Process Variables and the Performance of Cationic Rosin as an Internal Sizing Agent in Recycled Corrugated Container Pulp

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Cationic rosin has many uses in papermaking; however, its performance as an internal sizing agent differs depending on the circumstance, especially in the recycling of pulps. In this study, a comprehensive laboratory approach was used to investigate the process variables affecting the cationic rosin application in the paper recycling process. In this respect, four levels of alum (0.5, 1.0, 1.5, and 2.0%) and four levels of cationic rosin (0.5, 1.0, 1.5, and 2.0%) were considered to find the best alum/cationic rosin combination in acidic conditions (pH 5). After considering all aspects of the paper, such as the mechanical properties (tensile, burst, and tear indices), wet resistance (Cobb test and dynamic contact angle test), and chemical usage (economically and environmentally-friendly procedures), the 1.0% alum and 0.5% cationic rosin levels were selected for optimum performance. This research also showed that the combined effect of alum with cationic rosin was favorable. Moreover, the sequence of alum and cationic rosin addition, which is a challenge in paper mills, also should be considered. The results indicated that the addition of cationic rosin after alum obtained the best mechanical and wet resistance results. In addition, the results showed that both acidic and neutral pH were acceptable in this sizing process.

Keywords: Papermaking; Recycled Paper; Internal Sizing; Process Variables; Cationic Rosin; Alum; Old corrugated container (OCC)

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INTRODUCTION

Paper products have a high tendency to absorb water because of their lignocellulosic fibrous contents (Zou *et al.* 2004a). Although this property is useful in some applications, such as tissue, some products require water resistance. Packaging paper, for example, usually faces conditions that force the producer to improve its resistance against water penetration. In such conditions, the application of sizing agents can be effective.

Soap rosin, which is a successful sizing agent that has a long history in papermaking industries, usually works at a pH lower than 6.5. Changing the papermaking process to favor neutral-alkaline conditions puts pressure on this industry to seek new components in this respect. Alkylketene dimer (AKD) and alkylsuccinic anhydride (ASA) were the first agents to be used for this process (Zou *et al.* 2004a; Varshoei *et al.* 2013).

Rosin sizing agents are usually inexpensive, user-friendly, tolerant to other wet end additives, and have a longer shelf life than other sizing agents (*e.g.*, AKD). Therefore, there is a growing interest in using rosin sizing agents for neutral-alkaline papermaking.

In this respect, modified rosin sizes have been of interest in the field (Zhang *et al.* 2004). Although our information about different aspects of rosins application in paper mills (premixing rosin sizes, pH adjustment, applied temperatures, water hardness effect, optimum chemical dosages, *etc.*) has considered many issues (Nitzman and Royapaa 2003; Zou *et al.* 2004a,b; Bajpai 2005; Hubbe 2005, 2006; Zhijie 2006; Hamzeh *et al.* 2008; Bergvall 2013), the subject of cationic rosin seems to need more attention. Although its application became prevalent by the late 1990s (Ehrhardt and Gast 1988; Nitzman and Royapaa 2003), the scientific and laboratory information about different aspects such as the main mechanism underlying the hydrophobizing effect, its tolerance domain in complex wet end chemistry of recycled mill (high conductivity suspension, highly cationic demand,…), the effect of alum presence, the influence of sequence of alum/rosin addition, and the effect of suspension pH, *etc*., remain unclear (Daniel and Moore 1956; Watanabe *et al.* 1999; Hubbe 2005). Some of these areas, such as sequence of addition, pH adjustment, and assessing the tolerance, can provide a proper lead to optimize the process situation.

Increasing the waste paper recovery rate and the ratio of recycled fiber consumption during the papermaking process is important for optimizing wet-end additive performance (Khosravani and Rahmaninia 2012). Recently, a high percentage of packaging paper materials have contained recycled fibers, especially recovered old corrugated container (OCC) fibers. The complex wet-end chemistry of recycled fiber suspension, specifically the presence of anionic trash, may interact with cationic additives. The objective of this study was to further investigate the performance of cationic rosins in recycled suspensions.

