Original Research Article

Treatments of Recycled Pulps from Old Corrugated Containers. Part II. The Effects of Boron Compounds on Strength Properties

ABSTRACT

The selected boron compounds used in this study exhibit a more moderate reduction on burst strength, even though they may only limited improvements in other properties. However, at the fifth recycled stage, quite high burst strength values observed with at both selected boron treatment conditions that approximately 32.31% and 35.94% higher burst strengths at 5.0% level while 20.32% and 14.06% higher burst strengths at 10% boric acid and sodium borohydride level compare to control sample at similar recycling phase. The more less similar trend was also observed for tensile strength properties of test papers. The highest tensile strength (index) of 19.74 Nm/g and tensile stiffness value of 386 kN/m was observed at second recyling phase with boric acid. For tensile energy absorption (TEA) properties, only 10% sodium borohydride treated test papers showed higher TEA of 23.25 j/m^2 compare to counterpart control samples (C_2: 20.60 j/m^2).

The paper from secondary fibers has generally considered to be used in corrugated cardboard production. For this purpose, Sack Corrugated Test (SCT) and Corrugated Medium Tests were used to determine the strength resistance behaviors. The highest CMT value of 73.5kN/m was found with first recyling stage of control samples. For boron treated pulps, the highest CMT of 63.3 N was found at 10% boric acid treatment at second recyling phase followed by 5.0% boric acid treatment at second recyling phase, respectively. However, some level improvement of SCT properties was observed at certain level both boric acid and sodium borohydride treatment conditions. the highest improvements of SCT of test papers was found with 5.0% boric acid treatment at forth recyling phase that show approximately 39.74% improvement compare to control.

Keywords: Old Corrugated Container, recyling, boron compounds, tensile strength, burst strength, corrugated medium test,

INTRODUCTION

The multi-stage paper production stages affects on the the structure of cellulose by both chemically and physically [1]. To manufacture paper products from recovered cellulosic fibers (secondary fibers/pulps), the secondary pulp needs to have intrinsic strength and some certain properties. However, it was noted that some of the fillers have removed during recycling, which indicates that papermaking from secondary pulps require higher fillers [2]. Moreover, the cellulose fiber undergoes mechanical and drying cycles during papermaking and causing a very complex phenomenon and has not fully explained yet. These changes have usually called *hornification* that non-reversible hydrogen bonding reduction and hydrophilic nature of cellulose fibers [3-7]. In addition, the removing of hemicellulose and lignin from the cell wall during recyling also causes the collapse and negative impact on cellulose structure. In hornificated fibers, the amorphous region has typically reduced to some extent resulting increasing crystalline index with lowering re-wetting propeties of fibers [7-11].

Since environmental concern and protection of natural forestslands for papermaking industry, the recycling of post-consumer paper products has become an important issue in worldwide. Hence many technologies and alternative approaches have become established regarding waste paper recycling.

A typical paper sheet is a composite material that contains cellulosic fibers, air, fillers and some extraneous materials. However, fiber-fiber bonding is closely associated with fibers contact areas and important parameter for paper strengths [12]. Certain chemicals have been reported to be promote fibre bonding potentials and improve strength properties some level [3, 13-16]. It was proposed by Wistara and Young (1999) that the microstructure of cellulose must be modified to establishing further swelling capacity for better bonding potantial in paper sheet structure. Moreover, hemicelluloses have also important influences in regulating the physical properties of the pulps during recycling [15].

Although a number of chemical campounds have shown promising results on secondary pulps, and valuable restoring effects on cellulose fibers, there has not much information avalibale in literature regarding certain boron compounds treatements of secondary pulps and their effects on paper properties. A systematic approach have carried with boric acid and sodium borohydride on recycled OCC substrate to determine clear effects on recycling approach and chosen methods. In the first part of this study, *'Treatments of Recycled Pulps from Old Corrugated Containers. Part I. The Effects of Boron Compounds on Optical and Physical Properties'* has already send to *"submitted for publication"*. In the second part of this study, it is aimed to study for providing more fundamental understanding of the strength development of recycled fibres from old corrugated container (OCC) fibers.

MATERIALS AND METHODS

The additive and treatment free recycled pulps from old corrugated containers (OCC) were supplied from a commercially operated paper recycling plant, located in Istanbul, Turkey. The purity level of the boron compunds (boric acid and sodium borohydride) used is above 95%. The chemicals were supplied directly from the Etibank Borax plant, located in Bandırma, Turkey. The test sheets were prepared as 120 g/m^2 grammage (typical level for OCC manufactured papers) accordance with Tappi Standards (T-202 and T-205). The detailed information on boron compunds, experimental recycling procedures for treatment of OCC substrate and related similar informations have already given in first part of this study.

