



The Effects of Wetting-Drying on Bleached Kraft Paper Properties

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Abstract

The aim of the study is to investigate effects of wetting-drying processes on bleached kraft paper properties. According to results; it has been realized that continuously wetting-drying of paper samples supplied from three different brand (A, B, and C types) effect on both physical and strength properties. However, initial stages (up to 5th cycling stages) have dramatic effects resulting in a high degree of modification, considering the fact that each following stage is moderate trend on physical properties.

Contrary to breaking length and burst index that have a reducing trend as wetting-drying in progress, the tear index changed in both directions (increases or decreases). However, breaking length of samples were found to be reduced range of 11.4% to 67.8%. Nevertheless, the lowest breaking length was observed B type of papers with 1.79 km at 8th cycling stage. The lowest tear index of 2.64 mN.m²/gr was found at 5th cycling stage for C type papers while the highest tear index of 5.62 mN.m²/gr was found at 6th cycling stage for B type papers. It is clearly realized that the paper network structure are damaged and bonding potentials reduced during the wetting-drying process.

Keywords: Paper, wetting, drying, physical, strength.

Islatma-Kurutmanın Kraft Kağıt Özellikleri Üzerine Etkileri

Öz

Bu çalışmanın amacı ıslatma-kurutma işlemlerinin ağartılmış kraft kağıtlarının özellikleri üzerine etkilerini araştırmaktır. Elde edilen sonuçlara göre; üç farklı firmadan (A, B ve C tipi) temin edilen kağıt numunelerinin sürekli ıslatılmasının ve kurutulmasının hem fiziksel hem de mukavemet özellikleri üzerinde etkili olduğu anlaşılmıştır. Bununla birlikte, başlangıç aşamaları (5. ıslatma-kurutma aşamasına kadar) yüksek derecede modifikasyon ile sonuçlanan dramatik etkilere sahipken sonraki her aşamanın fiziksel özellikler üzerinde ılımlı bir eğilim olduğu gözlemlenmiştir.

Islatma-kurutma işlemi devam ederken azalan kopma uzunluğu ve patlama indeksinin aksine, yırtılma indeksi her iki yönde de değişmiştir (artar veya azalır). Bununla birlikte, numunelerin ıslatma-kurutma işlemleriyle kopma uzunluğunun %11.4 ile %67.8 aralığında azaldığı bulunmuştur. En düşük kopma uzunluğu 8. döngü aşamasında 1.79 km olan B tipi kağıtlarda gözlenmiştir. En düşük yırtılma indeksinin C tipi kağıtların 5. ıslatma-kurutma aşamasından sonra 2.64 mN.m²/gr değerinde olduğu, en yüksek yırtılma indeksinin ise B tipi kağıtların 6. ıslatma-kurutma aşamasında 5.62 mN.m²/gr değerinde olduğu tespit edilmiştir. Islatma-kurutma işlemi sırasında kağıt yapısının hasar gördüğü ve bağlanma potansiyellerinin azaldığı açıkça anlaşılmaktadır.

Anahtar Kelimeler: Kağıt, ıslatma, kurutma, fiziksel, mukavemet.

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1. Introduction

Thanks to technological development, the pulp and paper manufacturing has become easier with very efficient mass production. However, besides cellulosic fibers, a number of non-fibrous additives (i.e. fillers) are utilized to improve paper properties of opacity, smoothness, and print quality, so on. Although these additives effects on certain properties which should also be stabilized the paper products with chemically non-reactive state (Roberts, 1996; Scott and Abbott, 1995; Smook, 2002; Pesman and Laloglu, 2018).

However, wetting and drying of cellulose based products (i.e. paper), cause inevitable changes on physical and chemical properties that even if no chemical treatment is applied. Those changes in fiber structure are very complex and have a significant impact on the end use properties (Howard, 1990; Sahin, 2013). One of the basic changes could be noticed on the individual fiber properties (dimensional changes) that are impact on sheet structure (Clark, 1985). Atalla (1992) proposed that during wetting and drying, molecular organization of cellulose changes at the second and third levels with the formation of molecular mobility due to the removal of water. As a result of this re-organization, it effects on elasticity without deterioration. Moreover, elasticity and hydrophilic property of fiber surfaces is two of the most important factors in high fiber-fiber bonding (Clark, 1985; Sahin 2009 and 2013; Sahin and Arslan 2008).