EXPERIMENTAL

Old corrugated containers were selected from Iran Papyrus Co., Iran, transported to the papermaking lab, and stored in ambient conditions for 24 h. The waste papers were soaked in deionized water for 24 h. The soaked OCC fibers were slushed by hand and added to a laboratory Holander beater for disintegrating and refining, according to the TAPPI method, T200 sp-01 (2001), up to 300 ± 25 mL Canadian standard freeness (CSF) according to the TAPPI method T227 om-04 (2004). The pulp suspension pH after refining was approximately 7. This prepared pulp suspension was collected in a plastic container and used for all experiments. So the pulp conditions (conductivity, cationic demand, hardness, *etc*.) were the same in all treatments. The cationic aqueous rosin dispersion was prepared from Eka Co., Republic of Korea. The physical and chemical properties of this cationic rosin are shown in Table 1. To evaluate functional groups in the sizing agent, infrared (IR) spectra of the cationic rosin were taken on a Spectrum 400 (Perkin Elmer, USA) Fourier transform infrared (FT-IR) spectrometer, within the range of 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1} for 32 scans.

Table 1. Physical and Chemical Properties of Cationic Rosin

Properties	Description
Form	aqueous
pH	2 to 4
Viscosity	<100 mPa·s
Density	1050 kg/m^3
Solubility	Infinitely dispersible in water
Solids content	≈ 35%

Alum (Iran Shargh Co., Iran), a white powder with 17% active solids content, was diluted to 0.5% concentration with a pH of 2 to 4. Also, the pH of the OCC pulp suspension was adjusted using HCl or NaOH before the addition of other chemicals. For the first step of the experiment, alum, at four different dosage levels (0.5, 1.0, 1.5, and 2.0%) and cationic rosin, at different dosage levels (0.5, 1.0, 1.5, and 2.0%) were applied to find the best alum/cationic rosin combination under acidic conditions (pH 5). Then, the best combination was tested at approximately neutral pH (≈ 7.5). Also, the addition sequence of the alum and cationic rosin was investigated for acidic conditions. Lastly, the performance of the cationic rosin, without the addition of alum, was studied under acidic conditions. The chemicals were added to obtain a 0.5% consistency of OCC pulp, with 10 second intervals and 750 rpm agitation. The 130 gm^{-2} sheets were made, according to the TAPPI T205 sp-02 (2002) standard. Sheet drying was done using a drum dryer in 2 steps: 2.5 h at 70 ºC and 10 min at 90 ºC. After the sheets were prepared, the properties were measured (Table 2).

Changes in the contact angle of a 30 µL distilled water droplet with the sheet surface were monitored and dynamically measured using a PGX Goniometer, Switzerland.

It should be noted that all treatments had at least 5 replications, which provides the opportunity for verification of the experiments. Completely randomized design was considered for statistical analysis of results. After testing the normality, Duncan's new multiple range test was used to categorize the averages.

Table 2. Physical Properties and Relative Methods of Sheet Preparation

Properties	Standard
Basis Weight (g/m^2)	ISO 536
Cobb-60	ISO 535
Tensile Index	ISO 1924-2
Burst Index	ISO 2758
Tear Index	ISO 1974
Contact Angle	Instrument Manual

RESULTS AND DISCUSSION

FTIR Analysis

The FTIR spectrum of the cationic rosin is shown in Fig. 1. In this spectrum, the peaks at 2931 cm^{-1}, 1461 cm^{-1}, 1407 cm^{-1}, 1387 cm^{-1}, 1108 cm^{-1}, 947 cm^{-1}, and 823 cm^{-1} are related to the stretching vibrations of C-H bonding, C-H_3 bending, C-H_2 bending, doublet methyl group, C-O stretching, C-H stretching vibrations of alkene group (strong peak), and C-H stretching vibrations of alkene group (weak peak), respectively. Moreover, the peaks at 1783 cm^{-1} and 1695 cm^{-1} are related to carbonyl groups connected to the structure of cyclobutane and cycloheptane rings, respectively.

