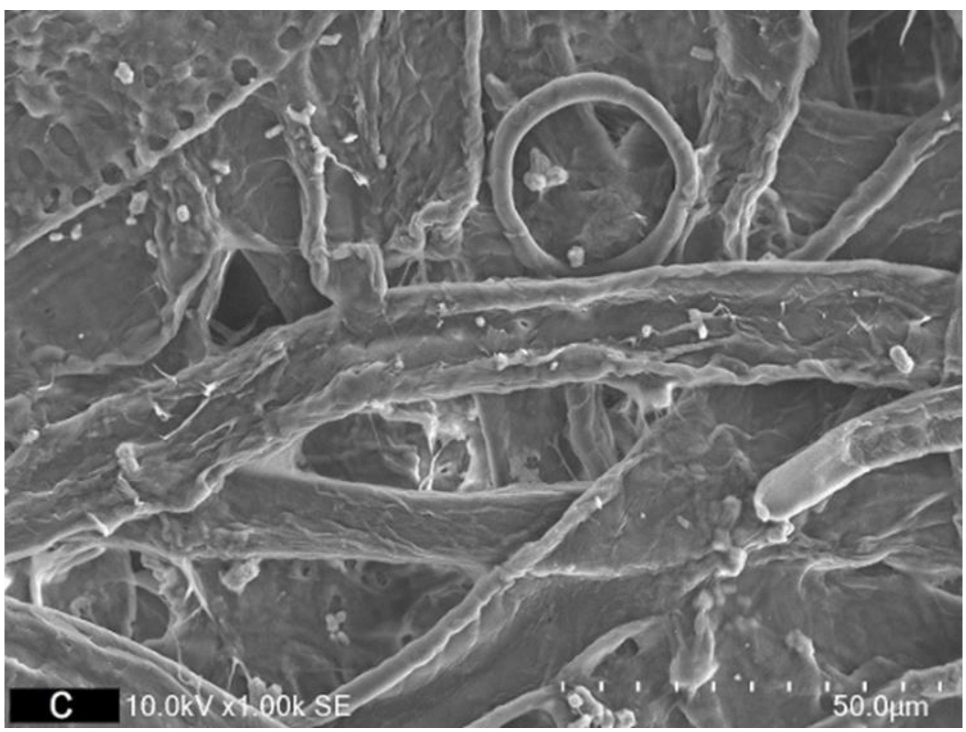

Fig. 2(c). Scanning electron micrographs of the bagasse paper (a, b) and bagasse paper with cellulose nanofibers and cationic polyacrylamide (c, d)

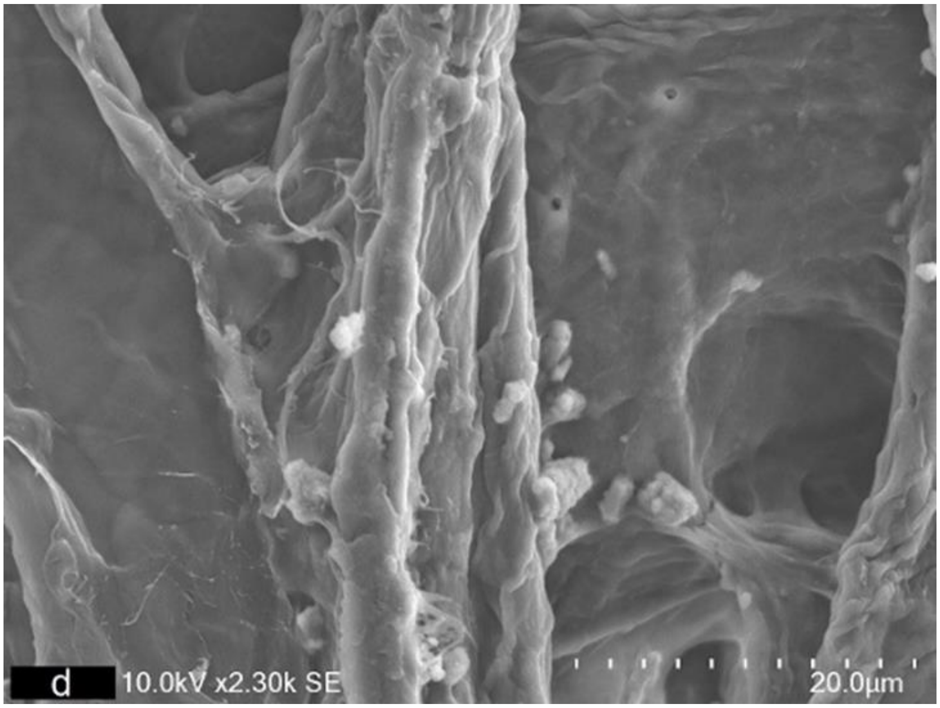

Fig. 2(d). Scanning electron micrographs of the bagasse paper (a, b) and bagasse paper with cellulose nanofibers and cationic polyacrylamide (c, d)

The gaps between the fibers were clearly observable in the 3-D images produced from atomic force microscopy of the control samples (Fig. 3a). With 2% cellulose nanofibers and 0.15% cationic polyacrylamide, the spaces between the fibers, fines, and cellulose nanofibers were filled, which increased fiber bonds and strengthened the paper.