It has already well established that pulp produced by mechanical method shows less shrinkage feature during drying compare to chemical pulps. One of the main reasons for this is the presence of lignin in mechanical pulps. Because lignin is interface on microfibrils that decreases the hydrogen bonding and cross-linking potentials (Sahin, 2009; Yeo et al., 2017). In another study, it was found that the low shrinkage rate of thermomechanical (TMP) secondary fibers that was caused by lignin, which is preventing bonding of cellulose microfibrils (Nanko et al., 1991; Singh and Roy 1996).

As it is known, water between microfibrils is called free water and bonding cellulose to form a film-like layer called bound water. However, the bound water is absorbed by the hydroxyl groups on microfibril surfaces to prevent overlapping each other (Goring, 1978, Sahin 2013). Moreover, with the removal of free water, not much modification occurs while highly elastic cellulose microfibrils prevent the collapse of the fibers in the lumens. On contrary, during the removal of the bound water, the distance between the microfibrils decreases even overcome the elastic limits. In this case, shrinkage/swelling occurs that impact on fibers elasticity, bonding potential and some other structural elements (Atalla, 1992; Goring, 1978; Sahin 2013).

In a general accepted opinion on cellulose chemistry, cellulose undergoes irreversibly changes (i.e. elasticity, bonding potential and hydrophilicity) during wetting-drying procedure while the surface and lumen of the fibers decreases, resulting in permanent collapses (Clark, 1985; Nazhad, 2005; Sutjipto et al., 2008; Wistara and Young 1999). These irreversible changes in the structure of cellulose are known as hornification (Çiçekler, 2019; Howard, 1990; McKee, 1971; McKenzie, 1984; Sahin, 2009; Wistara and Young, 1999). However, hornification mechanism may be summarized as the cellulose become a more tight and hard structure (densely hydrogen bonding) with less compatible to each other, and lower fiber-fiber bond potential.

It was proposed that non-dried fibers show higher initial swelling properties while re-swelling properties decreases (Çiçekler, 2019; Li et al., 1994; Wistara and Young, 1999). Nanko et al. (1991) investigated that depending on the subsequent drying event, the fibers first lose free water, and following contraction occurs during loss of bound water.

There have been numerous research studies conducted on the recycling effects on paper properties (Nanko et al., 1991; Sahin and Arslan, 2008; Wistara and Young, 1999). However, the hydrophilic natures of the cellulosic fibers within paper structure are very important for good fiber-fiber bonding. But the challenging aspects for wetting of papers understand how to control fibers wetting and bonding. Hence, there is a need to understand more clearly the changes that take place in the rewetted cellulose fibers in sheet structure. Moreover, kraft method is far most common paper manufacturing approach in worldwide. Therefore, the objective of this study is to investigate the influence of water over repeating drying and wetting of kraft paper, in terms of evaluating chemical and physical properties. In this regard, a basic approach was used to understand the properties of three similar full bleached paper types from different companies with certain wetting-drying cycling.

2. Material and Method

2.1. Material

Commercially available, fully bleached standard Kraft papers (80 g/m²) from three different brands were supplied from retail stores. Due to fully bleached chemical grade of paper samples, the sheets are above 85 ISO brightness values. These papers regarding produced at similar process from different companies are noted as; A, B, C types. From each type, 90 sheets were taken and 100 cm² circular test samples were prepared.

2.2. Wetting-Drying Progress

These test samples were subjected to continuously wetting and drying processes up to eighth stage. The sheets were soaked in the water at the atmospheric conditions for 8 hours. The wetting of samples in water was carried out in pure water for 8 hours then the drying was carried out in a temperature-controlled a heating oven at 103 °C (±2) for 2 hours.

After each wetting and drying phase, 10 samples were separated, numbered, and the remaining papers continued for wetting-drying progress. The control samples refer to cycle 0 that were not subjected to any wetting-drying process were used to compare with property changes. Cycling 1 refers to the first-time wetted and dried sheets; cycling 2 refers to the wetted and dried sheets for the second time (Fig. 1); and cycling 3 refers to the wetted and dried sheets for the third time. This cycling progress continued until the eighth wetting and drying stage.

