Effect of Carboxymethyl Cellulose, Cationic Surfactant and Alum on Strength Properties of Liner Paper Made from Old Corrugated Container (OCC)

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Abstract: This study was carried out to determine influence of the Carboxymethyl cellulose (CMC) on recycled pulp properties produced from Old Corrugated Container (OCC). Therefore OCC pulp was refined by PFI refiner to freeness degree of 250 ml, CSF. The refined pulp was treated by Carboxymethyl cellulose (1% of dry weight pulp) under specified conditions (1h, 60°C and pH 10.5). In the first stage, 1% CMC along with Dodecyltrimethylammonium Bromides (C_{12}TAB) was used as the cationic surfactant in two levels 0.1% and 0.2% and in the second stage, 1% CMC with Alum at two levels of 2% and 3% were used. The mechanical properties of the handsheets showed that, pulp treated with CMC and 0.2% C_{12}TAB had an increased burst and tensile indices (44.12% & 22.38%), compared to control sample. On the other hand, effect of the treatments on the recycled pulp's effluent indicated that in CMC-Alum's effluent led to a decrease on COD and TSS values by 61.1% and 90.95% respectively, in comparison with control sample.

Keywords: Old Corrugated Container, Carboxymethyl Cellulose, Alum and Dodecylltrimethylammonium

1. Introduction

Paper recycling has been practiced for many years. In spite of the economic value, recycled fibers have long been known to have inferior strength properties compared to those of virgin fibers. The change in the basic fiber characteristics (strength, length, swelling, and bonding potential) has been assumed to be the source of reduction in strength properties (Ellis and Sedlachek, 1993). Thus, one of the most challenging aspects of recycling is to understand how to increase and control fiber bonding potential (Cutler, 1995). Liner board is produced with various top plies and from various raw materials. It is produced from virgin fiber usually called Kraft Liner, whereas recycled fiber containing linerboard is called Test Liner. The resulted medium is a single-ply product. Medium is formed into fluted structure between two plies of linerboard to form the corrugated board for boxes. The major problem with recycling of old corrugated container (OCC) is the loss of its strength properties (Mousa et al, 2004). The fiber charge is of great importance for the properties of paper as well as for the behavior of fibers in the process. Charged fibers may affect the swelling and flexibility of fibers or affect the fiber bonding or specific bond strength (Barzyk and Ragauskas 1997). It has been suggested that the importance of

charged groups for paper properties is due to increased specific bond strength, while the role of swelling and fiber flexibility is only of secondary importance (Laine et al 2003). Different approaches for increasing the amount of charged groups on the fibers have been used, such as Carboxymethylation (Nelson and Kalkipsakis, 1964), Sulfonation (Allan and Reif, 1971 & Allan and Reif, 1971) or Oxidation (Saito and Isogai, 2005). Carboxymethylation as a method for introduction of charges and increasing the swelling of fiber and subsequently, the strength of paper, has been demonstrated many times over a period of years (Nelson and Kalkipsakis, 1964, Fors, 2000 and Walecka, 1956).

The purpose of this study was to find a new approach to chemically modify the properties of OCC fibers as a means to improve OCC fibers quality. In short, the modification can be directed either to internal or external structure of the cell walls in the fibers. The internal surface area of the cell wall is so large so that a huge amount of chemicals would be needed to change the properties of the internal surface significantly. So it was decided to modify the external surface of the fibers instead of the internal surface. In addition, a Polymer such as Carboxymethyl Cellulose (CMC) was chosen for the chemical modification.

Sodium Carboxymethyl Cellulose –NaCMC- (more commonly as CMC) is an anionic Polyelectrolyte derived from cellulose and one of the most important Cellulose derivatives. CMC is used as a wet-end additive, for surface sizing, and as a component of coating colors in papermaking (Holmbom & Stenius, 2000). Anionic Polyelectrolytes do not generally attach on Cellulosic fibers because of the electrostatic repulsion between the negatively charged cellulosic surfaces and the anionic polyelectrolyte (Laurell, 1952, Wiebe & Klug, 1957)

Previous studies conducted in this laboratory showed that CMC grades with a low degree of substitution (DS) will redound to irreversible absorbed external surface layers (Laurell, 1952, Blomstedt et al, 2007, Blomstedt & Vuorinen, 2006). The amount of sorbed CMC on pulp depended on several factors, including the degree of Polymerization (DP), DS and charge of the CMC, pH and Ionic strength of the sorption medium, and the beating level of the pulp (Mitikka Eklund et al, 1999). The absorption of CMC on cellulose pulps improved the strength properties of handsheets (Blomstedt et al, 2007) because the CMC treatment greatly increased the inter fiber bonding in hand sheets.

