The Performance of Alkylketene Dimer (AKD) for the Internal Sizing of Recycled OCC Pulp

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In this research, the ability of Alkyl Ketene Dimer (AKD) in sizing of recycled Old Corrugated Container (OCC) pulp in alkaline and neutral conditions was investigated. The results indicated that AKD could be a good and completely successful choice for obtaining sized liner made of recycled OCC pulp. In this study, 0.25, 0.5, 1% AKD (based on oven dry pulp) were considered. All treatments were successful in sizing but none of them showed considerable difference in Cobb-60 as a sizing indicator. Increasing the AKD consumption reduced tensile, burst and tear indices. Therefore, low addition levels yielded the best results in both neutral and alkaline pH. The pH of fiber suspension had no obvious effect on sizing under alkaline and neutral conditions, but all mechanical properties showed better results at alkaline pH compared to neutral pH. The contact angle test was used in selected optimum treatments from all aspects (0.25% AKD in alkaline condition), and the results were consistent with the other size test findings.

Keywords: AKD; OCC; Paper recycling; Cobb; Mechanical properties

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INTRODUCTION

One of the critical properties of paperboard to be used for packaging applications is its resistance to wetting by different liquids, especially water. Sizing agents added to the paper machine wet end can improve that paper's ability to resist liquids, along with improving their dimensional stability and surface quality. Internal (added at the wet end) and surface sizing (using a size press) are the main methods for application of different conventional sizing agents. Rosin products, which have been used for many years as internal sizing agents, are best suited for acidic papermaking conditions. A recent trend toward the use of neutral and alkaline papermaking conditions has forced papermakers to find new chemicals compatible with this new regime (Hubbe 2006).

Alkylketene dimer (AKD) is one of the main synthetic sizing agents used under neutral and alkaline conditions, and it has been considered by several researchers (Jin *et al.* 2010; Mukai *et al.* 2010; Lindström and Larsson 2008; Glad-Nordmark and Lindström 2007; Kumar *et al.* 2007; Mohlin *et al.* 2007; Hubbe 2006; Mohlin *et al.* 2006; Karademir *et al.* 2005; Hu *et al.* 2004; Karademir *et al.* 2004; Shen *et al.* 2003; Mendes *et al.* 2003; Karademir 2002; Mohlin *et al.* 2003; Shen and Parker 2001; Shen *et al.* 2000, 2001; Garnier *et al.* 1998; Chen and Biermann 1995; Krueger and Hodgson 1995; Bottorft

1994; Bartz 1992; Gess 1992; Walkden 1991; Crouse and Wimer 1991; Marton 1991; Gess 1991; Lund 1991; Marton 1990).

The mechanism of wood fibers sizing by AKD application has been argued widely. Most scholars believe that lactone tetrahedral ring of AKD reacts with the hydroxyl groups of cellulose and hemicelluloses to form beta-keto ester bonds (Fig. 1). However, some others mentioned in a recent review article suggest that such a bond plays no effective role in sizing (Hubbe 2006).

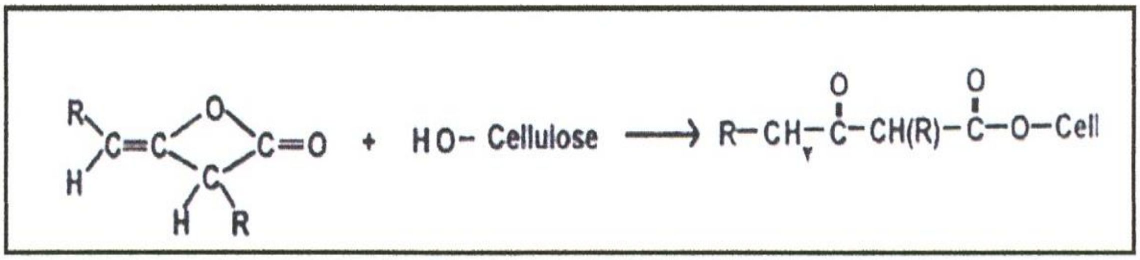

Fig. 1. The reaction of alkyl ketene dimer (AKD) with cellulose hydroxyl groups to form beta-keto ester

It seems that AKD can attach itself irreversibly to the surface of fibers and that such attachment is largely responsible for effective sizing. The direct observations of Bottorff (1994), conducted on papers treated and not treated with AKD using solid-state 13C NMR, have confirmed that beta-keto ester bonds can form in papers sized with AKD.