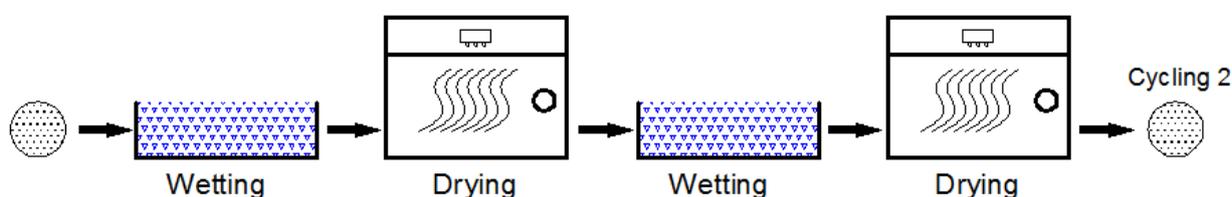


Figure 1. Simplified diagram indicating wetting-drying processes for Cycling 2

All the paper tests were conducted in a commercially running a paper mill's testing laboratory located in Konya, Turkey. This lab has specially designed according to paper testing laboratory conditions (temperature: 23±1 °C and relative humidity: 50%±2). The sheets for strength and physical properties were prepared in accordance with standard TAPPI T205 (2018) test method.

2.2. Determination of Physical and Strength Properties

Air permeability and surface roughness tests were performed with the L&W Bendtsen instrument according to ISO 5636-4 (2013) and ISO 8791-2 (2013) test methods, respectively). In this approach, the device detects the air that is flowing out between the blade of the measuring head and the sample that shows the values in ml/sec on the display. Bendtsen roughness is achieved by measuring the rate of airflow in ml/minute between the paper and head. However, an air stream through the paper is established and as soon as the flow rate is stable, the device shows the values in ml/min on the display. TAPPI T441 (2013) Cobb (60 second) test utilized to the quantity of water absorbed by paper in a specified time under standardized conditions. TAPPI T411 (2015) procedures used for measuring the thickness (caliper) sheet of paper, by the use of an automatically operated micrometer when a specified static load is applied for a minimum specified time. The tests were performed with the L&W instruments according to TAPPI T494 (2006) for breaking length, TAPPI T403 (2015) for burst index, and TAPPI T414 (2012) for tear index of paper samples, respectively.

3. Results and Discussion

3.1. Physical Properties of Paper Samples

Table 1 summarizes the comparative physical property changes against control (A0; B0 and C0, %) of three different test samples (A; B and C types) under similar wetting-drying procedures up to 8th cycling. It is observed that as the increasing cycling numbers positively impact on all three-type sheets' thickness that increases proportionally in all conditions. The highest thickness values were observed with A type of 126 μ (17.8% higher than A0) at 5th cycling, B type of 135 μ (19.5% higher than B0) at 7th cycling and 137 μ (24.5% higher than C0) at 8th cycling, respectively.

For the determination of water absorptiveness properties, Cobb test was conducted. It appears that all samples show a trend to higher water absorptiveness properties as continuously wetting-drying progress. The maximum Cobb value of 70 g/m² was observed in 8th cycling for A type samples, 93 g/m² was observed for B type samples and 92 g/m² for C type samples that those indicates approximately 204%; 272%; and 268% higher water absorptivity values compare to control samples (A0: 23 g/m²; B0: 25 g/m²; C0: 25 g/m²), respectively. These increases in Cobb values are probably due to the deterioration of the structure of Alkyl Ketene Dimer (AKD) and other hydrophobic additives (i.e. resins), which are typically used for internal sizing, and removing those from paper structure during the wetting-drying processes. Since these additives especially AKD gives the paper a hydrophobic feature (Hubbe, 2007; Lovaglio et al. 2019), the paper becomes a more hydrophilic structure when AKD is removed away from the structure. Accordingly, the Cobb values of the papers show increases after each wetting-drying process.

Table 1. Physical properties of the papers.