The standard paper strength tests were applied. These involves determination of tensile (T-494) and burst (T-403), strengths. Sack Crushing Strength Test or Short Compression Test (SCT) that is is indicates internal compression resistance of paper fibres and suitable for fluting in the middle layer of the cardboards, was applied on sheets accordance with ISO 9895 standard. The SCT properties of papers are expressed in Kilonewtons/Meter (kN/m).The Corrugating Medium Test (CMT) was also condcuted on hand sheets followed DIN EN ISO 7263 standard. The CMT determines the flat crush resistance of corrugating papers and made on laboratory corrugated samples for describing the usability for fluting. CMT is a way of estimating the crush resistance of corrugated board manufactured with those papers. The CMT is expressed in Newtons (N). Both SCT and CMT tests have used after forming currugated paper forms, and usually applied on corrugated papers alternatively to each other.

While many combinations was utulized during recyling procedure of cellulose fibers, some code number and abbrevatives were established throughout the study given in Figures and Tables. These are: C: Control, Ba: Boric acid; NaB: Sodium borohydride; 5 ve 10: chemical concentration %, weight/weight; 1, 2,3,4, and 5: recycling number.

RESULTS AND DISCUSSION

The burst strength values of the test papers produced from the control and treated with selected boron compounds during recycling are given comparatively in Table 1. It has realized that the burst strengths of control papers have increased in the first two recycling steps. Then, it has showed a downward trend in further recycling operations. The similar results have also been observed with sodium borohydride and boric acid treated pulps.

However, in general, the burst strength values of sodium borohydride and boric acid treated pulps show about 3.22% to 20.43% lower than the control samples up to fourth recyling steps. Interestingly, at the fifth recycled phase, quite high burst strength values observed with at both treatment conditions that approximately 32.31% and 35.94% higher at 5.0% concentration while 20.32% and 14.06% higher burst strengths at 10% concentration compare to control sample at similar recycling phase. It is important to note that selected boron compounds used in this study exhibit a more moderate reduction on burst strength, even though they may only limited improvements in other recyling phases.

Table 1. Burst strength properties of papers made from recycled OCC pulps

Sample	Burst strength (kPa)	Burst index (kPa m²/g)	% Change (from former treatment)	% Change (from control)
C_1	119	0.95	0.0	0.0
C_2	118	1.07	8.42	0.0
C_3	98	0.88	-17.75	0.0
C_4	102	0.93	5.68	0.0
C_5	70	0.64	-31.18	0.0
$5NaB_1$	95	0.86	0.0	-9.47
$5NaB_2$	115	0.92	6.97	-14.10
$5NaB_3$	92	0.84	-8.69	-4.54
$5NaB_4$	99	0.90	0.71	-3.22
$5NaB_5$	87	0.85	-5.56	**32.31**
$10NaB_1$	101	0.81	0.0	-14.73
$10NaB_2$	98	0.89	9.87	-16.82
$10NaB_3$	84	0.78	-12.36	-11.36
$10NaB_4$	85	0.83	6.41	-10.80
$10NaB_5$	68	0.77	-16.87	20.32
$5Bx_1$	104	0.83	0,.0	-12.63
$5Bx_2$	119	1.08	30.12	0.93
$5Bx_3$	93	0.82	-24.07	-6.81
$5Bx_4$	93	0.86	4.87	-7.53
$5Bx_5$	104	0.87	1.16	35.94
$10Bx_1$	114	0.91	0.0	-4.21
$10Bx_2$	110	1.0	9.89	-5.61
$10Bx_3$	88	0.80	-20.0	-9.09
$10Bx_4$	81	0.74	-7.50	-20.43
$10Bx_5$	66	0.73	-1.35	14.06

Figures 1 and 2 shows the effects of boron compounds concentration with recycling phases on burst strength properties of hand sheets. It has been observed that the increasing sodium borohydride concentration at higher recycling phase have no any positive effects while at lower recycling number (up to two) and sodium borohydride concentration shown to impriving burst strengths of sheets **(Figure 3).** Like sodium borohydride treatments, lower recycling phase (up to two) but in both level boric acid concentration have increasing effects on burst strengths of sheets **(Figure 4).** In this sense, increasing recyling phase beyon seconda recyling phase have not effective for improving burst strengths of papers made from selectec boron treated recycled OCC pulps.