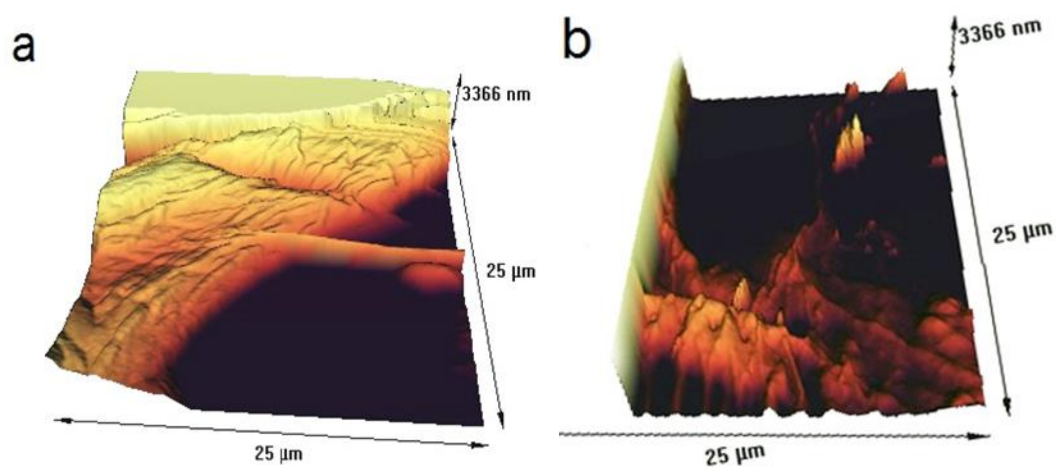

Fig. 3. Atomic force microscopy images of the bagasse paper (a) and bagasse paper with cellulose nanofibers and cationic polyacrylamide (b)

Freeness and Retention

The freeness increased with increased cellulose nanofiber loading up to 0.5% and decreased thereafter (Fig. 4). This result was attributed to the cellulose nanofibers causing the fibers to form flocks. The continuity between cavities was decreased by adding 1 and 2% cellulose nanofiber. Moreover, freeness diminished due to the hydrophilic ability, gel behavior, high absorbability, and water retention ability of the cellulose nanofibers; these characteristics increased the viscosity of the suspension as the nanofibers filled the cavities.

Also, increasing the amount of cationic polyacrylamide increased freeness. The greatest freeness (670 mL) was measured in the sample with 0.5% nanofibers and 0.15% cationic polyacrylamide. The lowest freeness (420 mL) corresponded to the sample with 2% cellulose nanofibers. The control sample freeness (505 mL) agreed with other published results (Hadylam *et al.* 2013; Su 2013; Jalali Torshizi *et al.* 2014).

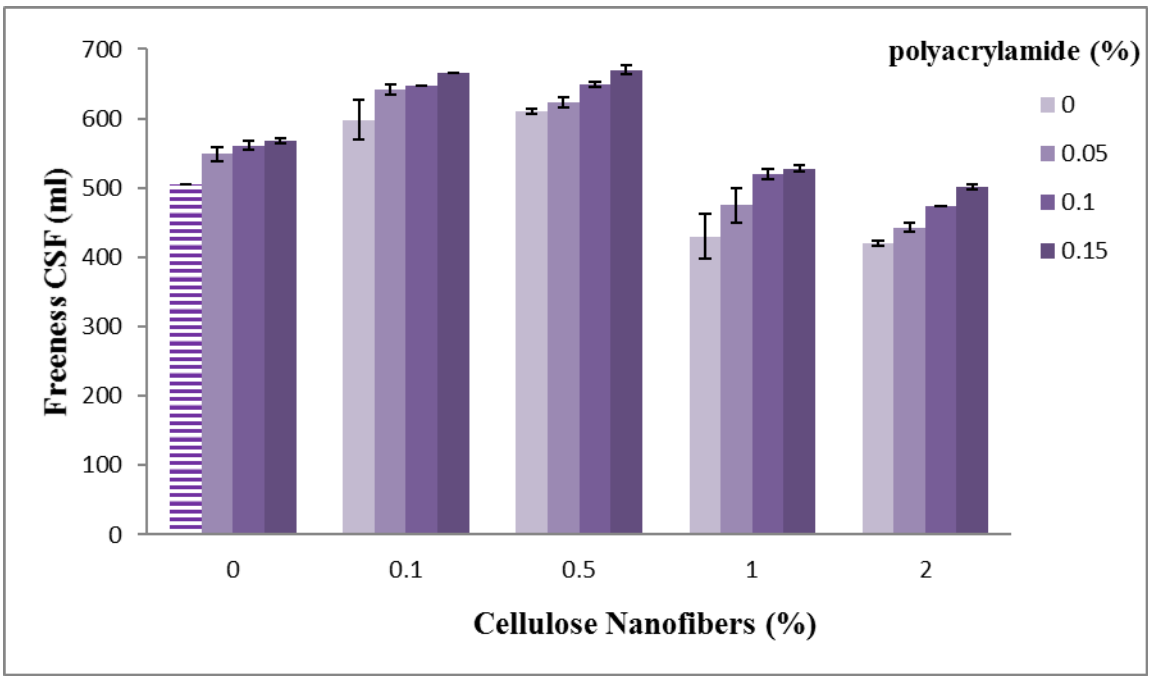

Fig. 4. The effect of cationic polyacrylamide and nanocellulose fibers on CSF

Both cellulose nanofibers and cationic polyacrylamide increased retention of the pulp ingredients (Fig. 5). The retention increased to 97.46% and 95.46% with the individual addition of 0.15% cationic polyacrylamide and 0.1% cellulose nanofiber, respectively, while the retention in the control sample was only 90.57%.

Incorporating cellulose nanofibers and cationic polyacrylamide together resulted in a higher retention than the control sample but a lower retention than individual addition of each additive. Incorporating cationic polyacrylamide and cellulose nanofibers separately increased retention because of the flocs creation, which trapped the fiber fines, but the simultaneous use of these two materials resulted in a decreased efficiency.