Cycling number	A	Diff. from A0 (%)	B	Diff. from B0 (%)	C	Diff. from C0 (%)
Sheets Thickness Properties (µ)						
0	107	0	113	0	110	0
1	117	5.9	124	9.7	121	10.0
2	119	11.2	132	16.8	127	15.6
3	120	12.1	129	14.1	127	15.6
4	121	13.1	130	15.1	135	22.7
5	126	17.8	134	18.6	130	18.2
6	120	12.1	133	17.7	130	18.2
7	126	17.8	135	19.5	134	21.8
8	124	15.9	134	18.6	137	24.5
Cobb₆₀ Values (gr/m²)						
0	23	0	25	0	25	0
1	24	4	56	124	78	212
2	31	35	87	248	81	224
3	34	48	88	252	82	228
4	36	57	87	248	85	240
5	55	139	93	272	88	252
6	62	165	92	268	92	268
7	66	187	91	264	89	256
8	70	204	87	248	86	244
Surface roughness (ml/min)						
0	196	0	205	0	240	0
1	926	372	924	351	1122	368
2	1211	58	1099	436	1245	419
3	1372	600	1086	430	1191	396
4	1358	593	1100	437	1329	454
5	1273	550	1200	485	1265	427
6	1308	567	1154	463	1360	467
7	1263	544	1233	502	1259	425
8	1354	591	1170	471	1520	533
Air Permeability (ml/min)						
0	806	0	922	0	767	0
1	985	22.2	1280	38.8	959	25.1
2	1158	43.7	1383	49.9	1155	50.6
3	1156	43.4	1567	69.9	1223	59.5
4	1301	61.4	1626	76.4	1375	79.3
5	1419	76.1	1804	95.7	1349	75.9
6	1453	80.3	1772	92.2	1328	73.4
7	1337	65.9	1826	98.1	1550	102
8	1445	79.3	1820	97.4	1546	102

It has been also observed that the increasing cycling number dramatically influence on roughness values while negatively effects on all three type test papers. For A group, the surface roughness values changed from 372.4%

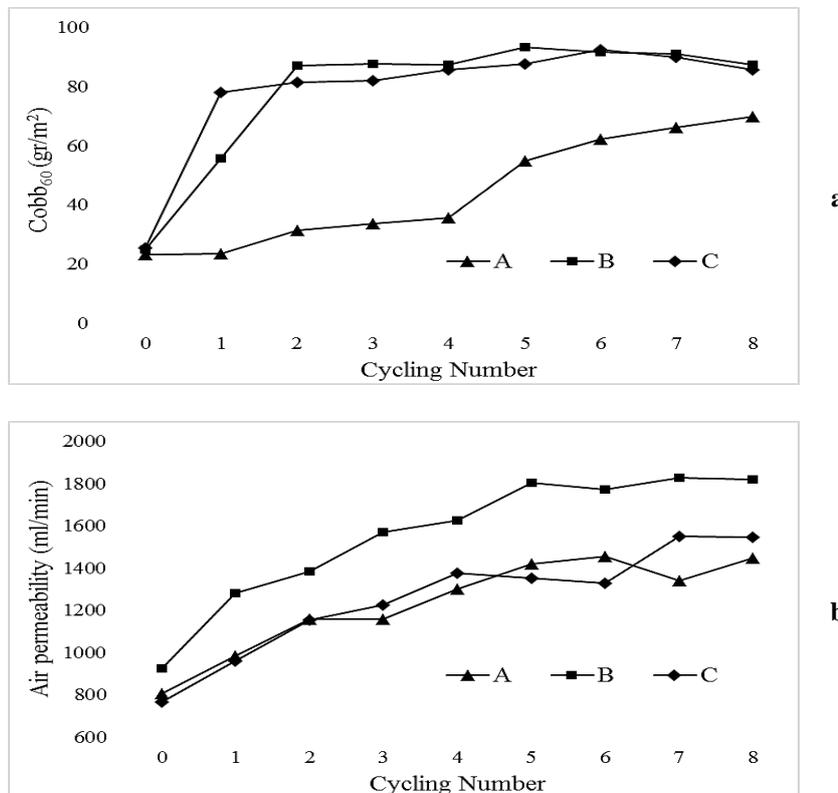
to 600%. The highest roughness value of 1372 ml/min was observed at 3rd cycle against control (A0: 196 ml/min). For B group, the roughness values changed in all conditions from 350.7 to 501.5%. However, the highest surface roughness value of 1233 ml/min was observed at 7th cycling. For C group, the surface roughness values changed in all conditions from 367.5 to 533.3%. The highest surface roughness value of 1520 ml/min was observed at 8th cycling stage.