The reaction between AKD and cellulose happens relatively slowly, and alkalinity can act as its catalyzer. Moreover, it has been shown that bicarbonates and polymers having amine functional groups are effective in accelerating this reaction and can be added to AKD emulsion. Some studies have indicated that thermal treatment could be considered in sizing with AKD. Roberts (1996) explained that thermal treatment has a positive impact on spreading and displacement of AKD on fibers surface. Lindström (2007) also considered the importance of eliminating water before the spreading and distribution of AKD molecules on the fiber surfaces. He concluded that when AKD is surrounded by water molecules it cannot act properly. Fortunately, it appears that spreading of the AKD on a molecular level does not take place to a significant extent until the paper web has been dried to 80 about percent solids. Figures 2 and 3 demonstrate the mentioned process and probable reactions in the AKD sizing process, respectively.

Recycling of waste papers reduces the volume of waste materials on the one hand, and creates considerable profits by returning an unusable material to the production cycle on the other hand. The recycling of papers reduces also the need for the pulping of virgin fibers throughout the world and the need to harvesting of forests as the lungs of the earth. The decrease in the costs of recycled paper products in comparison to virgin papers is in turn profitable. The Table 1 demonstrates the recycling conditions for paper in 2006 (FAO 2006). Meanwhile, rising paper consumption due to growing the world population along with enlarging diversity of papers' applications is putting more pressure on papermaking industries to use more waste paper.

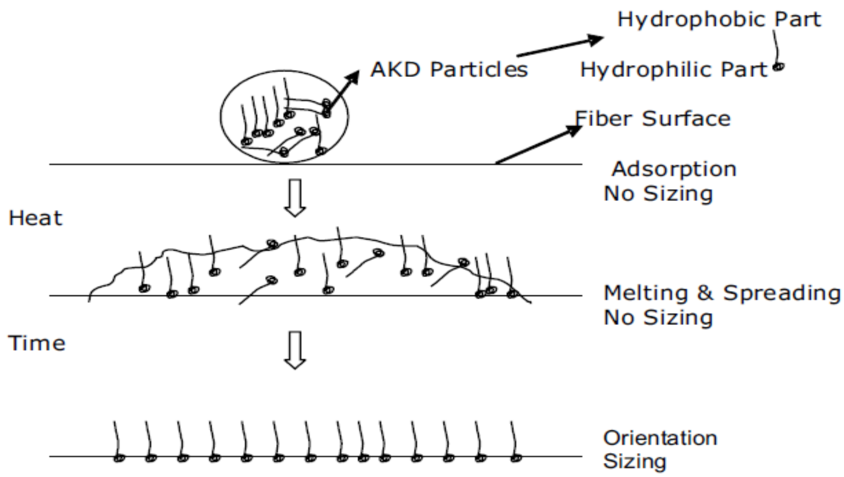

Fig. 2. Schematic Illustration of Mechanism of AKD Sizing (Kumar *et al.* 2010)

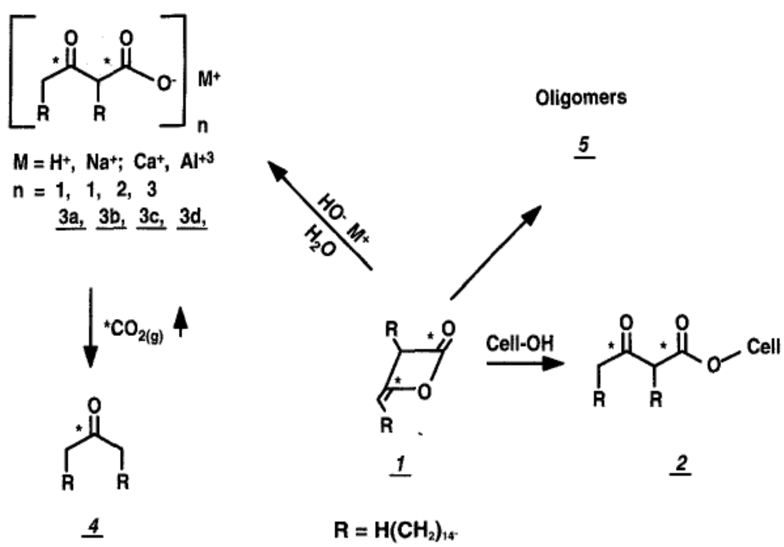

Fig. 3. Possible AKD reaction products produced during the sizing of paper (Bottorft 1994)