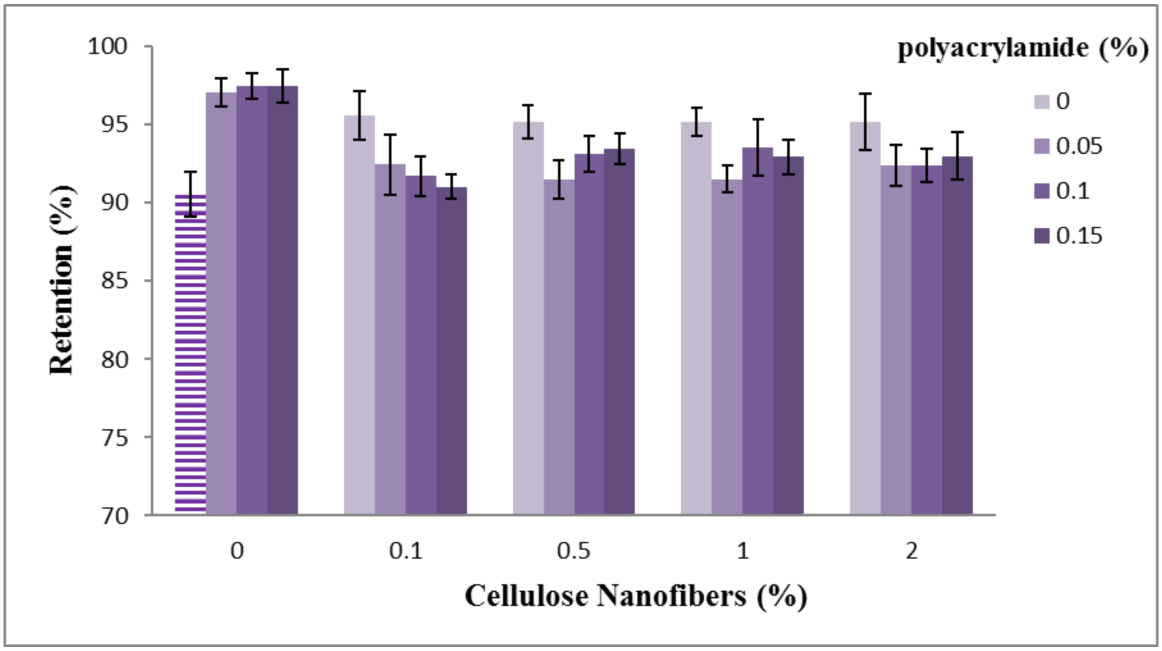

Fig. 5. The effect of cationic polyacrylamide and cellulose nanofibers on retention

Air Permeability Resistance and Bulk

With increased addition of cationic polyacrylamide and cellulose nanofibers, air permeability resistance increased and bulk decreased (Figs. 6 and 7). These effects resulted from a reduction in the paper porosity caused by the nanofibers and fines filling and entrapping in the sheet cavities, as well as an increase in fiber bonding, as previously mentioned (Su 2013; Hassan 2015).

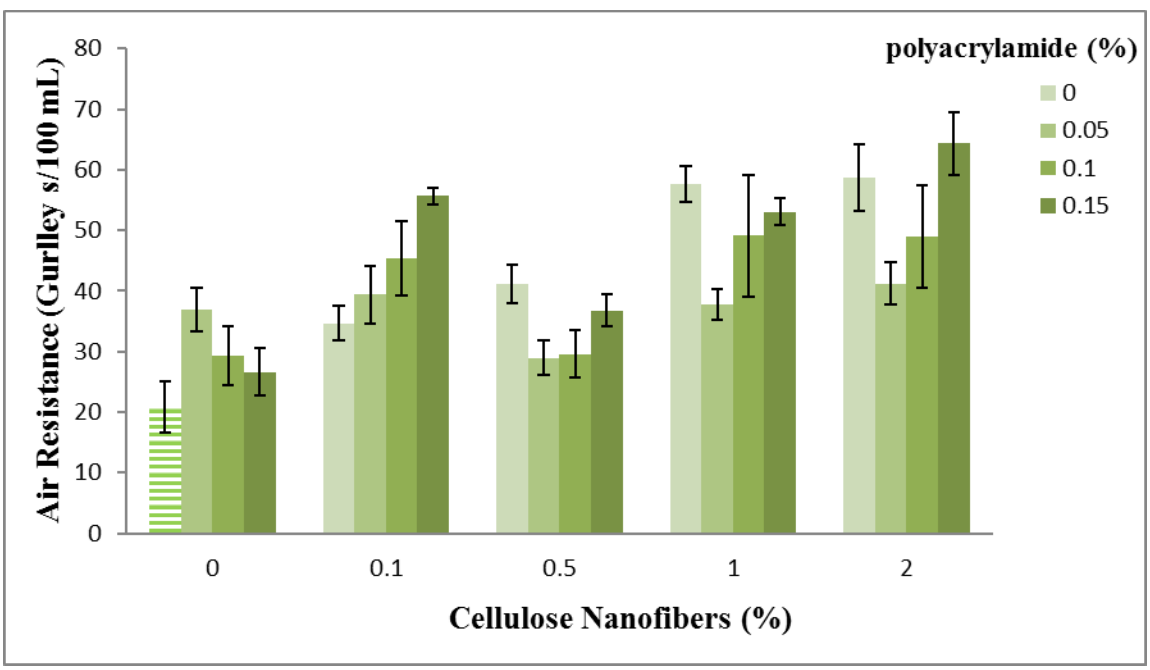

Fig. 6. The effect of cationic polyacrylamide and cellulose nanofibers on air permeability