In this study OCC pulp was treated first with Carboxymethyl Cellulose (CMC, degree of substitution 0.2 & 1% pulp) and then with Dodecylltrimethylammonium Bromides and Alum Antiseptic.

2. Material and Methods

Raw material for this experiment was 100% (OCC) pulp. The pulp was refined for 12000 revolutions with a PFI mill (T 248 sp-00 TAPPI) to freeness degree of 250 ml, CSF. The CMC with 750 Degree of polymerization (DP) and 0.2 substitutions was used in this experiment. The surfactant used in the experiments was Dodecylltrimethylammonium Bromides (CnH2n+1N (CH3)3Br, n= 12, C_{12}TAB).

CMC applied was partly insoluble in water. Stock CMC solutions (<10 g/l) was prepared in 2.5 M sodium hydroxide. The refined pulp was mixed with water and stock CMC solution to obtain a final pulp consistency of 5% (50 g/l) and an initial CMC concentration of 0.5 g/l (1% on pulp). The sorption (pH 10.5) was carried out in glass beakers. The temperature was raised to 60°C in 30 minutes. After 60 minutes, the pulp samples were cooled and washed with deionized water. Reference treatments were also carried out under similar conditions but without the addition of CMC.

The recycled pulp was CMC modified as described above. The surfactants (C_{12}TAB) with concentrations 0.1% and 0.2% & Alum 2% and 3% (both on dry weight pulp) were added to the diluted pulp suspension before sheet making (table 1). After Alum and surfactant addition, the pulp was allowed to stabilize for 1 hour. Liquid phase dissented for COD and TSS test. The laboratory sheets (120 g/m^2) were prepared by the standard method T205 sp-95.

Table1. Different treatments and related pH values

Treatments	CMC % on fiber	C_{12}TAB % on fiber	Alum % on fiber	pH
A	1	0	0	10.5
B	1	0.1	0	10.7
C	1	0.2	0	10.8
D	1	0	2	5.89
E	1	0	3	5.56
F	0	0.1	0	7.5
G	0	0.2	0	7.52
H	0	0	2	4.85
I	0	0	3	4.7
K	0	0	0	7.37

3. Results and discussion

Strength properties of CMC modified OCC pulps are shown in Table 2.

Table 2.Sheet properties of OCC pulp with and without CMC

Treatments	Tensile index (Nm/g)	Burst index ($KPam^2/g$)
K	60.31	4.5
H	63.46	5.46
I	61.25	4.97
F	63.46	5.24
A	65.6	5.69
G	64.2	5.46
B	71.27	6.17
C	73.81	6.49
D	72.33	6.24
E	69.33	5.69

The importance of the acidic groups in fibers lies in their capability of ionization without going to extreme values of pH (Scallan, 1983). These dissociable groups can have a large impact on final fibers properties, such as strength, wetting, adsorption and absorption capacity etc. Their effects on fiber swelling are well known. It is also known that an increase in the acid group content of cellulose fibers can result in increased strength properties of the paper sheets made from the fibers (Barzyk, 1997). The adsorption of different compounds onto cellulose fibers may increase with increased content of acidic groups. Increasing the amount of Carboxylic acids will increase the amount of –COOH groups and thus the adsorption of cationic substrate onto fiber surfaces. The CMC has two functionalities: first it modifies the surface by strong adsorption, and then it increases the charge density of fibers (Laine & Lindström, 2001 & Laine et al, 2000). The irreversible attachment of CMC onto cellulose surfaces is thought to be due to cooperative hydrogen bonding between the free cellulose segments on the CMC-backbone and the cellulose fiber surfaces on the fiber (Fors, 2000). Modification with CMC can be used to increase the charge density of fibers (Fras et al.2006). This results in a higher capacity of the fibers to adsorb Cationic surfactant and Alum as well as better mechanical properties.

3.1. Strength properties of CMC and C_{12}TAB modified OCC pulp

Swelling of external microfibril bundles as a result of CMC modification increases inter fiber bonding. Also carboxyl groups increase the bond and paper strength (Mitikka-Eklund et al 1999). Swelling of microfibrils on the fiber surface is believed to increase bonding after CMC modification. Although Anionic CMC is absorbed by anionic fibers when the DS is low enough for the adsorption to eliminate the electrostatic repulsion. Also an increase in burst and tensile index were observed after CMC modification (Figures 1 and 2).