Table 1. Paper Recycling in 2006 (FAO, 2006)

Region	Paper Recycling (MT)				Recycling Percent
	1990	1995	2000	2005	
Africa	1,515,700	1,166,700	909,800	734,970	---
Asia	52,077,715	44,076,152	33,493,771	24,322,100	57%
Europe	54,774,990	43,991,709	33,641,000	24,088,000	55%
North and Central America	47,806,928	45,945,000	33,246,500	28,788,008	38%
South America	4,867,700	4,455,000	2,665,000	2,417,000	---

However, recycled fibers can cause extensive problems because of their different nature compared to virgin pulps. For instance, complex wet-end in recycled fiber suspension (existing anionic trash, high conductivity, *etc*.) or decreasing fiber quality (hornification, less WRV, less hydroxyl groups, *etc*.) can be mentioned.

It seems that the presence of cations or less hydroxyl groups may interfere negatively with the bonding of the AKD and cellulose. Also, as the retention of AKD depends on its stabilization with cationic polyelectrolyte. The complex wet end system of recycled pulp may make it more challenging to control retention efficiency (Bottorff 1994; Hubbe 2006).

As the paper and paperboard packaging industry has paid special attention to use recycled fibers, especially fibers produced from recycling of old corrugated containers (OCC) and also because the resistance of packaging papers and paperboards against liquids, especially water, is of great importance, more comprehensive information is needed regarding AKD sizing of packaging papers produced from recycled fibers. In the present research, the effects of AKD on the properties of paperboard make from OCC recycled fibers were studied.

EXPERIMENTAL

The OCC required for this research was collected from Iran Papyrus Company randomly. There were no other contaminants, including non-paper wastes, white top papers, printed papers, office papers, newspapers, *etc*. Selected OCC was transferred to Shahid Beheshti University laboratory (ZirAb Campus) and kept under ambient conditions for 24 hours. The dryness of the sample was 6.7% after 24 hours. A sample weighing 384.12 grams (equal to 360 oven-dry grams of sample) was soaked in 5 L of water for 24 h and then reslushed manually.

Disintegrating and refining were applied at 1.5% consistency using a laboratory Hollander beater according to TAPPI standard T200 sp-01 until reaching 300 mL CSF freeness, as determined by CSF Tester. Thereafter, refined pulp was used for introducing desired treatments. The AKD was added to this pulp at four levels (zero, 0.25, 0.75, and 1 percent, based on oven-dried pulp) and at the two pH levels of of 8.5 (alkali) and 7 (neutral) using a mixer with 750 rpm during 60 seconds. The applied treatments have been shown in Table 2.

Table 2. Treatments Carried Out in the Research

pH	AKD (%)	Treatment
Neutral	0	Control Neutral
	0.25	0.25 % Neutral
	0.75	0.75 % Neutral
	1	1% Neutral
Alkaline	0	Control Alkaline
	0.25	0.25 % Alkaline
	0.75	0.75 % Alkaline
	1	1% Alkaline

The preliminary pH of the pulp was 6.5, so the levels of pH=7 and pH=8.5 were established by addition of sodium hydroxide. The handsheets were prepared and then pressed according to TAPPI standard T 205 sp-02, and dried using a drum dryer in two successive phases. In the first phase, the sheets were dried at 70 ^oC for 150 minutes, and in the second phase, the temperature was raised to 90 ^oC for 10 minutes. The basic weight was set to 130 g/m^2. Table 3 shows the determined properties, their units, and the used standard. The contact angle also was assessed using a Goniometer PG-X device.

Table 3. Tests Carried Out and their Standards

Test	Basis Wt.	Tear Index	Burst Index	Tensile Index	Cobb 60
Unit	g/m²	mNm^2/gr	kPam^2/g	Nm/g	g/m²
Test Method	IS0-536	IS0-1974	IS0-2758	IS0-1924-2	IS0-535

RESULTS AND DISCUSSION

AKD Performance for Sizing of OCC Paperboard at Alkaline and Neutral pH

Figure 4 shows the Alkyl Ketene Dimer (AKD) sizing performance on the liners obtained from old corrugated container (OCC) recycled fibers at different consumption rates of this sizing agent under alkaline and neutral conditions. As expressed before, although many subjects have been addressed about the use of AKD in different kinds of virgin fibers in previous studies (Hubbe, 2006), less attention has been paid to the use of the substance in recycled fibers with very complex wet-end chemistry. The results show that AKD imparted appropriate sizing in both alkaline and neutral conditions. Cobb values measured after 60 s decreased from 302 g/m^2 and 330 g/m^2 in a control treatment under neutral and alkaline conditions to 24 g/m^2 using 0.25% AKD, respectively. Although the Cobb's descending trend continued with the increase of AKD consumption, no considerable difference was observed between AKD levels and it can be concluded that the lowest value of AKD consumption in this research had offered an appropriate result.