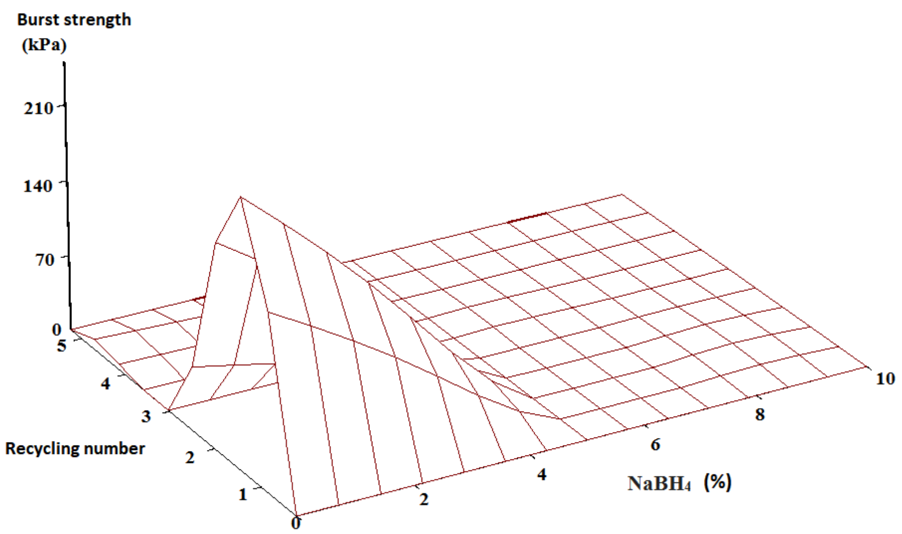

Figure 1. The effects of sodium borohydride concentration and recycling phase on burst strengths of papers

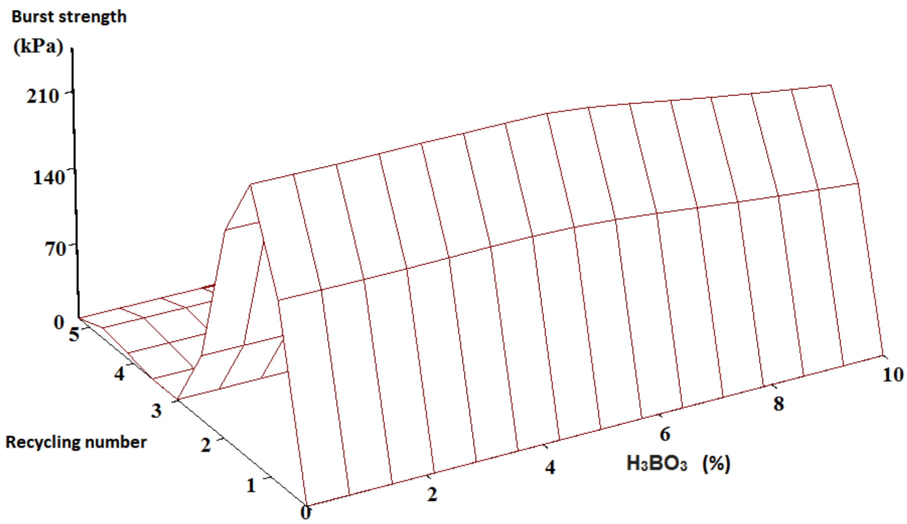

Figure 2. The effects of boric acid concentration and recycling phase on burst strengths of papers

In Table 2 the tensile strengths properties of the test papers are given comparatively. In general, the tensile properties (index) of control samples have not change much and even decreased only by 1.20% to 5.79%, continiously recycling procedure. It is important to note that there is not any improvements was observed with sodium borohydride treated pulps regardsless of concentration and recyling phase except 10% treatment conditions at second recyling stage ($10NaB_2$) that shows only 3.23% improvement compare to control samples.

For boric acid treatments, except in 5.0% conditions at first recycling stage ($5Bx_1$), 2.69 to 8.34% improvements of tensile strengths were observed compare to counterpart control samples. The highest tensile strength of 19.74 Nm/g was observed at second recyling phase ($5Bx_2$).

Stretch is usually reported percentage of elongation. As seen in Table 2, there is not much diffference regarding stretchs of papers. The changes were only ocur in marginal limits. However, tensile stiffness is the ratio of tensile force per unit width to tensile strain within the elastic region of the tensile-strain relationship. The highest tensile stiffness value of 386 kN/m was observed with 5.0% boric acid treatment at fifth recyling phase that is the only higher value for boron treated pulps regardless of recycling phase, than counterpart control samples. Tensile energy absorption (TEA) is the work done when a specimen is stressed to rupture in tension under prescribed conditions. It is expressed as energy per unit area (test span × width) of test specimen. For sodium borohydride treatments of secondary pulps, only 10% treated pulps at second recycling phase ($10NaB_2$) show higher TEA of 23.25 j/m^2 compare to counterpart control samples (C_2: 20.60 j/m^2). It is important to note that boric acid looks like effective only at 5.0% concentration phase (except first recyling stage).

