Insight on the Feasibility of Producing Durable Paper from Spruce Pulp using the Sulfate Process

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Bleached spruce sulfate pulp was used in this study to produce paper handsheets. Ethylene diamine tetra acetic acid (EDTA) was introduced as a chelating agent in concentrations of 0, 0.25, 0.5, and 0.75%. The handsheets were exposed to UV light at wavelengths ranging from 330 to 440 nm, with time intervals of 0, 10, 20, 30, 40, and 50 h. Finally, the strength properties were measured based on ISO standards. The strength indices of the handsheets were improved by adding the proper concentration of EDTA chelating agent, in comparison with the control sample. Furthermore, increasing the aging time reduced the breaking length, tear strength, folding endurance, burst strength, and tensile strength. Tear index, tensile strength, tearing strength, bursting strength, and folding endurance were decreased respectively by 41.9, 3.1, 28.2, 29.7, and 8.6 percent without EDTA treatment by increasing the aging time.

Keywords: Durable paper; Spruce pulp; Strength properties; EDTA

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INTRODUCTION

Deterioration in the physicomechanical, chemical, and optical properties of historic paper documents and artifacts stored in libraries and archives is responsible for an enormous loss of cultural heritage (Porck and Teygeler 2000). The paper components can be classified according to their origin, chemical structure, and function, such as fibers (composed mostly of cellulose, but also of lignin, hemicelluloses, and other minor components), mineral particles (talc, kaolin, calcium carbonate), natural sizing agents (starch or rosin), or synthetic ones (alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA)), colorants, and other substances (Area and Cheradame 2011).

Generally, increasing the durability of paper, preventing the degradation of its quality, and preserving its chemical structure intact are major concerns for collections managers of libraries. Durable paper is paper that retains its initial quality during use, and pure cellulose fibers are inherently durable. Pure cellulose can be easily hydrolyzed to glucose under controlled acidic conditions. When there is no acid present in the paper, the manufactured paper will exhibit great durability. Librarians have recently found archived paper documents made over 50 years ago that are seriously damaged and worn, with their strength and durability all but vanished. Because polymer cellulose is naturally durable, it is thought that the main reasons for its failure are the manufacturing process, additive materials, and maintenance conditions of the paper.

Kolar and Novak (1996) state that acidic hydrolysis has long been regarded as a possible damaging cause for paper. They argue that paper must be treated with a basic aqueous solution of calcium carbonate and magnesium bicarbonate to avoid the adverse effects acid has on the paper.

The effects of calcium hydroxide and magnesium bicarbonate solutions, as well as carbonated magnesium methoxide non-aqueous solution, on paper's resistance to wear were evaluated for three types of chemical pulps. The viscosity was measured using copper diamine ethylene to determine the damage to the samples after accelerated aging. The results demonstrated that for the tested pulps, the cellulose processed by the calcium hydroxide was damaged at a slower rate than the pulps pickled by the magnesium-bearing bases.

Research conducted at the Institute of Standard and Industrial Research of Iran in 2001 concluded that the durability and stability characteristics of archived document papers were determined as follows:

These papers must be made from the fibers of cotton, cotton linter, hemp, flax, or a mixture of any of the components. When a minute amount of bleached chemical pulp is added to reach a more desired performance standard for the paper, the amount of the pulp must be specified.

Afra (2006) reported that changing the temperature a mere 20 °C alters the damaging speed at a rate of 7.5%. Also, the moisture content of the paper must be kept constant during the accelerated aging process; otherwise, the resultant values would no longer be valid.

Moghaddam (2000) found that the range of light that can be damaging to paper ranges from wavelengths of 330 to 440 nm. He declared that paper yellowing occurs simultaneously, as a result of the heat and light in the environment. He also argued that paper turns yellow when exposed to a high amount of light and heat, but the whiteness of a paper is retained as long as it is stored at low temperatures. The final result depends on the dominant role of heat or light. Moreover, Moghaddam demonstrated that paper does not turn yellow or become brittle in an oxygen-free atmosphere, even if exposed to visible and UV light. However, the paper is expected to become yellow in normal conditions, even with no heat exposure. Therefore, special documents need to be stored in a neutral atmosphere.