Continuously wetting-drying cycling also influenced the air permeability properties of three different test papers. It can be observed that the treated samples show continuously increasing barrier against airflow up to 5th cycling stages. Further treatment looks like marginally affected on barrier against air permission. It was calculated approximately 22.2% to 80.3% higher for A type samples; 38.8% to 98.1% higher for B type samples; 25.1% to 102.1% higher for C type samples, respectively. It is clear that drying of paper network with continuously wetting-drying affects the distribution of voids in the network structure and increases the barrier against air and water intake, as observed in this study. It should be noted that air permeability is not a measure of porosity, and these two terms should not be used interchangeably. Two materials having the same porosity, one housing many small pores and the other having fewer but larger pores, could have very different air permeability.

However, this is in good agreement with the literature findings that the wetting-drying impact on not only cellulose morphology but also in sheet structure, because beside cellulose, the sheet network structure is modified by hydrogen bonding and/or cross-linking potential (Atalla, 1992; Clark, 1985; Sahin, 2013; Sahin and Arslan 2008).

It has already been explained by a number of researchers that the wetting and drying cycles of cellulose could result in physical changes such as; smoothness, thickness, hydrophilicity, air permeability properties (Çiçekler, 2019; Sahin and Arslan 2008, Sahin, 2013). The similar results have been observed in this study.

The comparative physical property changes of paper samples are shown in Figure 2. The continuously wetting-drying appears to be modified the physical properties in all conditions. However, first two cycling stages dramatic effects resulting in a high degree of modification, considering the fact that each following stage is lowering trend on physical properties.



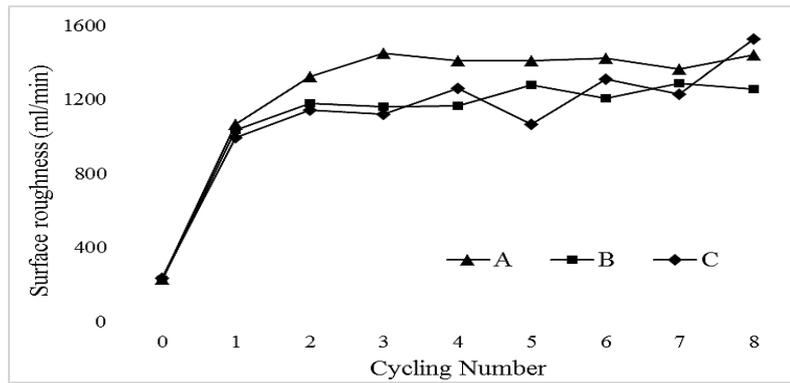


Figure 2. The physical properties of test papers (a: Cobb values; b: Air permeability; c: Surface roughness)

It is clearly visible that the treated test papers have relatively more water absorptiveness (Cobb) (Fig. 2a) than the controls. This is somewhat expecting considering very important processing for the paper substrate. It is noteworthy that both surface roughness (Fig. 2c) and air permeability (Fig. 2b) after the wetting-drying stages reached a maximum up to 5th, it decreased on further cycling stages.

3.2. Strength Properties of Paper Samples

Table 2 shows a summary of comparative strength property changes against control (A0, B0, and C0, %) of three different samples (A, B, and C types) under similar wetting-drying procedures up to 8th cycling. As expected, continuously wetting-drying cause lowering tensile and burst strengths some degrees while in contrast tear strength changed in both directions (increases or decreases) that difficult to interpret.

Table 2. Strength properties of the papers.