From the results observed in Table 2, it can be summarized that treatment of OCC secondary fibers with both boron compounds at 5.0% treatment levels have some restoring/improving effects on the tensile strength values at certain treatment phases.

Table 2. Tensile strength properties of papers made from recycled OCC pulps

Sample	Tensile strength (kN/m)	Stretch (%)	TEA (j/m^2)	Tensile stiffness (kN/m)	Tensile index (Nm/g)
C_1	2.40	1.69	31.20	356	19.34
C_2	2.15	1.34	20.60	341	18.22
C_3	2.09	1.28	19.15	313	18.0
C_4	2.08	1.27	16.10	255	18.26
C_5	2.24	1.21	18.15	328	18.98
$5NaB_1$	2.02	1.88	26.75	269	16.10
$5NaB_2$	1.85	1.52	20.40	273	16.67
$5NaB_3$	1.93	1.25	17.05	272	17.79
$5NaB_4$	1.87	1.27	16.10	254	17.32
$5NaB_5$	2.02	1.29	17.85	291	18.53
$10NaB_1$	1.77	1.96	25.0	212	14.71
$10NaB_2$	2.05	1.59	23.25	274	18.81
$10NaB_3$	1.72	1.20	14.10	259	17.73
$10NaB_4$	1.80	1.80	16.20	257	17.39
$10NaB_5$	1.54	0.95	10.33	266	17.50
$5Bx_1$	1.93	1.72	23.25	254	16.69
$5Bx_2$	2.23	1.45	22.90	302	19.74
$5Bx_3$	2.13	1.32	19.50	290	18.85

$5Bx_4$	2.16	1.29	19.80	296	18.94
$5Bx_5$	2.30	1.14	19.15	386	19.49
$10Bx_1$	1.96	1.71	24.0	253	15.68
$10Bx_2$	1.93	1.09	14.83	289	17.31
$10Bx_3$	1.97	1.42	19.25	267	18.41
$10Bx_4$	1.74	1.20	14.20	253	16.57
$10Bx_5$	1.42	1.10	10.71	228	13.40

Figures 3 and 4 shows the combine effects of sodium borohydride and boric acid concentration with recycling phases on tensile strength properties of test papers. It has been observed that the increasing sodium borohydride concentration at low recycling phase marginally improving effects **(Figure 3).** In contrast to sodium borohydride, low level boric acid concentration and higher recycling phase positive effects on tensile strengths of sheets **(Figure 4).** In this sense, increasing boric acid contentration to 10% at up to third recycling phase not effective for improving tensile strengths of papers.

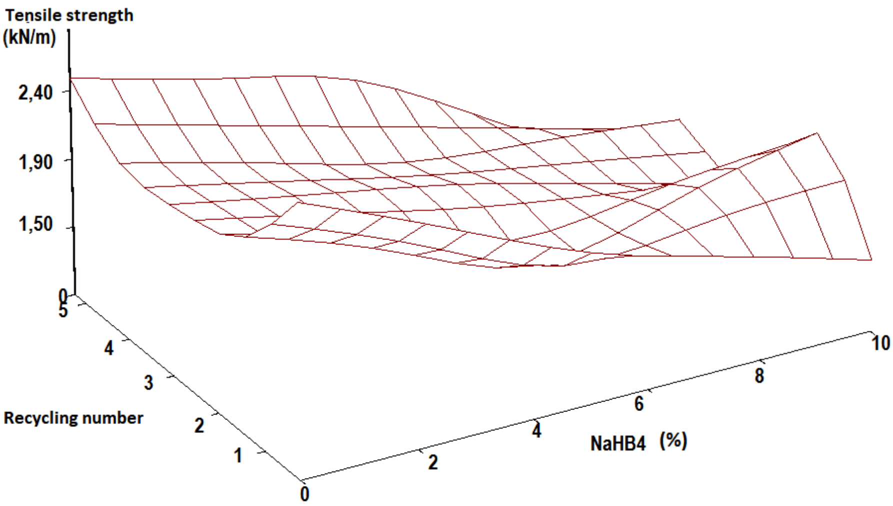

Figure 3. The effects of sodium borohydride concentration and recycling phase on tensile strengths of papers