The FTIR spectrum was characteristic of the fatty acids and resin acids that are usually found in tall oil. The peaks at 665 cm^{-1}, 716 cm^{-1}, and 1277 cm^{-1} were assigned to amine groups, which are responsible for the cationic character. The first two may be related to the N-H of primary and secondary amines, while the latter C-N stretching was characteristic of aromatic amines.

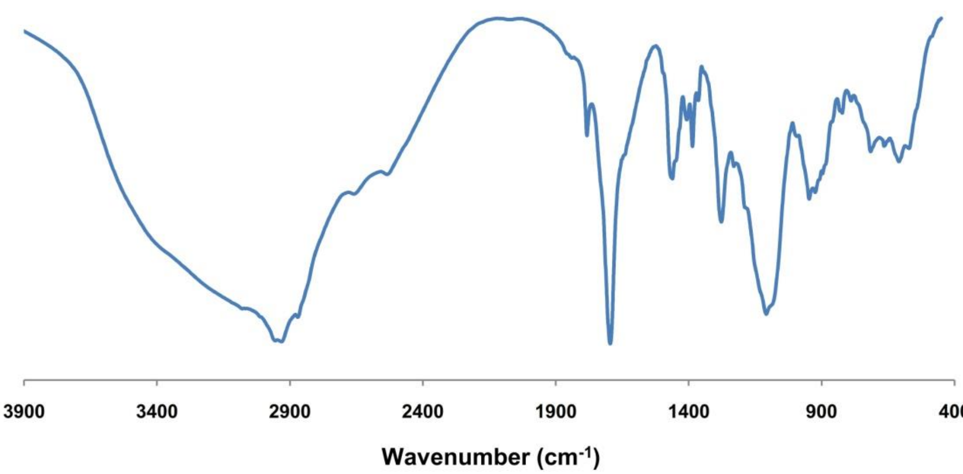

Fig. 1. The FTIR spectrum of cationic rosin

Effect of Alum and Cationic Rosin Dosages on Water Resistance

According to Fig. 2, all dosages of alum/cationic rosin could properly increase the water resistance of recycled paper. The Cobb-60 measurement of the control sample (pulp with no chemical addition) decreased from 288 gm^{-2} to less than 15.5 g/m^2, which was even lower than the current standard (≥ 50 g/m^2). Although the recycled OCC pulp had moderately high conductivity (800 µS/cm in control samples) with a high content of anionic trash, the alum/cationic rosin system acted effectively.

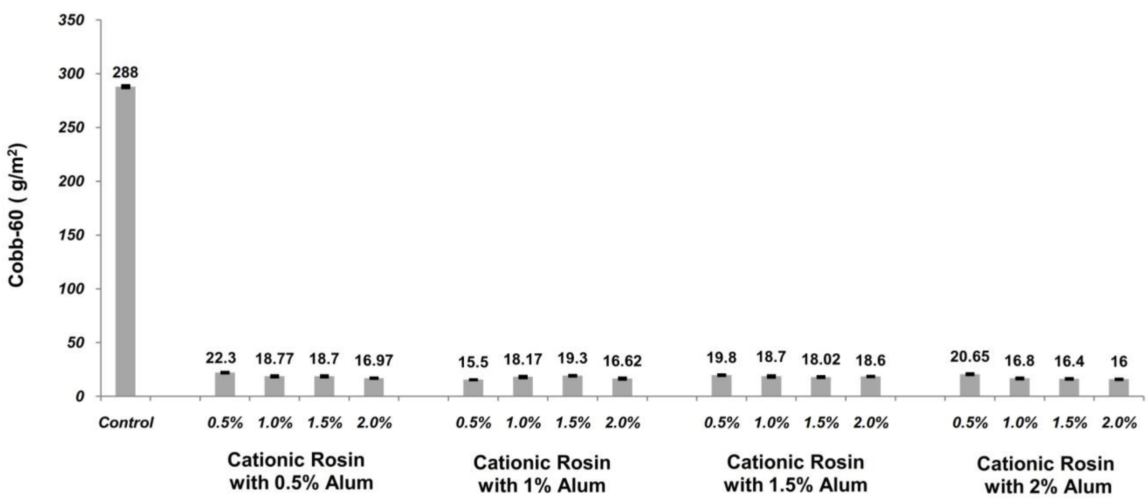

Fig. 2. Effect of alum/cationic rosin dosage on the internal sizing of recycled OCC paper

Internal sizing has four main elements: retention of size, distribution on fiber, attachment of size to fiber, and anchoring and orientation of the size molecule. Alum has an important role in this phenomenon, especially in the 1st, 3rd, and 4th elemental stages (Wang *et al*. 2000; Batten 2005).