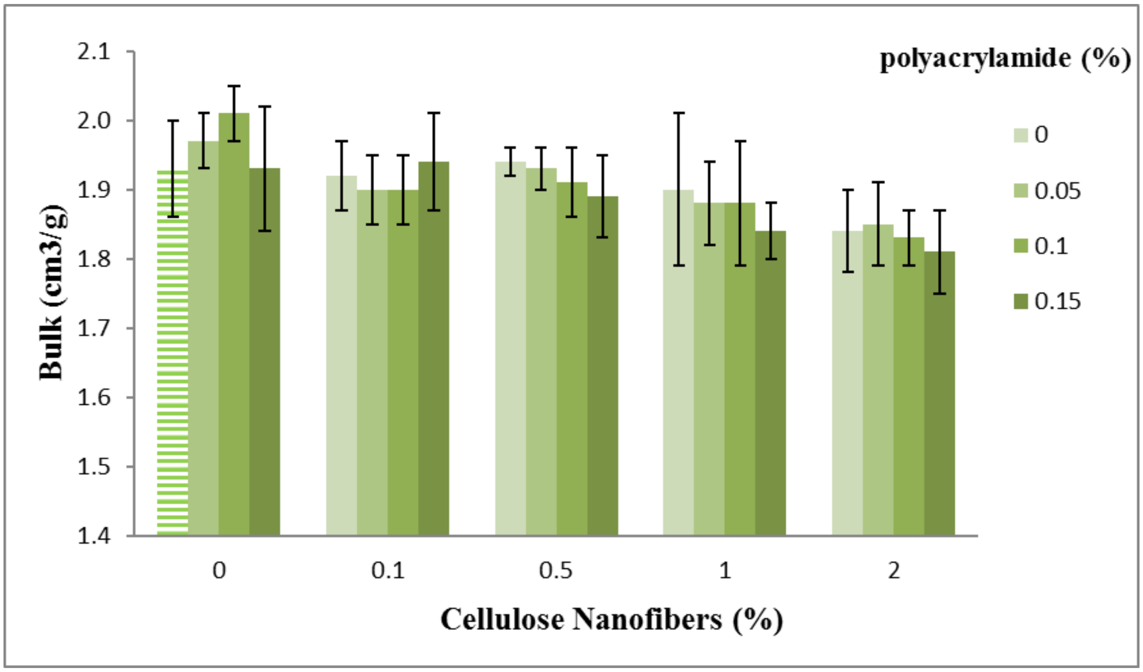

Fig. 7. The effect of cationic polyacrylamide and cellulose nanofibers on bulk

Strength Properties

Tensile and burst strength

Increased cationic polyacrylamide and cellulose nanofiber content caused increases in tensile and burst strengths (Figs. 8 and 9).

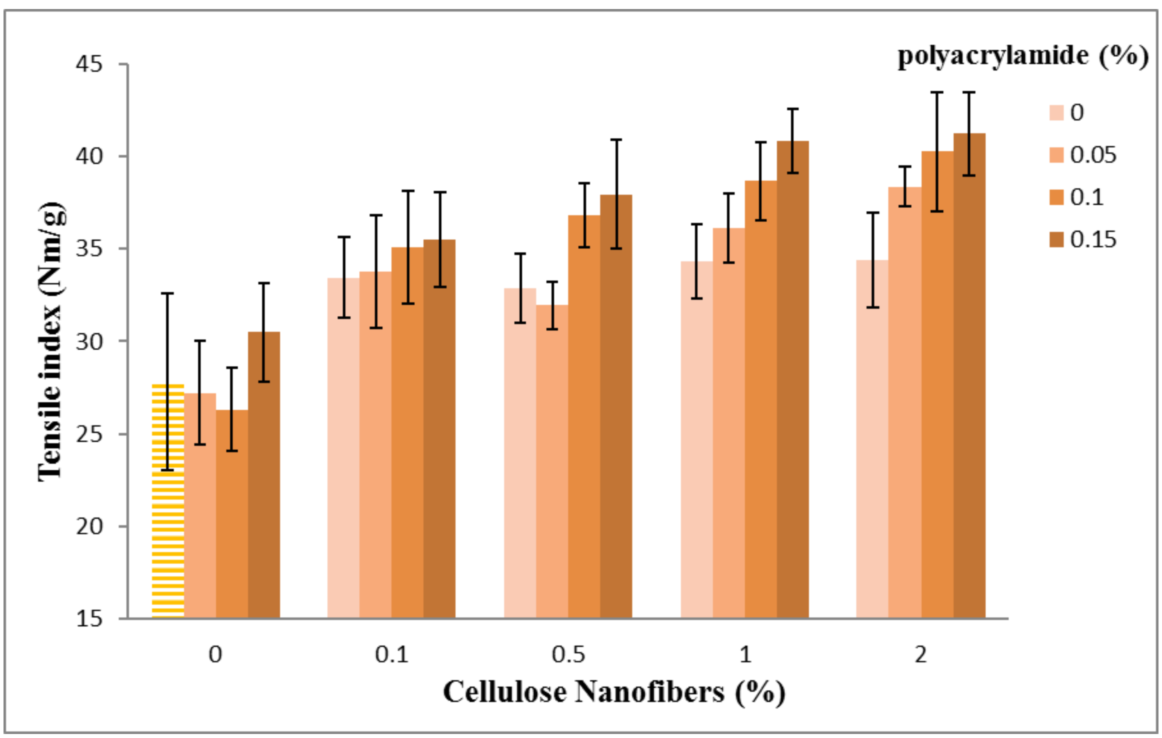

Fig. 8. The effect of cationic polyacrylamide and cellulose nanofibers on tensile index