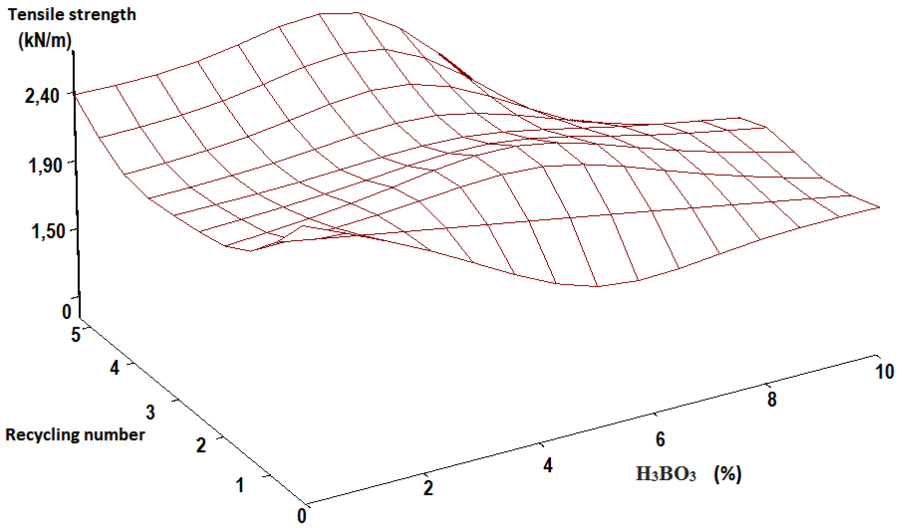

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Figure 4. The effects of boric acid concentration and recycling phase on tensile strengths of papers

The Corrugate Medium Test (CMT) values of the test papers are given in Table 3. It can be seen that there is not certain restoring trend realized for the CMT values of test papers. It looks like selected boron compunds have not positively effects ob CMT of papers. The highest CMT value of 73.5 N was found with first recycling stage of control samples. However, for boron treated pulps, the highest CMT of 63.3 N was found at 10% boric acid treatment at second recycling phase ($10Bx_2$) followed by 5.0% boric acid treatment at second recycling phase ($5Bx_2$), respectively.

Table 3. Corrugated Medium (CMT) strength properties of papers made from recycled OCC pulps

Sample	CMT (N)	Change (%, from former stage)	Change (%, from control)
C_1	73.5	0.0	0.0
C_2	60.7	-17.41	0.0
C_3	50.0	-17.62	0.0
C_4	46.0	-8.0	0.0
C_5	45.7	-0.06	0.0
$5NaB_1$	69.3	0.0	-5.71
$5NaB_2$	54.3	-21.64	-10.54
$5NaB_3$	46.7	-13.99	-6.60
$5NaB_4$	43.7	-6.2	-5.00
$5NaB_5$	39.0	-10.76	-14.66
$10NaB_1$	61.7	0.0	-16.05
$10NaB_2$	59.0	-4.38	-2.80
$10NaB_3$	40.1	-3.03	-19.98
$10NaB_4$	37.0	-7.73	-19.56
$10NaB_5$	29.7	-1.72	-35.01

5Bx$_1$	63.3	0.0	-13.54
5Bx$_2$	**62.3**	-1.58	2.63
5Bx$_3$	43.3	-30.49	-13.40
5Bx$_4$	41.7	-12.70	-7.17
5Bx$_5$	36.0	-21.21	-21.22
10Bx$_1$	60.7	0.0	-17.41
10Bx$_2$	63.3	5.43	4.28
10Bx$_3$	43.3	-31.59	-13.40
10Bx$_4$	39.0	-9.90	-15.21
10Bx$_5$	29.7	-23.84	-35.01

Figures 5 and 6 shows the effects of boron compounds of sodium borohydride and boric acid with recycling phases on CMT properties of test papers. It has been observed that the increasing sodium borohydride concentration have not any effcets on CMT values while increasing reycling number negatively effects on test papers. Interestingly, more less similar trend was also observed with boric acid treatment conditions as seen in Figure 6.