In sizing with soap rosin, alum has a vital effect on the retention of soap rosin in the fibers (*i.e.* 1st step of sizing). Thus, a recycled fiber suspension with higher conductivity and more anionic deposits is better suited for aqueous phase aluminum to act as a cationic trash collector. Thus, the active alum for the rosin-aluminum reaction and forming of aluminum rosinate should decrease, and the important step of internal sizing (*i.e*., retention of size) would be incomplete. However, in the alum-cationic rosin system, the cationized nature of rosin itself is a positive factor in the retention of the size of the fiber, and it compensates for the deficit in the 1st step of rosin sizing (Sakamoto and Au 2002). The results in Table 3 comparing the Cobb-60 measurements of soap and cationic rosin confirm this explanation.

Table 3. Comparison of the Cobb-60 Measures between Soap and Cationic Rosin

Treatment	Cobb-60 (g/m^2)
Soap rosin (1% Alum and 0.5% Soap rosin)	21.6
Cationic Rosin (1% Alum and 0.5% cationic rosin)	15.5

The percent usage of chemicals is a vital factor, especially considering the cost and environmental aspects of mill activities, so the optimal dose of 0.5% cationic rosin was selected. In the next step, the performance of this dose in combination with different alum consumption levels, was investigated according to the mechanical properties and Cobb-60 measurement, as previously mentioned.

Effect of Alum/Cationic Rosin Dosages on the Mechanical Properties

As Fig. 3 shows, using 0.5% cationic rosin with different dosages of alum improved water resistance factor but it did not have a negative effect on the burst, tensile, or tear indices. Compared with other conventional sizing agents such as AKD, ASA, and soap rosins, this system successfully achieved the proper effect without reducing the mechanical properties of the paper (Hubbe 2006; Ekhtera *et al.* 2008; Varshoei *et al.* 2013). In internal sizing, the main mechanism of increasing water resistance is to block the hydroxyl and carboxyl groups, the hydrophilic portion of pulp. Here, the mechanism is the same, however, the presence of alum as a cationic polymer with the cationized rosin aids in the formation of ionic bonds among the anionic fibers and fines, which compensate for the loss of hydrogen bonding. Considering all aspects, such as less chemical usage and the obtained results, using 1.0% alum with 0.5% cationic rosin was selected as the best treatment option.

Confirming the Alum/Cationic Rosin Treatment on Water Resistance Using Dynamic Contact Angle Measurement

After alum/cationic rosin application, the dynamic contact angle (DCA) of a water droplet with the paper surface was tested (Fig. 4). The DCA of treated papers (about 110 to 120°) was significantly different from the control samples (90º ≥), which indicated that the applied sizing system successfully decreased the surface tension of fibers. Also, these results showed that the paper treated with 1.0% alum/0.5% cationic rosin required more time for the water droplet to be absorbed than the control paper; in the control paper, the contact angle drastically decreased in only 26 s.