As stated before, the formation of beta-keto ester bonds between AKD and the hydroxyl groups of cellulose and hemicellulose is one of the proposed mechanisms to explain AKD sizing. Since the bond is of covalent type, it appears to be been less affected by the recycled pulp’s wet-end chemistry, and hence it gave rise to successful sizing. Of course, it shouldn't be forgotten that AKD is effective only under alkaline and neutral papermaking environments. Conversely, the complexity inherent in wet-end chemistry would have a negative effect in the case of internal sizing in an acidic environment of recycled papermaking, especially when employing rosin systems that depend strongly on electrostatic relationships during their curing process. Although it was supposed that the recycled fiber wet end may interfere with the adsorption of AKD and consequently decrease its sizing effect, the present results show no considerable effect on sizing. Moreover, no difference was observed between the alkaline and neutral pH with regard to sizing. So, the AKD performance hasn't been affected by the change of the pH from neutral to alkaline.

The sizing results also have been confirmed by assessment of water drop shapes and disappearance during 25 seconds between control treatment and 0.25% AKD in the alkaline condition (Fig. 5). As was observed after 25 seconds, there weren't any obvious changes in the shape of water drops on paper treated with 0.25% AKD, but in contrast, the water drops disappeared during that interval by absorption into the paper. The above-mentioned results are in accordance with those obtained by other researches about virgin pulps (Hubbe 2006).

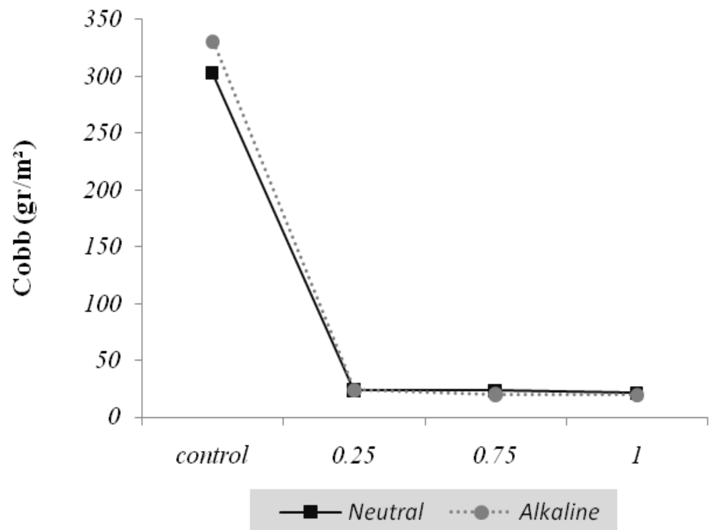

Fig. 4. Effect of AKD sizing on Cobb-60

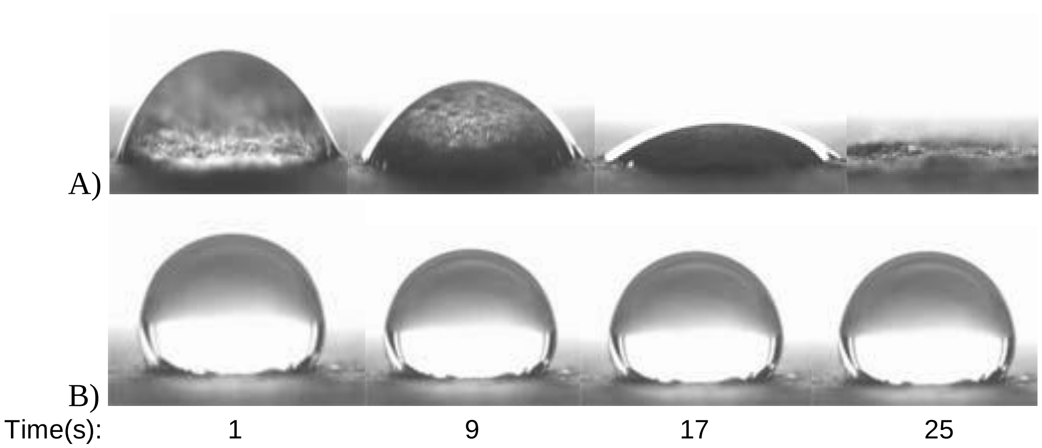

Fig. 5. Comparing contact angle between (A) control paper (un-sized), and (B) paper sized with 0.25% AKD, all at alkaline pH