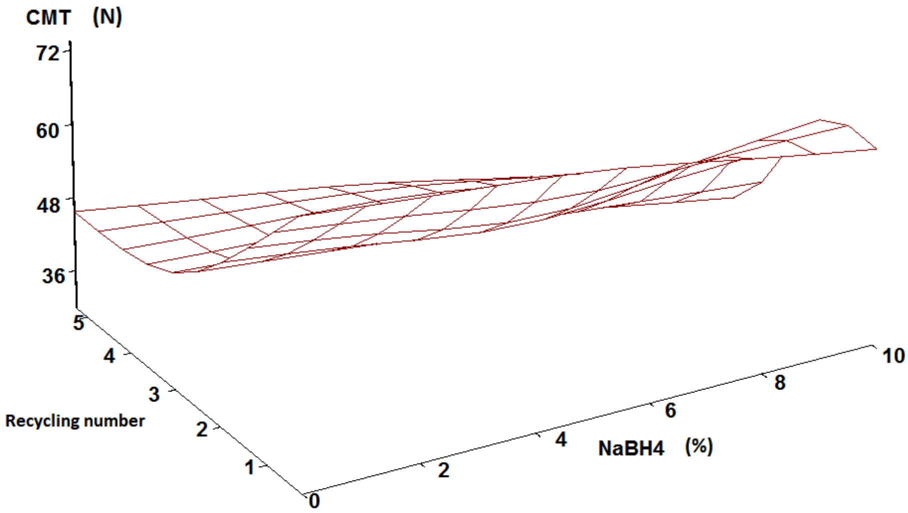

Figure 5. The effects of sodium borohydride concentration and recycling phase on CMT properties of papers

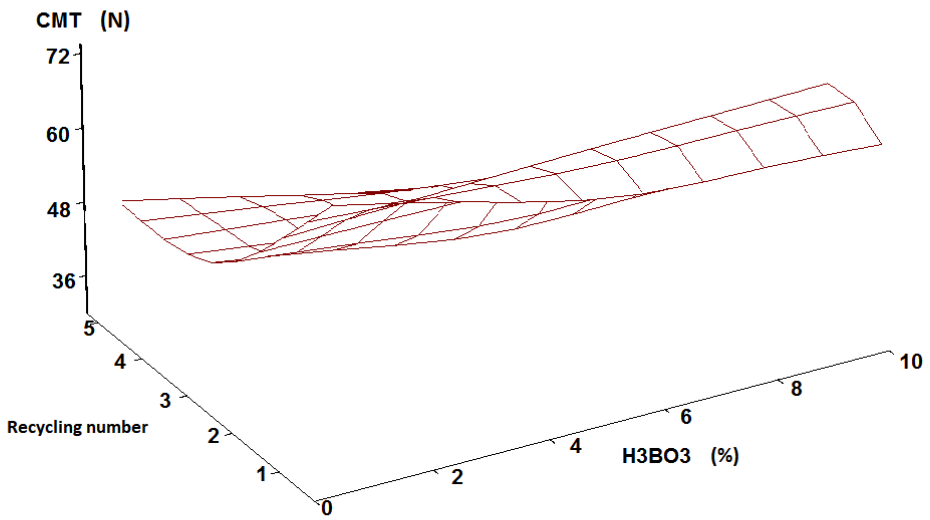

Figure 6. The effects of boric acid concentration and recycling phase on CMT properties of papers

The paper from secondary fibers has generally considered to be used in corrugated cardboard production. For this purpose, Sack Corrugated Test (SCT) is used to determine the surface crush strength resistance behaviors. In this test, the content of paper is more sensitive than fiber content as compared to conventional testing methods. In Table 4, the SCT values of the test papers produced from the treated secondary fibers with the control and boron compounds are given comparatively. As seen in Table 4, the SCT properties of the (control) papers showed a steady decline as the recycling stage increased. It is very complicated to interpret the data presented in Table 4. However, some level improvement of SCT properties was observed at certain level with both boric acid and sodium borohydride treatment conditions. However, the highest SCT value of 1.18 kN/m was found for control sample (C_1). The highest improvements of SCT of test papers was found with 5.0% boric acid treatment at forth recyling phase ($5Bx_4$) that show approx. 39.74% improvement compare to control samples (C_4: 0.78 kN/m vs $5Bx_4$: 1.09 kN/m), followed 16.44% improvement by fifth recycling phase at same boric acid contrentration.