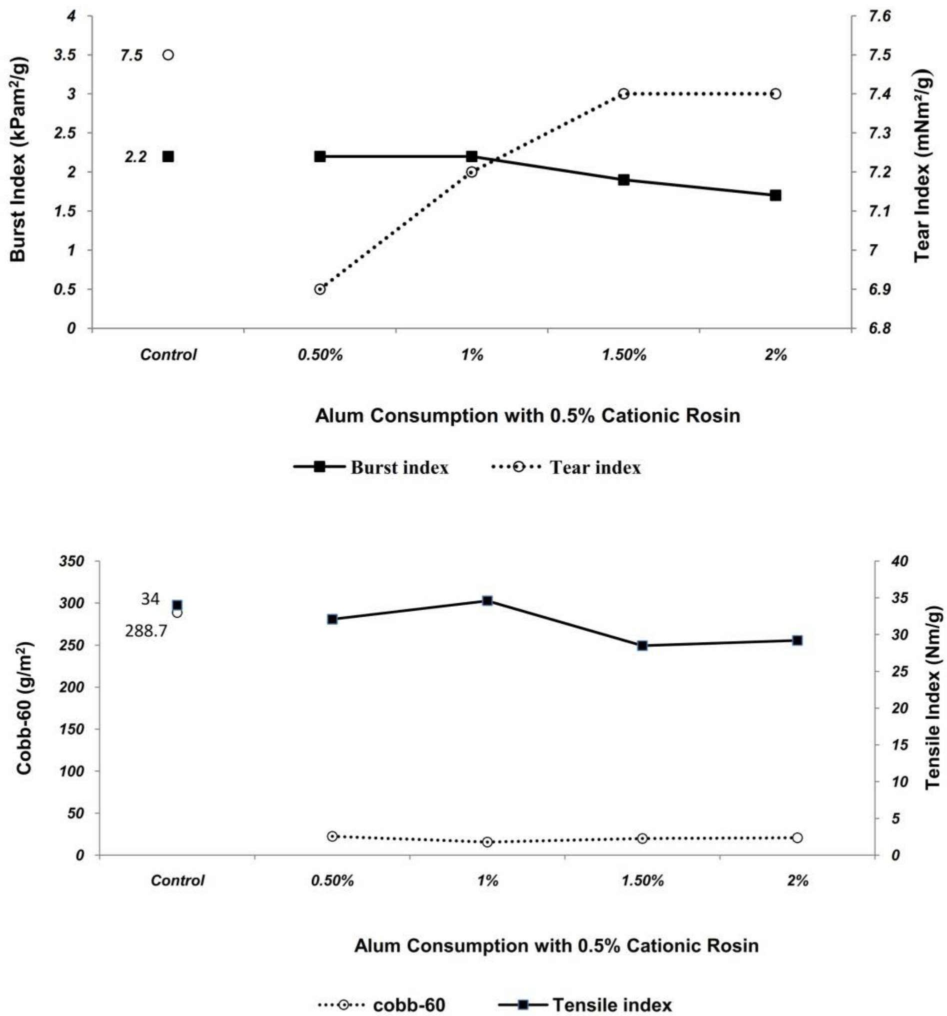

Fig. 3. Effect of different dosages of alum with 0.5% cationic rosin, as an internal sizing agent, on the burst and tear indices (up), and the tensile index and Cobb-60 (down) of recycled OCC pulp

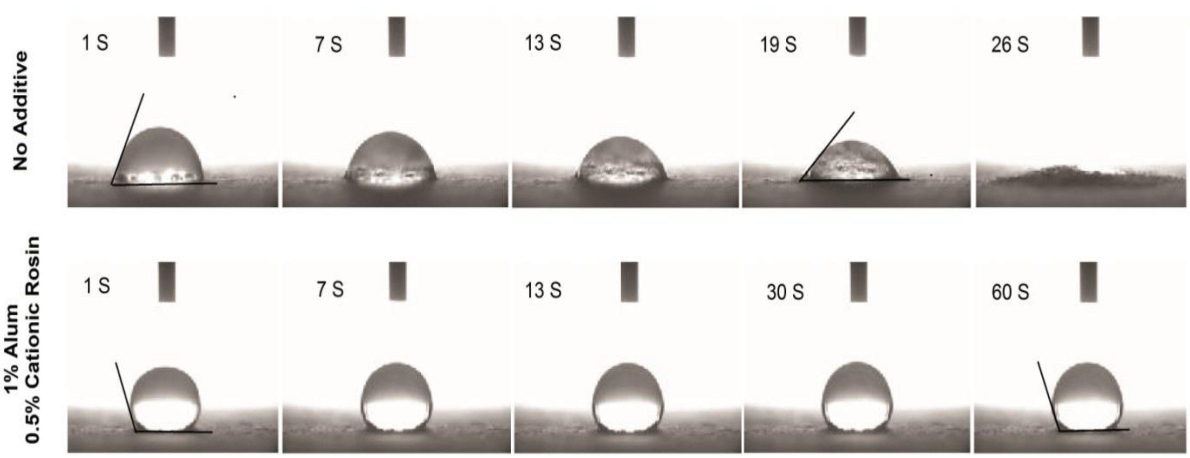

Fig. 4. Differences in the contact angle of the water droplet with the paper surface between control papers (no additive) and treated papers (1.0% alum/0.5% cationic rosin)