Cycling number	A	Diff. from A0 (%)	B	Diff. from B0 (%)	C	Diff. from C0 (%)
Breaking Length (km)						
0	5.64	0	5.56	0	5.79	0
1	4.29	-23.9	4.68	-15.8	5.14	-11.4
2	4.16	-26.3	4.11	-26.2	4.24	-26.9
3	3.78	-33.1	3.42	-38.6	3.59	-38.0
4	3.38	-40.0	3.14	-43.5	2.94	-48.9
5	2.72	-51.7	2.26	-59.4	2.81	-51.5
6	3.01	-46.6	2.63	-50.8	2.64	-54.3
7	3.84	-31.9	2.24	-59.8	2.43	-58.0
8	2.85	-49.5	1.79	-67.8	2.22	-61.6
Burst Index (kPa.m²/gr)						
0	2.26	0	2.12	0	2.60	0
1	2.08	-8.1	1.97	-6.9	2.42	-6.6
2	1.92	-1.5	1.62	-23.7	1.94	-25.5
3	1.65	-27.1	1.38	-34.7	1.70	-34.4
4	1.50	-34.1	1.29	-39.3	1.31	-49.5
5	1.29	-42.7	1.24	-41.6	1.26	-51.9
6	1.58	-30.3	1.25	-41.0	1.36	-47.6
7	1.51	-33.5	1.00	-53.2	1.33	-49.1
8	1.43	-36.8	1.00	-52.6	1.10	-57.5
Tear Index (mN.m²/gr)						
0	4.36	0	5.11	0	4.07	0
1	5.66	29.8	5.00	-2.11	4.01	-1.45
2	4.21	-3.27	4.50	-12.0	3.30	-19.0
3	4.19	-3.83	4.03	-21.1	3.13	-23.1
4	4.09	-6.08	3.87	-24.4	5.38	32.1
5	4.39	0.90	4.69	-8.25	2.64	-35.2
6	4.36	0.00	5.62	9.98	3.05	-25.1

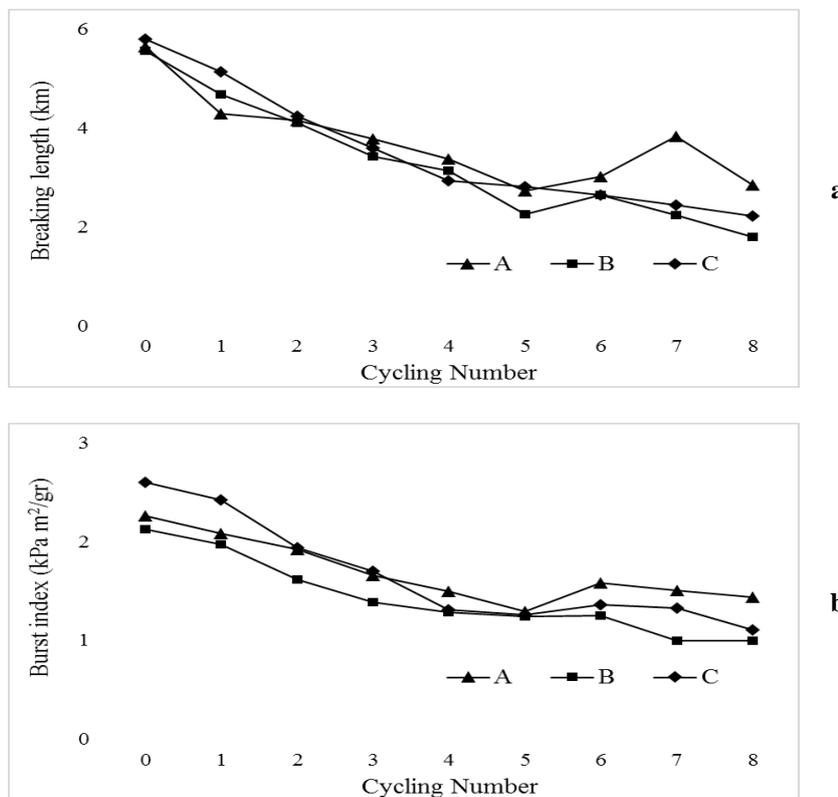
7	4.81	10.4	4.40	-13.8	4.48	10.1
8	3.99	-8.33	3.95	-22.7	2.92	-28.2

The breaking lengths of paper samples were found to be reduced range of 23.9% (A1) to 51.7% (A5) for A groups, 15.8% (B1) to 67.8% (B8) for B groups and 11.4% (C1) to 61.6% (C8) for C groups, respectively. The lowest breaking length was observed with A type of 2.72 km (51.7% lower than A0) at 5th cycling, B type of 1.79 km (67.8% lower than B0) at 8th cycling and 2.22 km (24.5% lower than C0) at 8th cycling, respectively.