Table 4. SCT strength properties of papers made from recycled OCC pulps

Treatment	SCT (kN/m)	% Change (from former treatment)	% Change (from control)
C_1	1.18	0.0	0.0
C_2	1.16	-1.72	0.0
C_3	1.09	-7.62	0.0
C_4	0.78	-28.44	0.0
C_5	0.73	-0.64	0.0
$5NaB_1$	0.96	0,0	-17.24
$5NaB_2$	0.88	-9.38	-26.27
$5NaB_3$	0.87	-1.14	-19.27
$5NaB_4$	0.78	-11.36	0.0
$5NaB_5$	0.92	17.94	8.00

10NaB$_1$	0.90	0.0	-22.41
10NaB$_2$	1.09	21.11	-7.63
10NaB$_3$	0.92	-15.59	-15.59
10NaB$_4$	0.84	-8.69	7.69
10NaB$_5$	0.67	-20.24	-8.21
5Bx$_1$	0.99	0.0	-14.65
5Bx$_2$	1.15	16.16	-2.54
5Bx$_3$	1.0	-13.04	-8.26
5Bx$_4$	1.09	8.26	39.74
5Bx$_5$	0.85	-22.02	16.44
10Bx$_1$	0.98	0.0	-15.51
10Bx$_2$	1.13	15.31	-4.23
10Bx$_3$	0.92	-18.58	-15.59
10Bx$_4$	0.82	-10.87	-5.13
10Bx$_5$	0.66	-19.51	-9.59

The results observed in Table 4 has used to interpret selected boron compounds and recycling phase effects on SCT properties of test papers. Hence, the effects of sodium borohydride and boric acid with recycling stages effects on SCT properties presented in Figure 7 and 8, respectively.

It can be seen that middle level of recycling (up to third) with 10% sodium borohydride has somehow improving effects on SCT properties (Figure 7). However, treatment of secondary OCC fibers with boric acid was found to have the only positive effect on the SCT properties at low concentration (5.0%) and at middle level recycling stages (up to third) (Figure 8).

In general, it has been observed that the increase in recycle number and selected boron content concentrations have usually negative impact on the SCT properties of the test papers, but the SCT value changes was found to be within marginal levels for certain treatment conditions (see in Table 4)

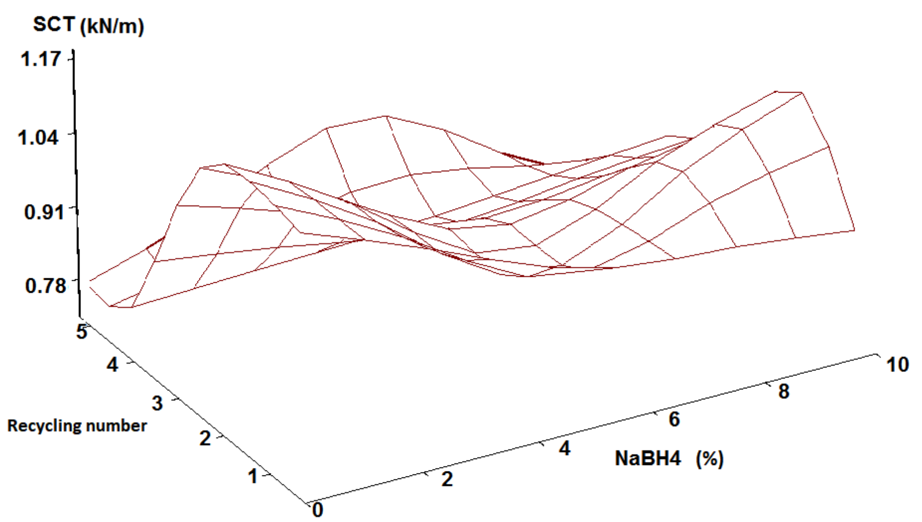

Figure 7. The effects of sodium borohydride concentration and recyling phase on SCT properties of papers

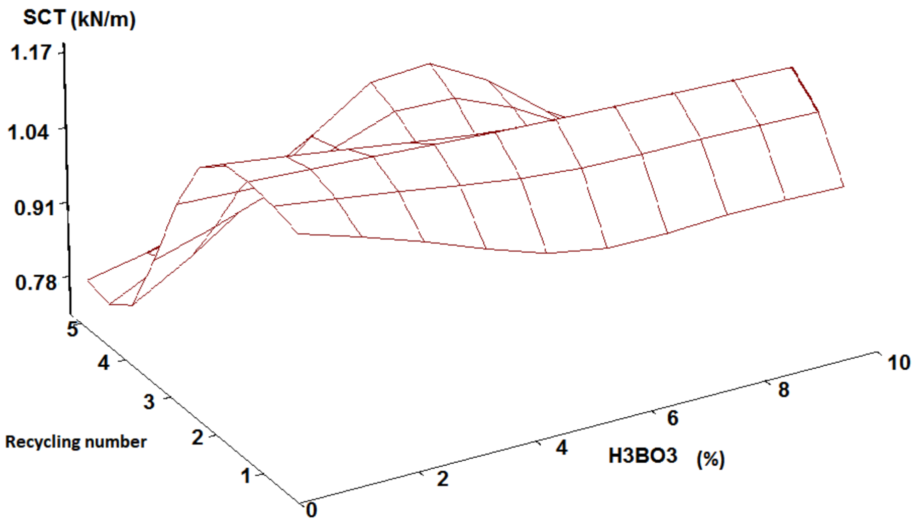

Figure 8. The effects of boric acid concentration and recyling phase on SCT properties of papers