Effect of pH and the Alum/Cationic Addition Rosin Sequence on Water Resistance and Mechanical Properties

The sequence of alum and rosin addition has been considered in previous investigations (Kraus *et al.* 2002; Katz *et al.* 2003; Zou *et al.* 2004b). In this study, all of the results met the minimum requirement of a test liner for water resistance (50 ≥ gm^{-2}; Fig. 5). In sizing with soap rosin, the creation of rosin aluminates should happen in the wet-end of the pulp suspension. Thus, the sequence of addition to the pulp slurry is important. However, in cationic rosin, the formation of aluminum rosinate occurs during the drying stage of the papermaking process, when the pulp suspension status is less important.

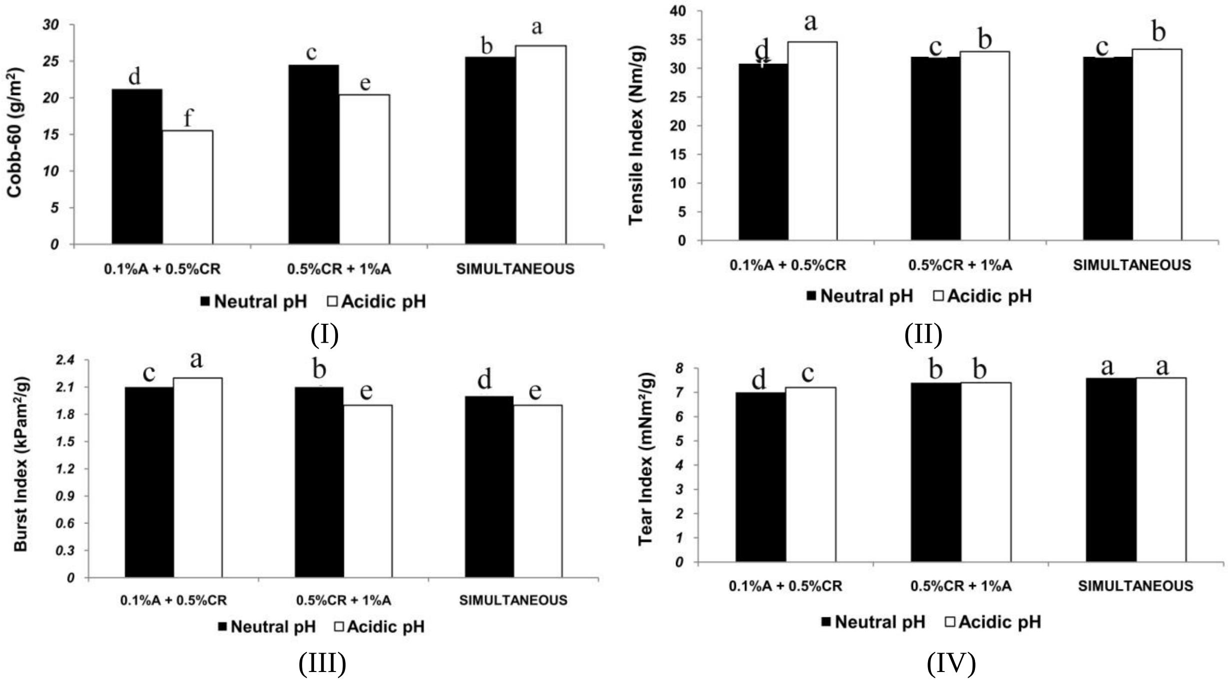

Fig. 5. Effect of pH and alum/cationic rosin sequence of addition on water resistance (I) and mechanical properties (II, III, and IV) (A: Alum and CR: Cationic Rosin)