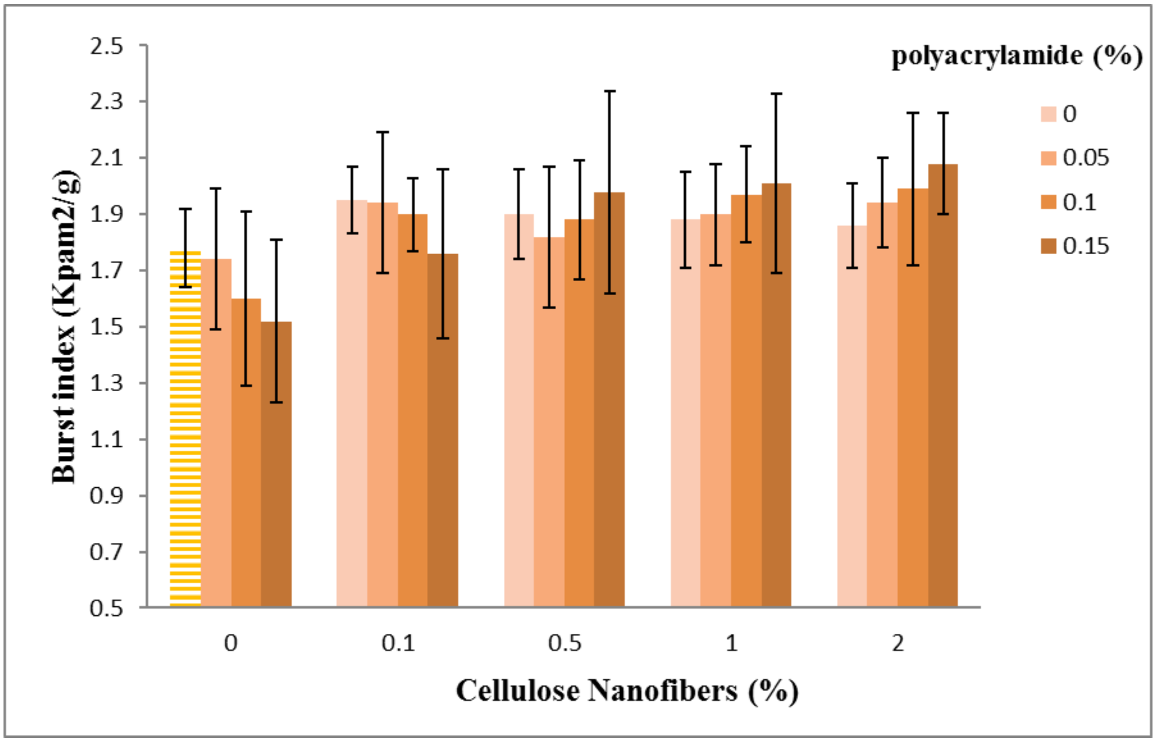

Fig. 9. The effect of cationic polyacrylamide and cellulose nanofibers on burst index

The tensile strength in the control samples was 27.80 Nm/g; in the samples containing 2% nanofiber and 0.15% cationic polyacrylamide, the tensile strength increased to 41.22 Nm/ g (Fig. 8), representing a 33% strength improvement. For the control, the burst strength was 1.78 kPa m^2/g, which was enhanced to 2.08 kPa m^2/g with the complex addition treatment, an increase of about 15% (Fig. 9). The increase in cellulose nanofibers resulted in higher hydrogen bonding between fiber surfaces. Because of the high specific surface area in CNF and physical entanglements between the nanofibers and bagasse fibers, hydrogen bonding between fibers increased, which improved the fiber network strength under mechanical loading, resulting in a uniform distribution of tension in the paper web. This effect has been confirmed by previous reports (Hadylam *et al.* 2013; Su 2013; Hassan 2015).

Compared with the control samples, tear resistance varied in the studied treatments (Fig. 10). Tear resistance is influenced by many factors, including average fiber length, hydrogen bonding area, and natural fiber strength. With increasing cellulose nanofiber content, the average fiber length decreased, the hydrogen bonding area increased, and inherent (natural) strength of the nanofibers was higher compared with the bagasse fiber. These effects were due to amorphous and poor section removal of the cell walls in CNF compared with the bagasse fibers. These reasons explain why the tear resistance fluctuated among the results. In general, with an increased amount of nanocellulose fiber, tear resistance was reduced due to the decrease in average fiber length, which agreed with previous studies (Hadylam *et al.* 2013; Hassan Janzadeh *et al.* 2014; Hassan 2015).

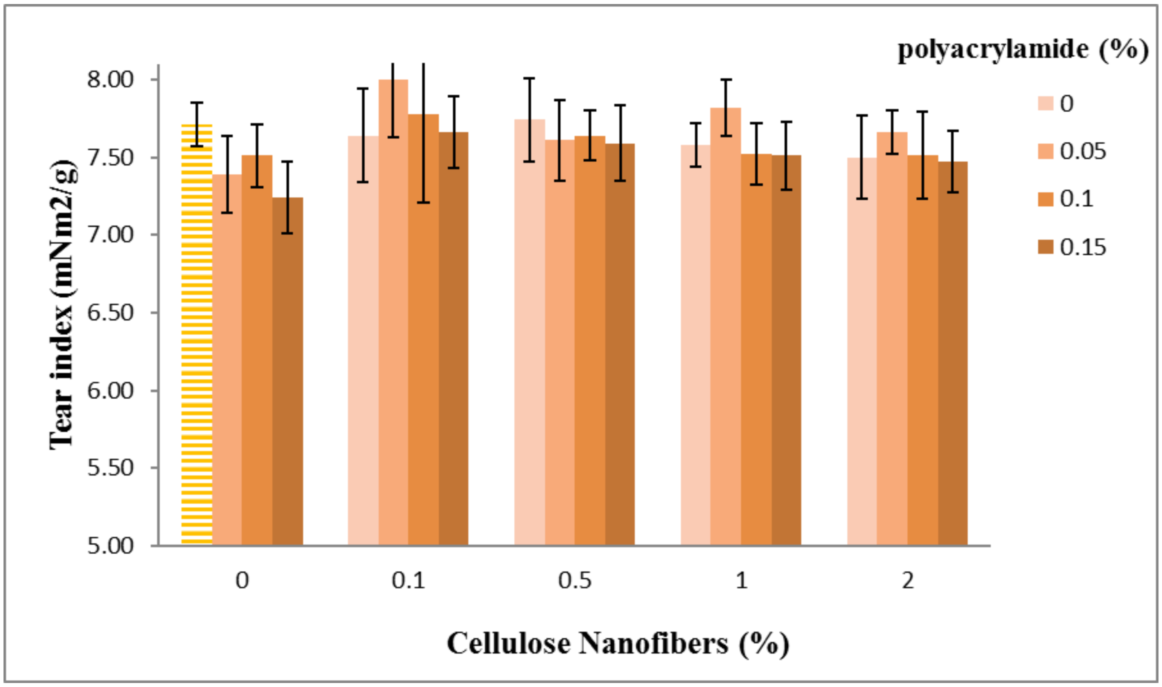

Fig. 10. The effect of cationic polyacrylamide and cellulose nanofibers on tear resistance

Optical Properties

Opacity and brightness

Favorable optical properties of papers vary according to their application. For example, opacity properties are very important for printing and writing papers, while for tracing paper, lampshades, and some packing papers, brightness is very important. The individual addition of cellulose nanofibers to the pulp reduced the opacity (Fig. 12) and increased the brightness (Fig. 11).