The effect of accelerated aging on the optical properties of paper has been investigated by numerous researchers, including Mirshokraei and Abdolkhani (2005), Kasmani *et al.* (2013), Nemati *et al*. (2013), and Vaysi and Kord (2013). However, no research work has been conducted regarding the feasibility of producing durable paper from spruce pulp using the sulfate process. This study was thus implemented to explore the feasibility of making durable paper from spruce sulfate pulp.

MATERIALS AND METHODS

Materials

Spruce sulfate pulp (bleached), with the specifications shown in Table 1, was transferred to the laboratory. Ethylene diamine tetra acetic acid (EDTA) chelating agent, which was introduced to help remove metal ions, is effective for the oxidation of cellulose at concentrations of 0, 0.25, 0.5, and 0.75 wt% of dry fibers. The pH of the solution was kept in the range of 7 to 7.5.

Table 1. Properties of Spruce Sulfate Pulp

Property	Value	Property	Value
Kappa number	1.3	Fiber length (mm)	3.25
Freeness before refining (mL CSF)	750	Diameter of fibers (μm)	47.77
Freeness after refining (mL CSF)	285	Wall thickness (μm)	4.44

Handsheet Formation

Having performed the initial operations for manufacturing the handsheet paper, the pulps were refined in accordance with ISO standard 5269-2 (2011) using a PFI mill, at approximately 18,000 rpm, to reach a freeness degree of 300 ± 25 mL based on the Canadian freeness standard. The freeness testing was conducted with standard ISO 5267-2(2001). Finally, 70-gm^{-2} handsheets were prepared from each pulp sample, in accordance with code M 5:67 of the SCAN standard.

Determination of Properties

After the creation of the handsheets, the samples were exposed to an optical aging test. For the purpose of this study, an accelerated optical aging apparatus with an output wavelength of 330 to 440 nm was applied. The optical aging testing was conducted with standard ISO 5630-3(1996). The aging was performed in time intervals of 0, 10, 20, 30, 40, and 50 h. At the conclusion of the aging, the strength properties of the aforementioned papers were measured three times based on the National Iranian Standards equivalent of the ISO standards as listed below:

Burst strength index	ISO 2758 (2014)
Tear strength index	ISO 1974 (2012)
Folding endurance	ISO 5626 (1993)
Tensile strength index	ISO 1924-3 (2005)
Breaking length	ISO 1924-3 (2005)

Data Analysis

It should be noted that all additive materials were added to the pulp after refining. Analysis of the data was performed as a completely random design, while the comparison and grouping were done using Duncan's test at a 95% significance level. SPSS statistical software (IBM Software, Armonk, New York; version 11.5) was used for the statistical calculations.

RESULTS AND DISCUSSION

Table 2. Analysis of Variance (F-Value and Significance Level) of the Results for EDTA and Time

Variable	Breaking length (km)	Tear index (mN.m^{2}g^{-1})	Fold endurance (n)	Bursting index (kPa.m^{2}g^{-1})	Tensile index (Nmg^{-1})
EDTA	0.112 ns	0.084 ns	20.744 *	0.515 ns	0.152 *
Time	54.157 *	48.722 *	75.779 *	102.846 *	75.761 ns
EDTA * Time	0.033 ns	0.013 ns	0.744 ns	0.093 ns	0.190 ns

* 95% significance level
ns no significance

The F-values and significance level are listed in Table 2. Figures 1 to 5 illustrate the effects of both EDTA and aging time on the strength properties of the durable handsheet papers. It is evident from these figures that the control samples, for all concentrations of EDTA, are in a more damaged condition in comparison to the other treatments.

Effect of EDTA on Strength Properties of Handsheet Papers

The effect of EDTA on both the tensile strength and number of folding was significant at a 95% level. On the other hand, breaking length, tear index, and burst index were not significant at a 95% level (Table 2). Figures 1 to 5 indicate that increasing the concentration of the EDTA chelating agent caused the parameters of breaking length, tear index, folding strength, burst index, and tensile index to improve for the handsheet samples. Therefore, the positive role of EDTA in the improvement of the breaking length, tearing strength, folding strength, bursting strength, and tensile strength was evident.