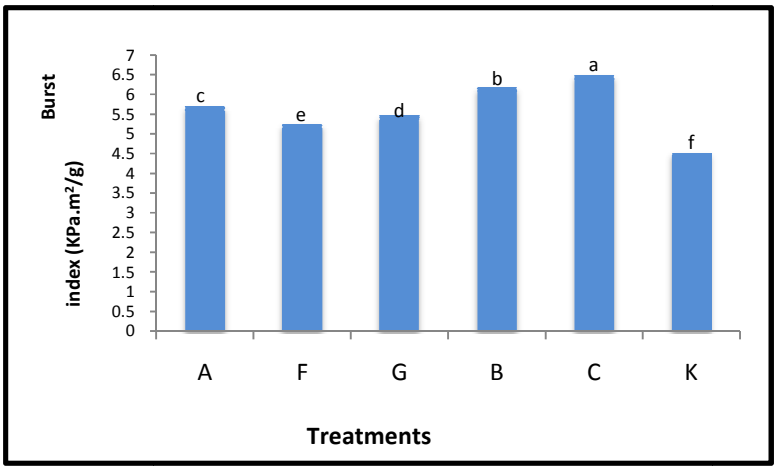

Fig. 1.The effects treatment CMC and surfactant on burst index.

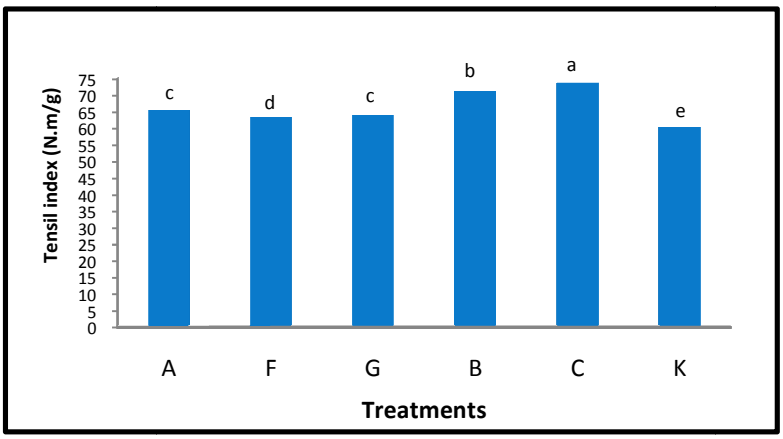

Fig. 2.The effects treatment CMC and surfactant on tensile index

Only a few attempts have been made to study the effect of surfactants on paper properties. Adding surfactants to mechanical and chemical pulps (Bruun, 1975& Christensen, 1969) and sulfite pulps (Touchette, 1960) would have decreased strength properties. The results of the present study show a remarkable increase in tensile and burst strength if the OCC pulp had been first treated with CMC and then with a surfactant. Carboxyl groups in the fibers are easily accessible to C_{12}TAB molecules. Topochemical modification with CMC can be used to increase the charge density of fibers. The increased charge, results in a higher capacity of adsorption of cationic surfactant in fibers as well as better mechanical properties (Fras, 2006). Pulp treated with CMC and 0.2% C_{12}TAB had increased burst and tensile indices (44.12% & 22.38%). At the initial stage of adsorption the electrostatic attraction between negatively charged fiber groups and the positive Ammonium ions is strong, and ionic bonds between the Ammonium group and Carboxyl on the fibers will be formed.

Strength properties of CMC and Alum modified OCC pulp was related by using Page Equation. This presented that the loss of strength with recycling is due to a loss of bonded area.

The Page Equation is given in Equation (1).

$1/T = 9/8Z + (12gC/PLBRBA)$

T tensile breaking length

Z zero span breaking length

C fiber coarseness

P fiber perimeter

L fiber length

b fiber-to-fiber specific bond strength

RBA relative bonded area

It is proved that Carboxymethyl substitution enhances the strength of both cotton and wood pulps (Walecka, 1956). The improved strength was due to increased plasticity of the fibers, increased bonding, increased bonded area, or increased aggregate bond strength (Talwar, 1958). The Barzik analysis indicates that the increase in strength for modified CMC fibers was due to an increase in RBA. Also the increase in RBA is due to increase strength sheets.