Wistara et al. (1999) reported that the recycling affects lowering surface energy of cellulosic fibers. This hypothesis has been suggested that the disruption of hemicelluloses may occur during recyling of cellulose. They have proposed that some compounds could be capable oxidizing fiber surfaces resulting increasing carboxylic and OH groups on the surface of the fibers during recycling.These clearly effects substitution of -OH groups and resulting further swelling and, improve physical properties of sheets [15]. In our study, there has not much improvements of paper strengths was observed while some properties have been found to be restore at certain boron compounds treatement conditions.

CONCLUSIONS

The corrugated container manufaturing is an important sub parts of papermaking industry. This is because of wide utulization of these products in packaging and transportation needs of other cunsumer products. Thereby, the recycling of these products has important issue and cost reducing effects on similar products that they usually re-manufactured from those recyled fibers. The selected boron treatments of the recovered secondary OCC pulps are aimed to improve some strength propertie of sheets made. Although the use of boric acid and sodium borohydride during recycling of OCC pulps as treatment agent show some variables and limited restoring/improving results on some selected strength properties, the results have found in this study might be a basement for further studies.

LITERATURE

1. **Atalla, R.H. 1992.** Structural change in cellulose during papermaking and recycling. *In* : Rowell, *et.al*. Eds. Material Interaction Relevant to recycling of Wood-Based Material: Proceeding of Materials Research Society Symposium; 1992 April 27-29, San Francisco, CA.
2. **Waterhouse, J. F. 1994.** Improved utilization of recycled fines. A Progress Report No 92, The Institute of Paper Science and Technology, Georgia.
3. **Clark, J. d'A. 1978.** Pulp Technology and Treatment of Paper. Miller Freeman Publications, Inc. San Francisco, USA.
4. **Carlson, G. and Lindstrom, T. 1984.** Hornification of Cellulosic Fibers During Wet Pressing. Svenk Papperstidning, No. 15: R119-R125.
5. **Howard, R.C ve Bichard, W. 1992.** The basic effects of recycling on pulp properties, Journal of Pulp and Paper Sci.: 18(4): J151.
6. **Diniz, F.J.M.B., Gil, M.H., Castro, J.A.A.M. 2004. Hornification**- its origin and interpretation in wood pulps. Wood Sci. Technol., 37, 489-494.
7. **Hubble, M. A., Venditti, R. A., Rojas, O. J. 2007.** What happens to cellulosic fibers during papermaking and recycling? A review. Bio Resources 2(4): 739-788.
8. **Bouchard, J., Douek, M. 1994.** The effects of recycling on the chemical properties of pulps. Journal of Pulp and Paper Science, 20 (5): J131-J136.
9. **Brancato, A., Walsh, F. L., Sabo, R., Banerjee, S., 2007.** Effect of recycling on the properties of paper surfaces. Ind. Eng. Chem. Res., 46, 9103-9106.
10. **Cao, B., 1998.** Effect of pulp chemical composition on the recyclability. Ph.D Theses, University of Minnesota, p183, USA.
11. **Somwang, K., Enomae, T., Isogai, A., Onabe, F. 2002.** Changes in cristallinity and re-swelling capability of pulp fibers by recycling treatment. Japan Tappi Journal, 56 (6): 863-869.
12. **Torgnysdotter, A., Kulachenko, A., Gradin, P., 2007.** The link between the fiber contact zone and the physical properties of paper: A way to control paper properties. Journal of Composite Material, 41 (13).
13. **Bhat, G.R., Heitmann, J.A. and Joyce, T.W. 1991**. Novel techniques for enhanching the strength properties of secondary fiber. Tappi J.74(9), 151-157.
14. **Gurnagul, N. 1995.** Sodium hyroxide addition during recycling; Effects on fiber swelling and sheet strength. Tappi J.: 78(12); 119.
15. **Wistara, N., Young, R.A. 1999.** Properties and treatments of pulps from recycled paper. Part I. Physical and chemical properties of pulps. Cellulose (6), 291- 324.
16. **Wistara, N., Zhang, X., Young, R. A. 1999.** Properties and treatments of pulps fro recycled paper. Part II. Surface properties and cristallinity of fibers and fines. Cellulose 6, 325 – 348.