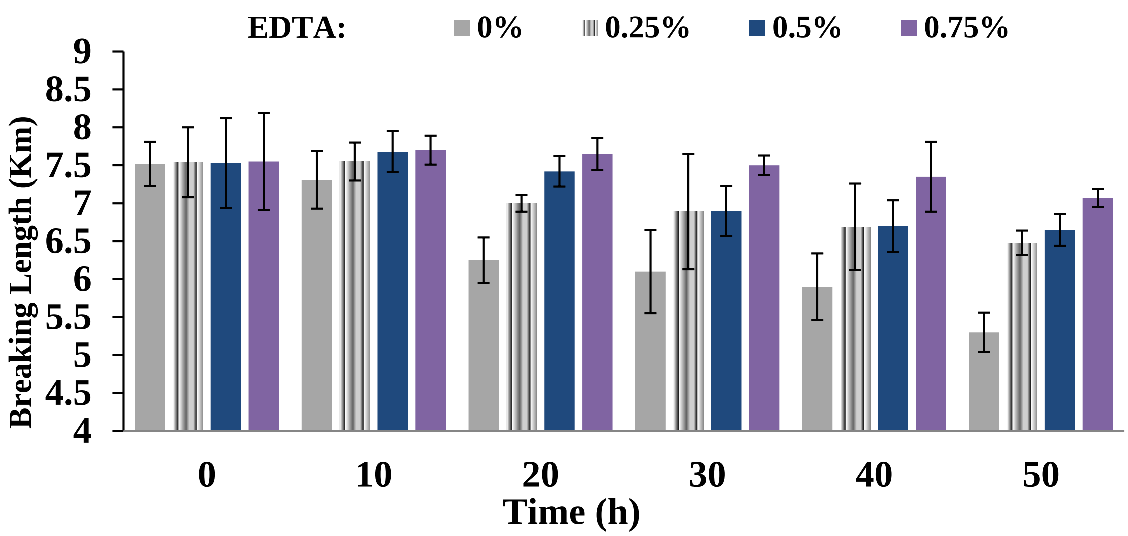

Fig. 1. Effect of aging time and EDTA concentration on breaking length

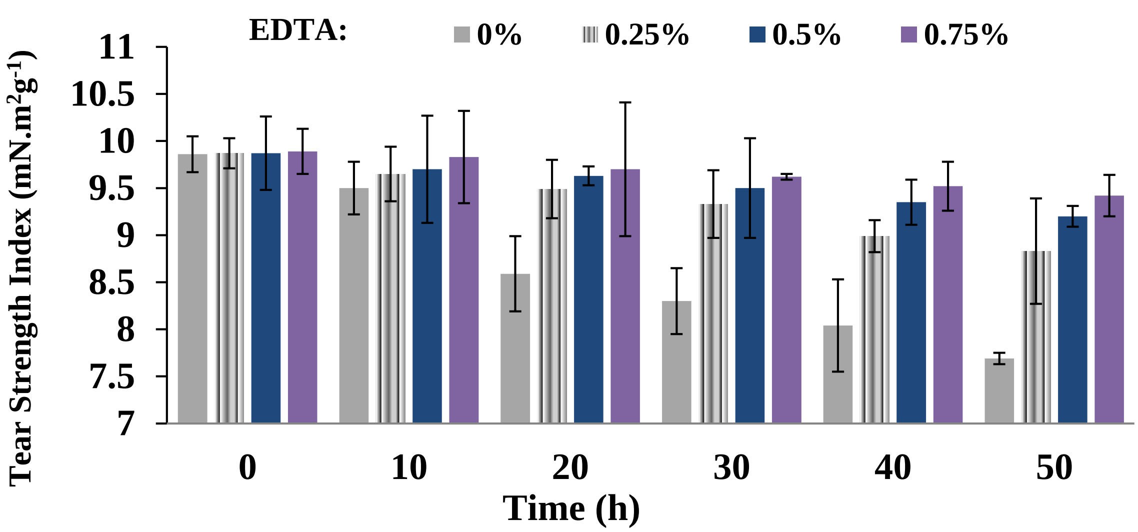

Fig. 2. Effect of aging time and EDTA concentration on tear strength

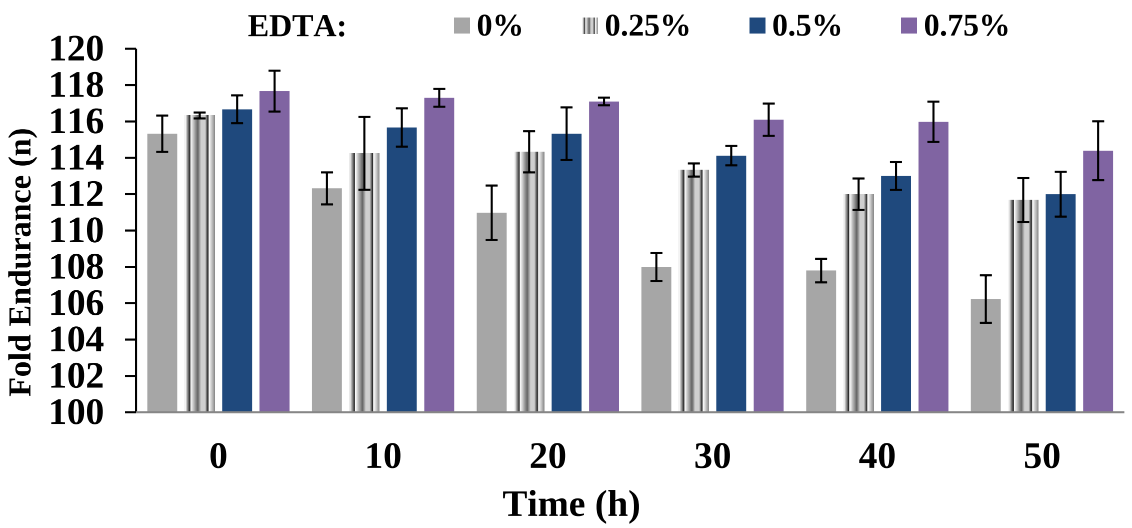

Fig. 3. Effect of aging time and EDTA concentration on fold endurance

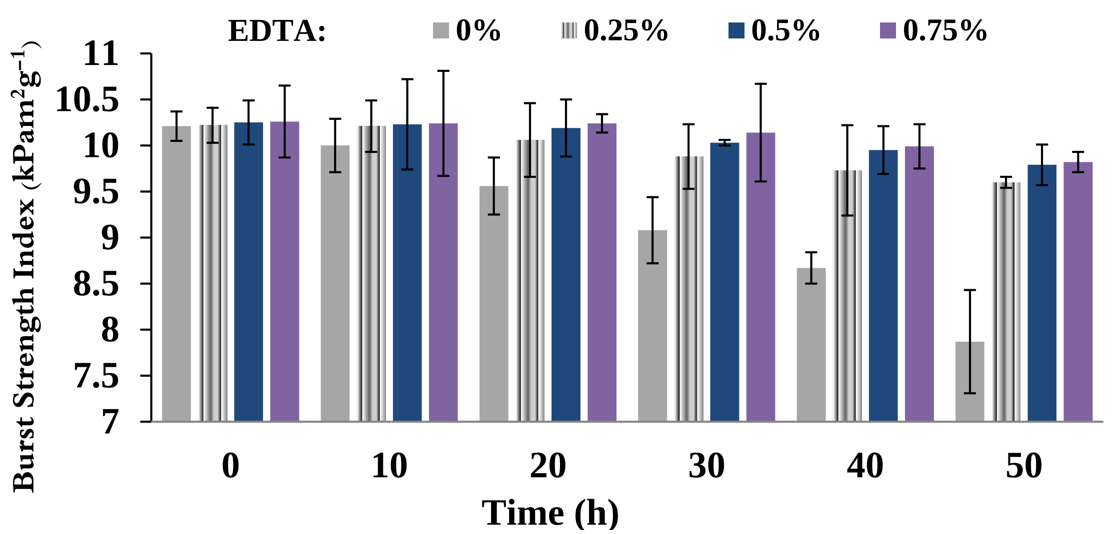

Fig. 4. Effect of aging time and EDTA concentration on burst strength

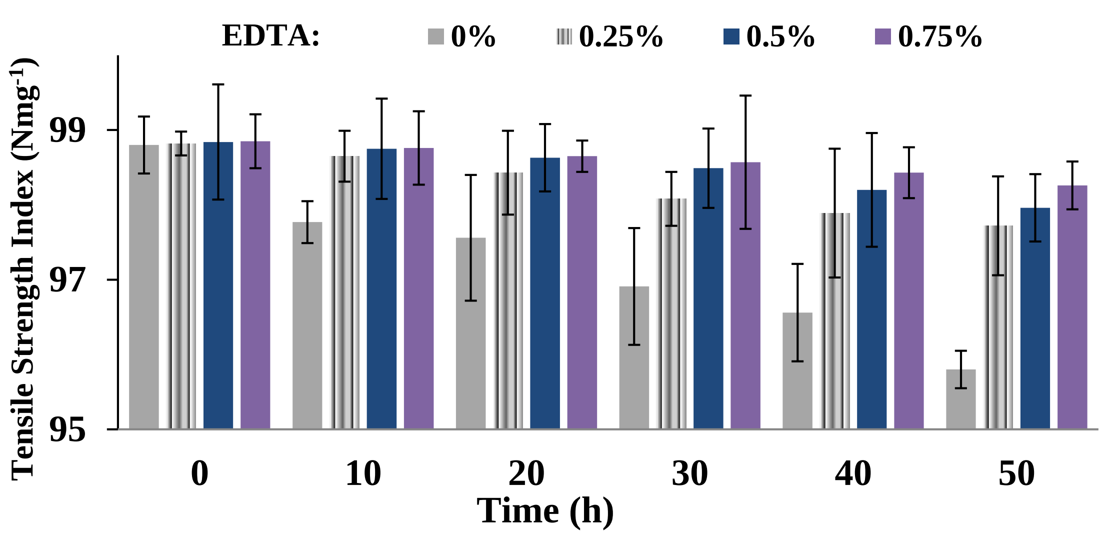

Fig. 5. Effect of aging time and EDTA concentration on tensile strength

Effect of Aging Time on the Strength Indexes of Handsheet Papers

The effect of time on the tearing length, number of folding, tearing strength, and bursting strength was significant at a 95% level (Table 2). Increased aging time significantly affected the properties of the papers and caused a reduction in tearing length, tearing strength, folding strength, bursting strength, and tensile strength.

Mutual Effect of EDTA and Aging Time on Strength Indexes of Handsheet Paper

The mutual effect of EDTA and aging time on the tearing length, number of folding, tearing strength, bursting strength, and tensile strength was not significant at a 95% level (Table 2). For all studied properties, it was possible to observe a negative effect of the increased aging time, by increasing concentration of EDTA.