Although all manners of addition considered in this work were acceptable, the addition of alum in the 1st step, before cationic rosin usage, was shown to improve the water resistance of prepared recycled paper in both acidic and neutral conditions. Therefore, the addition of alum to recycled OCC pulp (with a high anionic trash content) would deactivate the anionic charges and momentarily lower the pH, thus providing a suitable condition for that action of cationic rosin. In fact, alum plays an important role as a valuable anionic trash collector. In contrast, adding the cationic rosin first, would interfere with the anionic trash and drastically decreases its cationic charge and retention on the fiber surface (Bajpai 2005; Batten 2005). The simultaneous addition of both the cationic rosin and alum exhibited weaker results, which showed that the alum did not have enough contact time to have an effect on the anionic trash collection; thus the cationic rosin was less effective compared with the alum/cationic rosin sequence of addition.

This trend was the same in neutral and acidic conditions. Although this rosin system was overall more successful in acidic pH, all of the treatments showed acceptable responses, compared with the standard value for test liners (50 ≥ gm^{-2}).

Considering the burst and tensile properties, the trend was the same as the Cobb-60 test, *i.e.*, the alum/cationic rosin addition showed higher results for these properties, although the differences were minimal. There was not a considerable difference in the tear strength. For most treatments, the acidic pH resulted in better mechanical results. These results showed that using cationic rosin not only had a positive effect on the mechanical properties of paper, but in some cases, even notably improved such properties.

Influence of Alum on the Performance of Cationic Rosin in Acidic Conditions

Except for the tear index, which showed no change, the combination of alum with cationic rosin had a positive effect on all of the measured properties (Table 4). As previously mentioned, recycled OCC pulp with a high cationic demand may exhibit a negative influence on the retention of cationic rosin on the fiber's surface. Alum in the pulp suspension acted as an anionic trash collector, thereby decreasing the potentially negative effects of the anionic particles on sizing. According to some reports, alum has an important role in the rosin molecule orientation on cellulosic fiber, which may increase the hydrophobicity of the final products (Batten 2005; Liu *et al.* 2006; Liu *et al.* 2008). Moreover, the tensile and burst indices increased, resulting from the consumption of alum with cationic rosin.

Table 4. Effect of Alum on the Sizing Process with Cationic Rosin in Recycled OCC Pulp

Treatment	Properties			
	Cobb - 60 (g/m^2)	Tensile Index (Nm/g)	Burst Index ($kPam^2/g$)	Tear Index (mNm^2/g)
1.0% alum and 0.5% cationic rosin	15.5	34.6	2.2	7.2
0.5% cationic rosin with no alum	30.6	30.6	1.7	7.8

CONCLUSIONS

1. The results showed that OCC pulp could be sized successfully with alum/cationic rosin without any concern of its complex wet end conditions.
2. Even in hard conditions of OCC pulp wet end, this dual components system was successful at lower dosages of alum (1.0%) and cationic rosin (0.5%), which is economically and environmentally important.
3. The use of alum as a rosin stabilizer and anionic trash collector should be considered because of its combined effects with cationic rosin.
4. The addition of alum before cationic rosin obtained better results than the simultaneous addition and cationic rosin to the suspension. This trend was the same for neutral and acidic conditions.
5. Although this rosin system was overall more successful in acidic conditions, all of the treatments showed acceptable responses when compared with the standard value.
6. Cationic rosin had a positive effect on the mechanical properties mentioned and in some cases, improved the mechanical properties of paper.

ACKNOWLEDGMENTS

The authors express their appreciation to the Iran Papyrus Co., Iran Shargh Co., and Eka for providing the chemicals used in this research. The authors also thank Dr. Hossein Kermanian, Dr. Omid Ramezani, and Eng. Zahra Razmpour of the Shahid Beheshti University for their technical supports during the laboratory experiments. The authors also extend thanks to Dr. Amir Khosravani and Dr. Habibollah Younesi for their scientific consulting during the last steps of this study.

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Article submitted: December 18, 2015; Peer review completed: March 17, 2016; Revised version received and accepted: April 23, 2016; Published: April 28, 2016.
DOI: 10.15376/biores.11.2.5333-5342