AKD Effect on Tensile Index of OCC Paperboard at Alkaline and Neutral pH

Figure 6 shows the effect of AKD sizing on the tensile Index of the liners made of OCC recycled fibers in different percentages of its consumption in two alkaline and neutral environments. The presence of AKD in the structure of the OCC recycled papers reduced tensile index. According to the mechanism considered for the AKD, the quadrilateral lactone ring in AKD reacts with cellulose and hemicelluloses hydroxyl groups to form the beta-keto ester bonds (Fig. 2). This reaction will cause in the cellulose and hemicelluloses hydroxyl groups to be unavailable for formation of hydrogen bonds with each other, leading to a reduction of connections between fibers. The tensile strength is a property that is mostly affected by the interfiber bonding status. Hence, the AKD addition will reduce this resistance naturally. According Fig. 6, increasing AKD consumption will reduce tensile strength more. Therefore, except for the control treatment, the lowest level of the AKD consumption gave in the highest dry-strength in this research.

Moreover, it is observed that the tensile index was higher for sheets formed at alkaline pH. This result is reasonable and perceivable, because under alkaline conditions (even in the presence of AKD), the fibers' electrostatic negative charge and the fibers' bonding potential will be increased because of activation of a greater number of hydroxyl groups in this environment compared to neutral pH (Crouse and Wimer 1991).

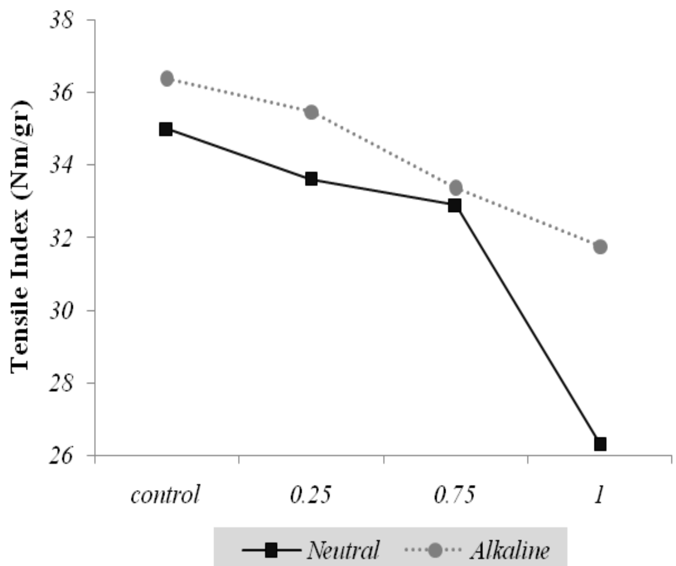

Fig. 6. Effect of AKD sizing on Tensile Index

Effect of AKD on the Burst Index at Alkaline and Neutral pH

Test results for bust index were similar to those for tensile index, as shown in Fig. 7. Once again, the internal AKD sizing adversely affected strength. As the burst strength is similar to tensile strength with respect to being dependent on interfiber bonding, the same discussion given in the previous paragraph could be applied here as well.

Effect of AKD Sizing on the Tear Index at Alkaline and Neutral pH

Figure 8 shows the effect of AKD sizing on the tear strength of the liners made from the OCC recycled fibers with different AKD levels under the alkaline and neutral environments. The fibers length is regarded as the most important factor affecting the tear strengh, but under constant fibers length conditions, the increased potential of hydrogen bond formation can positively affect this property.