Durable paper is paper that retains its initial qualities upon use and after prolonged periods of storage or archiving (Pourmomtaz and Tehrani 2001). The main reasons for paper failure are identified as acidic hydrolysis, oxidation, and photochemical processes. Increasing fiber length and decreasing the contents of metal ions such as Cu^{2+}, Fe^{2+}, Fe^{3+}, and Mn^{2+}, and aromatic compounds in the paper is expected to improve the durability of the produced paper (Khakifirooz *et al*. 2009).

The methods used to determine the effect of accelerated aging on paper include measurement of the paper's strength properties, such as folding strength, tensile strength, tearing strength, and bursting strength. Among these properties, the folding strength most adequately indicates the intensity of the aging with maximum accuracy and sensitivity.

Mechanical properties of paper samples in a study under dry-heat and moist-heat accelerated aging have been studied in diverse experimental conditions; folding endurance was identified as a highly sensitive means for monitoring changes in paper structure (Havlinova *et al*. 2009).

Because different papers exhibit different strengths or base weights, some researchers have declared that the tension introduced during the folding process must be consistent with the tensile strength. On the other hand, other scholars have suggested that the folding test should be done with a constant number of folds, with the required loading, to determine the required factor. Finally, interpretation of the results obtained from the accelerated aging require an awareness of the relationships between accelerated aging and natural aging.

CONCLUSIONS

1. Increasing the accelerated aging time negatively affects the strength properties, such that the breaking length, tensile strength, tearing strength, bursting strength, and folding endurance are all reduced.
2. Tear index, tensile strength, tearing strength, bursting strength, and folding endurance were decreased respectively by 41.9, 3.1, 28.2, 29.7, and 8.6 percent without EDTA treatment by increasing the aging time. The corresponding changes, in samples that had been treated at the 0.75 percent level of EDTA, were decreases of only 6.8, 0.6, 5, 4.5, and 2.9 percent.
3. Increasing the concentration of the EDTA chelating agent positively affects the strength properties of the handsheet paper.

4. Tear index, tensile strength, tearing strength, bursting strength, and folding endurance were increased respectively: 33.4, 2.6, 22.5, 24.8, and 7.7 percent by increasing EDTA content from 0.75 percent and with 50 h aging.
5. Two variables, namely accelerated aging time and EDTA, do not evoke a significant effect. Furthermore, the small effect the two variables do exhibit shows a decreasing trend.

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