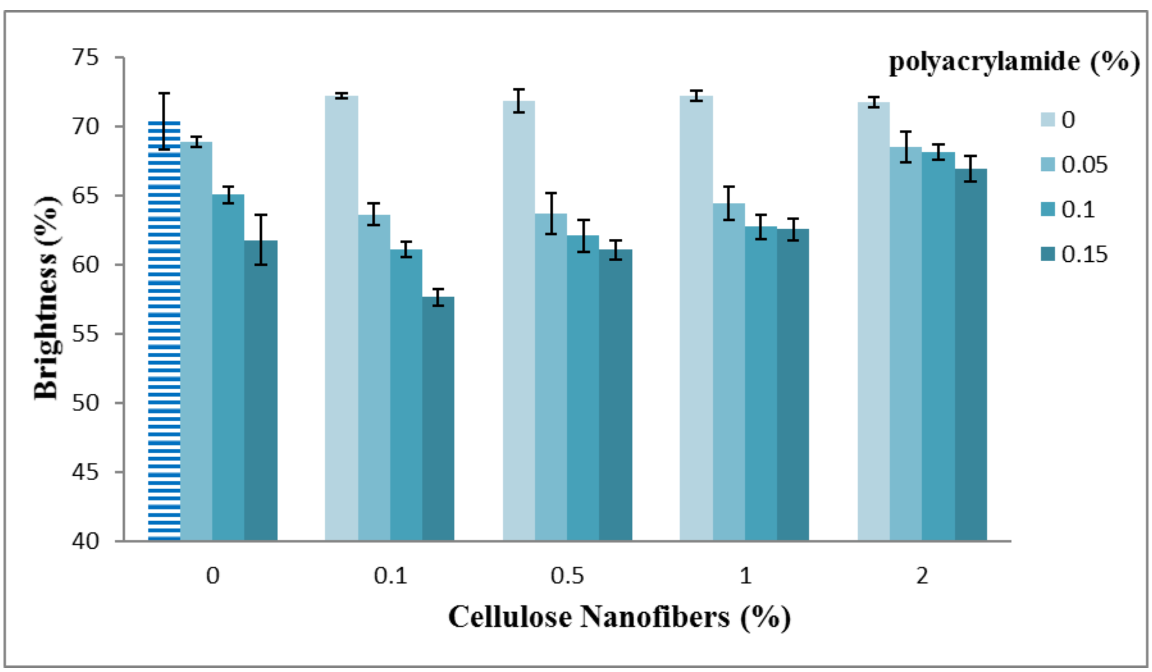

Fig. 11. The effect of cationic polyacrylamide and cellulose nanofibers on brightness

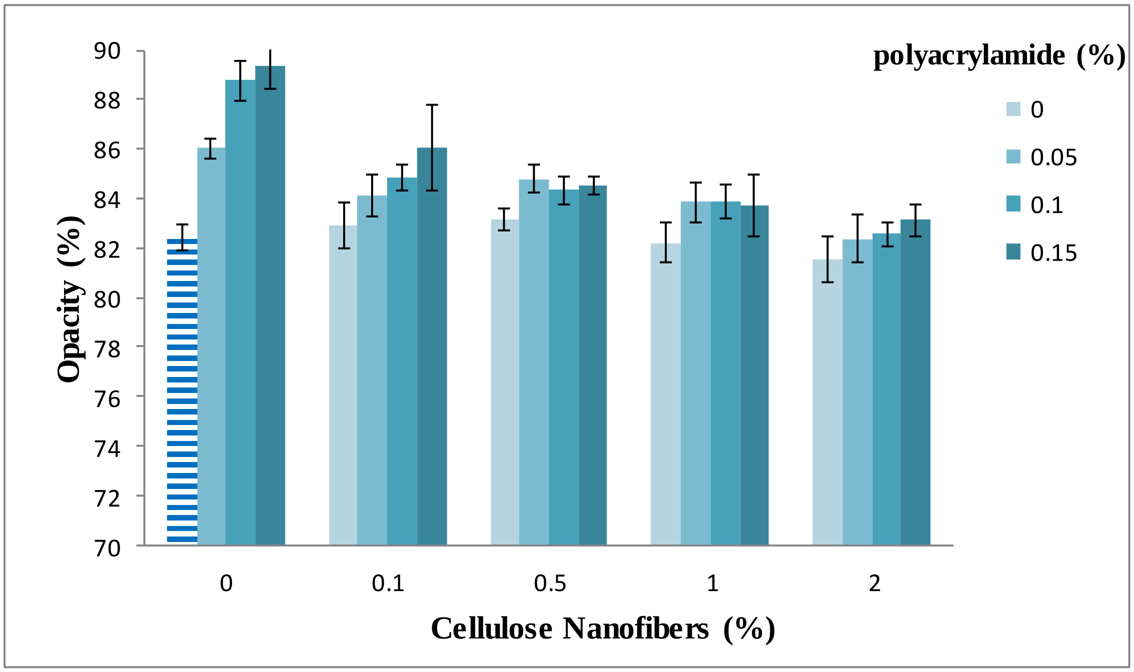

Fig. 12. The effect of cationic polyacrylamide and cellulose nano fibers on opacity

Light easily passes through the walls of cellulose nanofibers, as the cellulosic wall has no porosity, and thus increases the brightness and reduces the opacity. A reverse trend was observed for the individual addition of cationic polyacrylamide, for which the opacity increased and brightness decreased.