However, like breaking lengths, more less similar trend was also observed for burst indices that, increasing cycling stages lowering effects on burst indices of samples in all conditions and all three type papers. The burst indices were found to be reduced range of 1.5% (A2) to 42.7% (A5) for A groups, 6.9% (B1) to 53.7% (B7) for B groups and 6.6% (C1) to 57.5% (C8) for C groups, respectively. The lowest burst index was observed with A type of 1.29 kPa.m²/gr (42.7% lower than A0) at 5th cycling, B type of 1.00 kPa.m²/gr (53.23% lower than B0) at 7th and 8th cycling and 1.10 kPa.m²/gr (57.5% lower than C0) at 8th cycling, respectively.

The tear indices of paper samples show different property changes compare to burst index and breaking length. For A type samples; the lowest tear index of 3.99 mN.m²/gr found at 8th cycling stage that shows approximately 8.3% lower tear index compare to control (A0: 4.36 mN.m²/gr) while the highest tear index of 4.36 mN.m²/gr was found at 1st cycling stage that shows approximately 29.8% higher than control. Similar results were also observed for both B and C type samples. For B types; the lowest tear index of 3.87 mN.m²/gr found at 4th cycling stage that shows approximately 24.4% lower compare to control (B0: 5.11 mN.m²/gr) while the highest tear index of 5.62 mN.m²/gr was found at 6th cycling stage that shows approximately 9.98% higher than control. For C type paper samples; the lowest tear index of 2.64 mN.m²/gr found at 5th cycling stage that shows approximately 35.2% lower compare to control (C0: 4.07 mN.m²/gr) while the highest tear index of 5.38 mN.m²/gr was found at 4th cycling stage that shows approximately 32.1% higher than control. As mention previously, severe treatment conditions could cause depolymerization reactions of some chemical constituents (i.e. cellulose fragments, low molecular weight hemicelluloses). However, tear index has a very complicated effect in the terms of fiber properties, especially morphological structure of the fibers (Fernandez and Young, 1996; Sutjipto, et al.2008).

The breaking lengths (Fig. 3a), burst (Fig. 3b) and tear (Fig. 3c) indices values of paper samples plotted against cycling numbers.



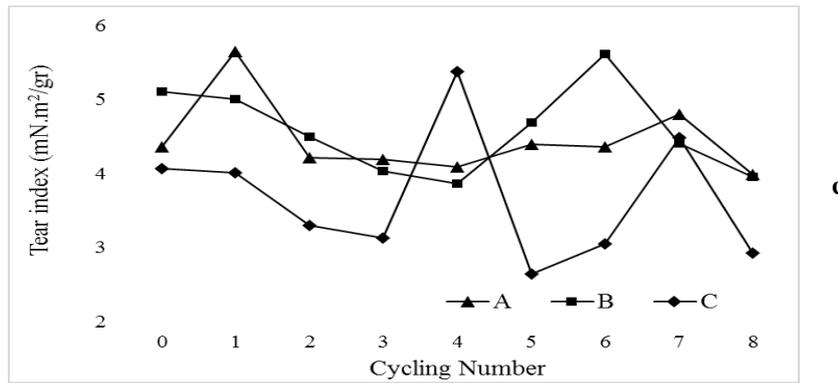


Figure 3. The physical properties of test papers (a: Breaking length; b: Burst index; c: Tear index)

It can be realized that the similar trend as breaking length and burst index was shown and reveals paper fiber network degradation at prolonged wetting-drying in progress. It is well known that a substantial amount of the hemicelluloses could be soluble in water environment that can be soluble much more readily than cellulose. Having this information, it is reasonably to explain that there is no sign of extensive cellulose hydrolysis occur in wetting-drying system. However, it can be clearly shown that both breaking length and burst index loses occur at all wetting-drying stages.

However, the initial phase of water penetration is controlled by diffusion and takes place at room temperature. Hence, water can quickly penetrate into fiber and may affect some chemical degradation along with removal of non-fibrous additives. In this sense, the paper network modification could be controlled by solubilization of chemical groups such as short cellulosic fragments, fillers and hemicelluloses. These conditions are not only affecting paper physical properties but also hydrolysis of some chemical constituents as well. As a result of fiber drying, the lumens become narrower and the ability to make hydrogen bonds between the cellulose chains decreases. The fibers become harder, collapse, and lose their swelling properties. Reducing effects of strength at prolonged cycling stages supports this information. Since the burst index and breaking length dominantly depend on fiber bonding, the reduction of those properties can be an indication that cycling conditions reduce or weaken fiber bonding with changes in fiber strength. It was well established that, the strength properties of papers have usually reduced with wetting-drying. However, their properties may be improved by treatment with various chemicals (Sahin, 1997).