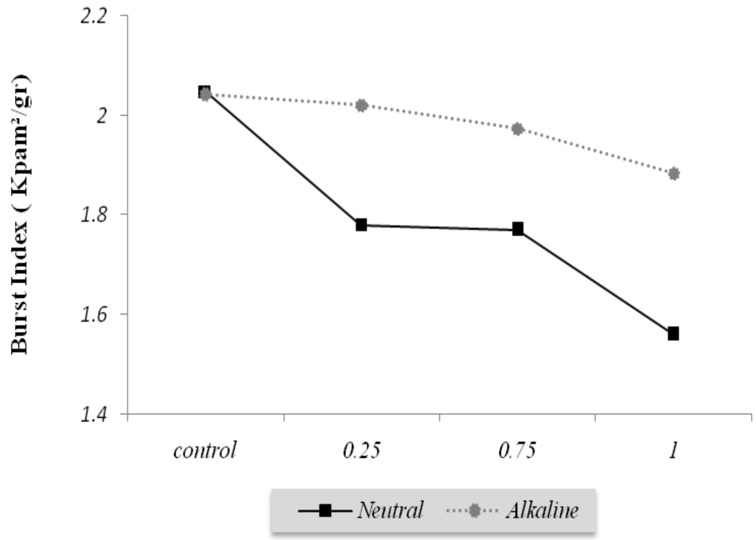

Fig. 7. Effect of AKD sizing on burst index

The maximum value of the tear resistance was observed in the case of the control treatment. It seems that a lack of AKD in the paper structure and so the avoidance of interfering with the hydrogen bond sites is responsible for this observation. By adding the sizing agent, the tear index tends to be reduced and the descending trend continues with increasing more dosage, consistent with increased beta- keto ester bonds between AKD and the cellulose and hemicelluloses hydroxyl groups. With regard to the effect of alkaline and neural environments on the AKD performance, it is observed that like the other previous properties, the positive effect of the alkaline environment is more obvious compared to the neutral one and the increase of the environment alkalinity can mitigate the adverse effect of this substance on the tear strength.

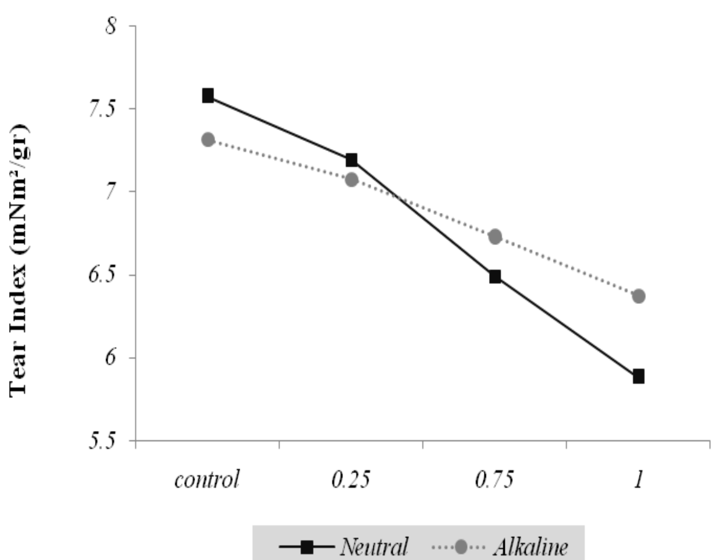

Fig. 8. Effect of AKD sizing on tear Index

CONCLUSIONS

1. Although it was supposed that recycled fiber could interfere with the retention of AKD, no obvious effect was found. It seems that more research using tougher conditions would be needed to show such an effect. Also, it seems that the sizing mechanism of AKD after its adsorption is not so much based on the electrostatic relationships, and this process is mainly affected by bonding and formation of beta-keto ester bonds. Those methods of internal sizing that are based on the electrostatic charges effects, such as rosin sizing, would definitely encounter more problems in the suspension of the recycled fibers and would likely even lead to the sizing failure.
2. The increase of the AKD consumption from zero to 1% in this research reduces the Cobb test values, but the best result was obtained at the lowest percentage of AKD consumption, *i.e*. 0.25%. Because on the one hand, no considerable difference was obtained through using greater amounts of AKD and in the other hand, the over-consumption of AKD reduces such properties as burst index, tear index, and tensile index, the results suggest that the AKD addition ought to be no greater than then minimum that is required to reach the sizing specification.
3. The internal sizing performance using AKD for the recycled fibers was not affected by suspension's neutral or alkaline pH in this research. But the dry-strength properties evaluated in the research, namely the burst index, the tensile index, and the tear index increased with the increase of pH during papermaking. This result can be attributed to the increase of the fibers' negative electrostatic charge because of the activations of a greater number of hydroxyl groups in this environment compared to neutral pH. Consequently, the fibers have a greater potential to form hydrogen bonds. Crouse and Wimmer (1991) have also referred to this point.

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