Additional use of Alum and pH reduction in E treatment, cause pretention of Carboxyl groups and also reduces absorbing Cationic Ion with fibers. The balance between aluminum components and absorption behavior depends on Alum concentration. Increasing concentration of Alum will reverse to cellulose fiber charge in lower pH, using 3% of Alum. The result is reduction of tensile and burst index rather to other treatments. Treated fiber with negative Carboxymethyl Cellulose increases fibers adsorption of Cationic material. Ions from Alum act as an electrical bridge and increase the bonding between fibers. Aluminum Ion can make ionic bonding between fibers. Using CMC and 2% Alum improves paper tensile and burst strength (Figures 3 and 4) . Alum reduces zeta potential of particles and makes colloid particles and coagulant. Adding suitable amounts of Alum with suitable concentration and pH to treated fiber with CMC increases strength paper.

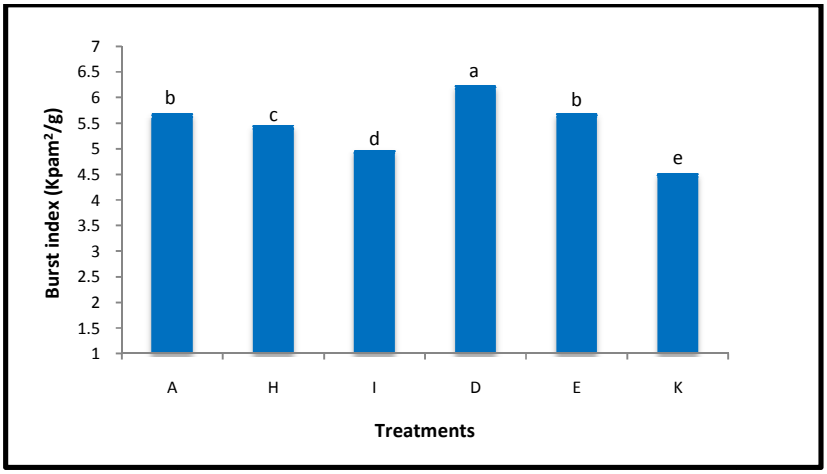

Fig. 3.The effects of CMC and Alum on burst index

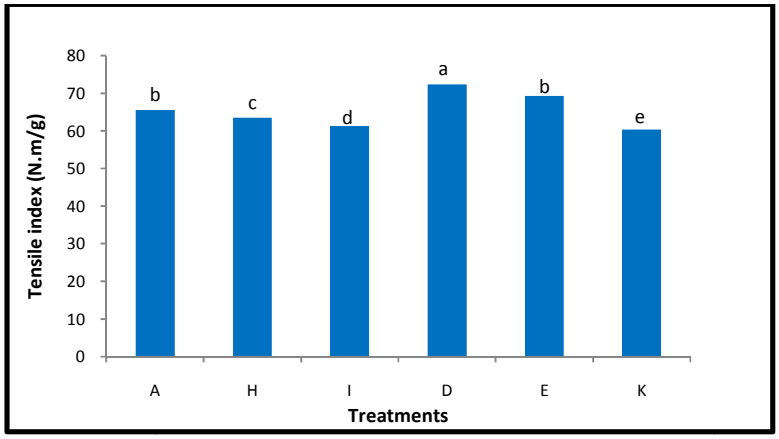

Fig. 4.The effects of CMC and Alum on tensile index

3.2. Effect treatments on effluent

Regarded that the very first purpose of recycling paper is to protect the environment, treatments for improving recycle paper strength should not be in contrast with environmental health. In this study we tried to investigate treatment effects on effluents. By measuring TSS, COD and pH of separated liquid from treated pulp, Alum and CMC treatment is determined as the best treatment (Table 3).

Table 3: Effect CMC - C_{12}TAB and CMC - Alum treatments on TSS and COD of effluent

Treatment	TSS	COD	Temperature (^{o} c)
C	1048	1716	30
D	54.3	433	30
K	600	1113	30

Aluminum salt is widely used as coagulant in water, wastewater treatment and some other applications. It's mode of action is generally explained in terms of two distinct mechanisms: Charge neutralization of negatively charged colloids by cationic hydrolysis products and incorporation of impurities in an amorphous hydroxide precipitate (so-called sweep flocculation), (Duan& Gregory, 2003). Effluent of CMC - Alum treatment decreased COD and TSS values by 61.1% & 90.95% respectively.

4. Conclusions

CMC with Cationic surfactants and Alum opens up new possibilities for modification of OCC fibers and their recycled paper product properties. The main advantages indicated by these preliminary experiments are acceptable tensile and burst strength of the handsheets. Cationic surfactants and Alum can be easily attached to the surface of CMC-modified anionic fibers. Surprisingly, these treatments can substantially improve the tensile and burst strength of the prepared hand sheets.

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