Figure 4 shows that the tear and tensile strengths are inversely related to each other. The shape of plot is typical for sheets when physical properties are low (Sahin, 1997 and 2007). Howard (1990) suggested that paper made from recycled fiber's usually shows decreasing tensile, burst and folding properties but density, surface roughness, thickness, and tear strength increased.

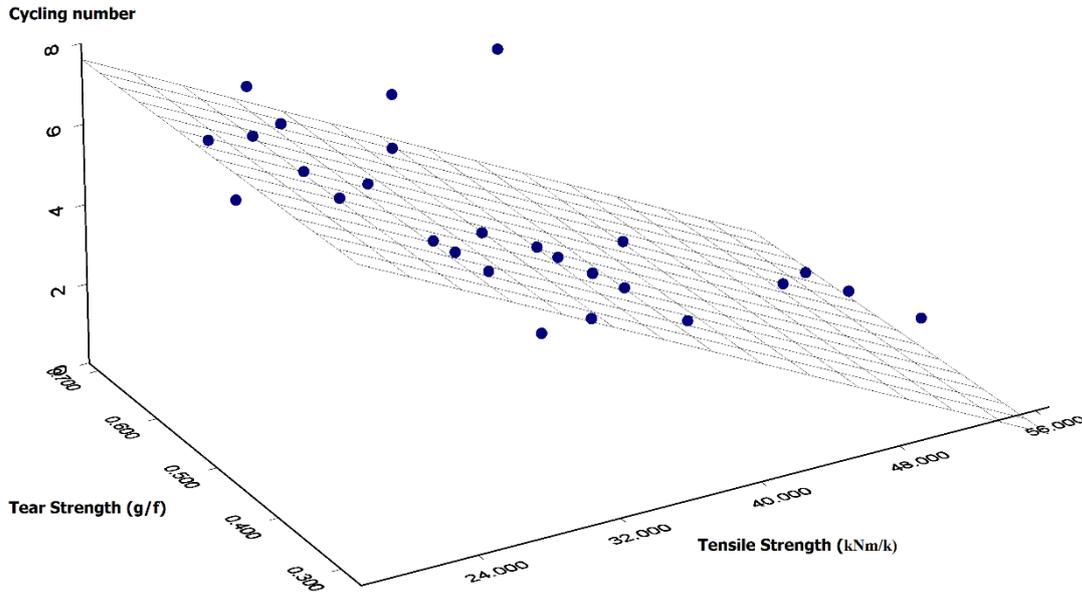


Figure 4. Tear-tensile strength properties against wetting-drying cycling

However, these dramatic changes especially noticed in up to 4th recycling stages. In our study, it was observed that the tear strength of sheets shows different property changes compare to burst and tensile (breaking length) strengths. Since there were no regularities in the sheet network that no regular bonding expected and therefore a decrease in bonding strengths (tensile and burst) while variables in tear strength was observed. Tear strength is affiliated to the bonding potential and fiber length (Sood et al., 2005; Latifah et al., 2009). These irregularities in tear strength are thought to result from bond potential.

4. Conclusions

The continuously wetting-drying of paper samples found to be impact on the paper properties. As a result of these treatment procedures, it has been observed that there are differences between the physical and mechanical properties of the papers produced by the three companies. The reasons for this may be due to using different chemicals and additives such as binders, retention aids, calcites wet- and dry-strength additives. Since the usage rates of the chemicals, fillers and additives used in the recipes are not the same, there are differences in the values obtained in the study. There may also be differences in the long and short fiber ratios they use. The short and long fiber ratios used in paper production can be changed according to fiber quality, chemicals and additives. In paper industry, typically short and long fibers are used together to improve strength and print properties of sheets. Commonly, office grade kraft papers typically contain %70 long and %30 short fiber fractions. Hence, the short and long fiber ratios used in paper production can be changed according to fiber quality, chemicals and additives. Physical and strength properties of all three type papers have been affected by wetting-drying processes. A significant increase was seen especially in Cobb values, due to washing chemicals such as starch and internal sizing agent (AKD, ASA etc.) during washing-drying progress. Because of hornification, strength properties of the papers except tear strength reduced in parallel with number of cycling stage.

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