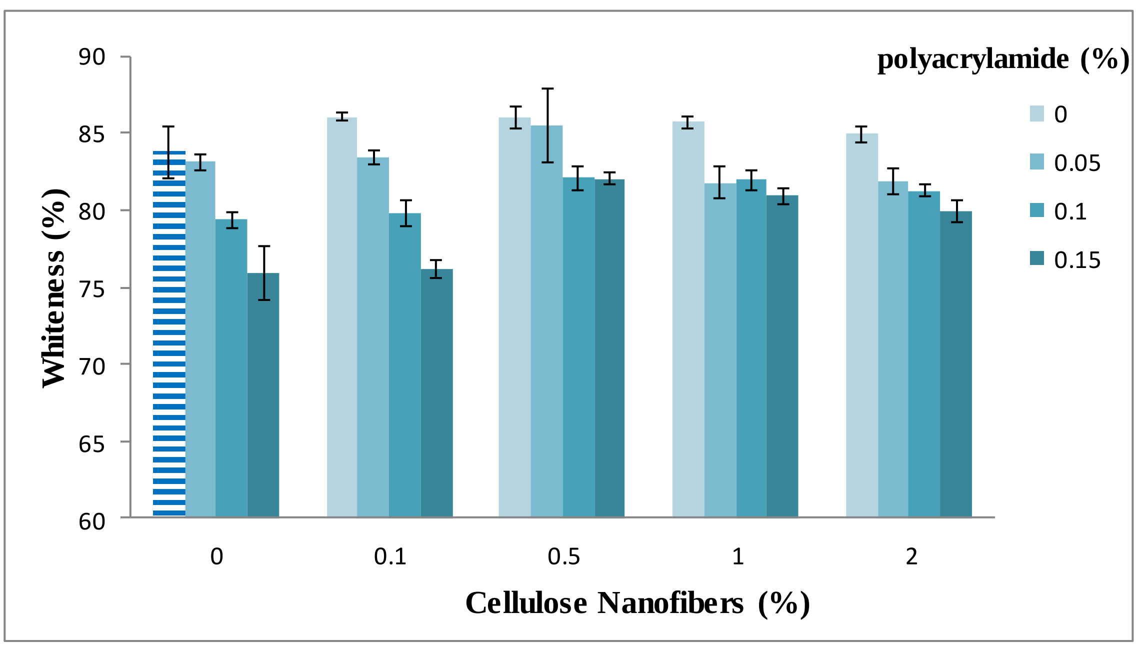

Fig. 13. The effect of cationic polyacrylamide and cellulose nanofibers on whiteness

Yellowness and whiteness

Yellowness decreased and whiteness increased with the addition of cellulose nanofibers (Figs. 13 and 14). Conversely, increasing the amounts of cationic polyacrylamide alone or in combination with CNF increased yellowness and reduced whiteness.

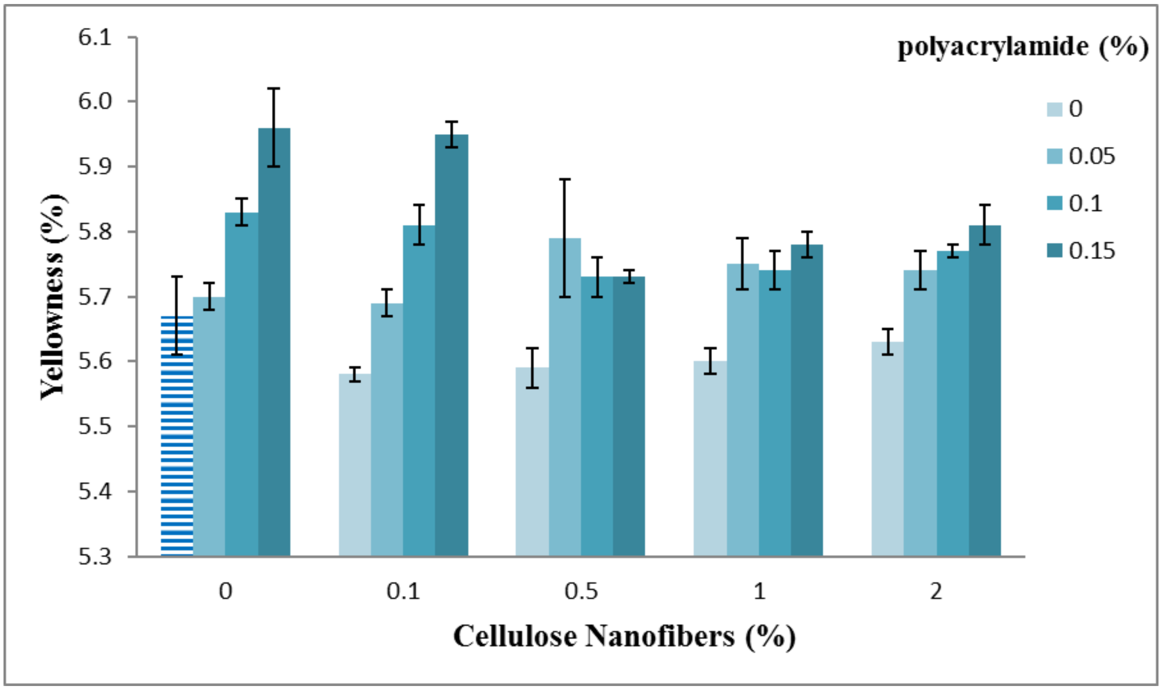

Fig. 14. The effect of cationic polyacrylamide and cellulose nanofibers on yellowness

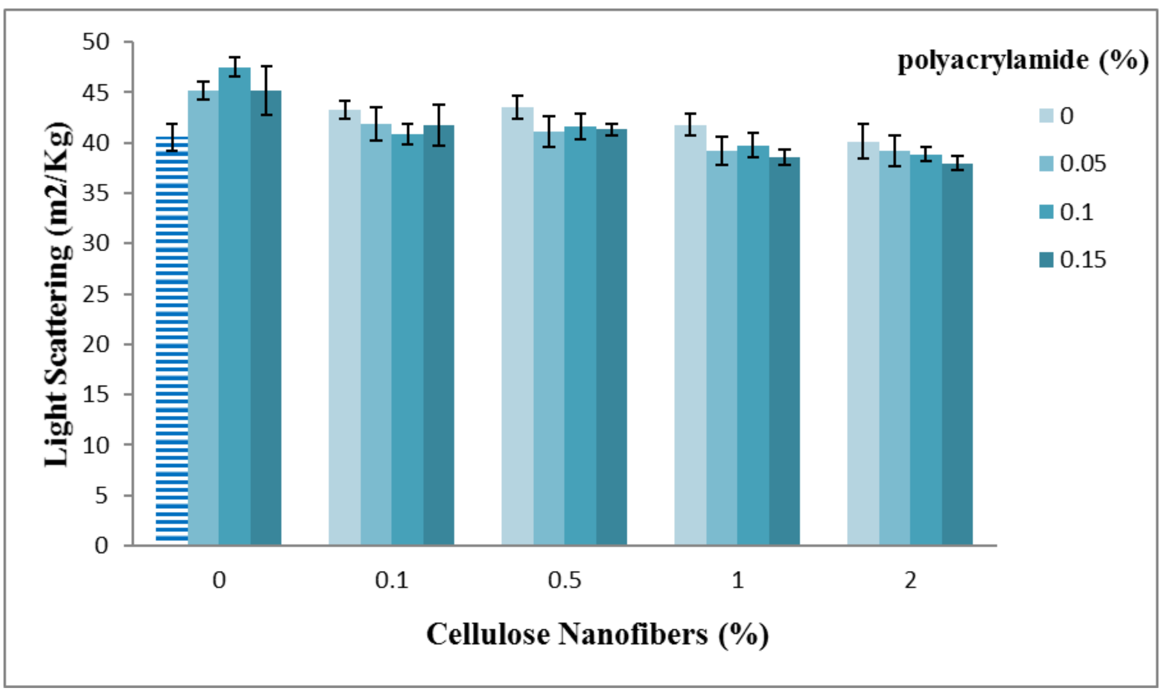

Fig. 15. The effect of cationic polyacrylamide and cellulose nanofibers on light scattering

Light scattering and absorption coefficient

The light absorption coefficient was greatly reduced in samples containing only cellulose nanofibers (Figs. 15 and 16). The light scattering coefficient in samples with either cellulosic nanofibers or cationic polyacrylamide increased compared with the control, but in samples that combined the two additives, the light scattering coefficient was significantly reduced.

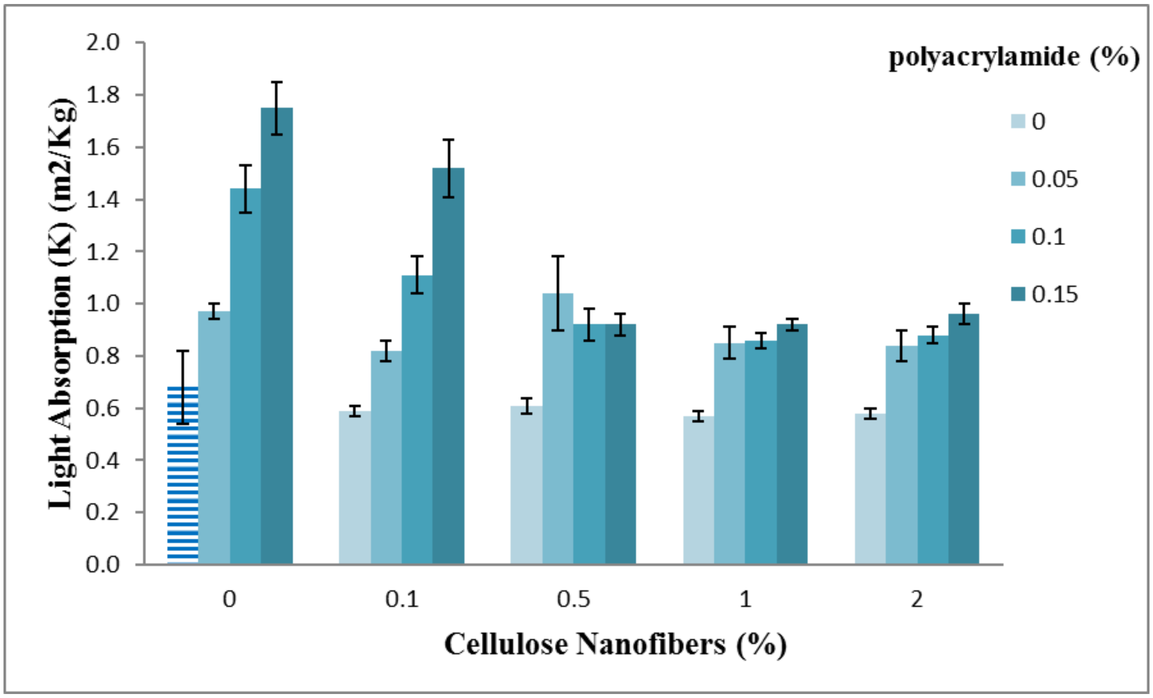

Fig. 16. The effect of cationic polyacrylamide and nanocellulose fibers on light absorption

CONCLUSIONS

1. The combined addition of cellulose nanofiber and cationic polyacrylamide to bagasse paper improved its physical, optical, and mechanical properties, including freeness.
2. The freeness for the control sample was 500 CSF; with 0.5 nm nanofiber and 0.15% cationic polyacrylamide, the freeness reached 670 CSF, which could be useful on high-speed paper machines. Furthermore, the addition of cellulose nanofiber and cationic polyacrylamide decreased the bulk and increased air permeability resistance.
3. The light scattering coefficient, brightness, and whiteness all increased with the addition of cellulose nanofiber; however, the light absorption coefficient, yellowness, and opacity decreased.
4. Incorporating cellulose nanofiber and cationic polyacrylamide increased the strength properties considerably. The highest strength properties were observed in the samples containing 2% cellulose nanofiber and 0.15% cationic polyacrylamide.

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