EFFECTS OF DIFFERENT RATIOS OF STARCH-CONTAINING AKD ON PAPER PROPERTIES IN INTERNAL SIZING OF VARIOUS PULP TYPES

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The main objective of this study is to determine the effects of different ratios of starch-containing AKD emulsion in various pulp types sizing processes on paper properties. A secondary objective of the study is to evaluate the influences of starch content in AKD emulsion and AKD dosage applied to pulps. Three different pulp types were sized: unbleached kraft, bleached kraft and chemithermomechanical pulps. In preparation of AKD emulsions, three different ratios of starch were used. AKD was applied to all pulps under the same conditions at four different dosages based on oven-dried fiber weight. Test papers were produced and Cobb values (water absorptiveness), some mechanical and optical properties of the papers were determined. In addition, SEM, XRD and contact angle analyses were applied to papers produced with optimal sizing parameters. As a result of the study, it was found that the effects of AKD cause different behaviors depending on the pulp types. AKD was highly efficient in sizing chemithermomechanical pulp, decreasing the Cobb value by 90.9%. Depending on the pulp type, the starch content used in the emulsion preparation and the AKD dosage applied to the papers have various effects on the paper properties.

Keywords: AKD, starch, internal sizing, pulp, paper

INTRODUCTION

Paper is made up of cellulosic fibers that encompass hydroxyl groups that provide it hydrophilic properties. One of the most important properties of paper and board for applications such as packaging and printing is its resistance to wetting by various liquids, notably water. Chemical additives (sizing agents) are introduced into the papermaking process to improve paper hydrophobicity.[1] The main methods of applying various conventional sizing agents are internal and external (surface) sizing. Rosin products, which have been adopted as internal sizing agents for numerous years, are most appropriate for acidic papermaking conditions. Due to a recent trend of using neutral and alkaline papermaking conditions,[2,3] papermakers have been forced to find newer agents compatible with the recent regime. Alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD) are common sizing additives utilized in the wet-end under alkaline and neutral papermaking conditions.[4] In terms of hydrolytic stability and reactivity towards cellulose, these sizing agents are contradictory, with AKDs being the least reactive species and being quite consistent towards hydrolysis, while ASAs being very reactive towards cellulose, but also sensitive to hydrolysis.[5] The degree of covalent bonding of these compounds to cellulose under papermaking conditions is controversial.[6,7]

According to G. Garnier *et al.*, AKD only moderately wets cellulose surfaces, possibly because AKD can rearrange surfaces in an autophobic thin film structure.[8] This spreading system may clarify why AKD has a non-zero contact angle with cellulose and silica surfaces, although the surface tension of AKD in bulk (≈33 mN/m) is considerably lower than the crucial surface tension of the solids in question (≥ 45 mN/m).[7] AKD products, typically produced by the dimerization of stearoyl chloride, represent a second set of examples that can be utilized to explain the key qualities and behavior of effective sizing chemicals.[1] The diagram in Figure 1 summarizes widely held theories of how AKD compounds form, spread, and attach to the cellulosic surface of the fiber.

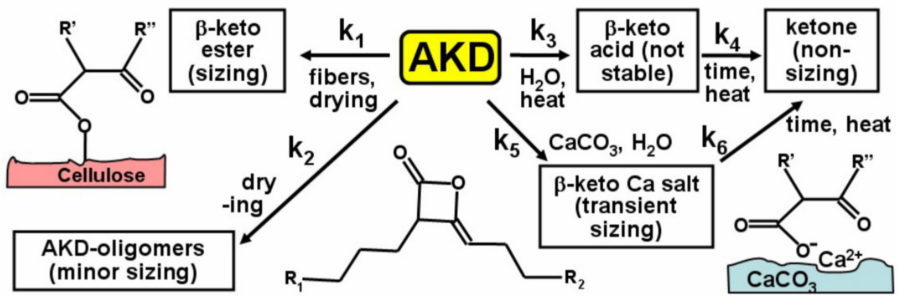

Figure 1: Major reactions between AKD and cellulose surfaces[1]

The interaction between AKD and cellulose is slow and the alkalinity can act as a catalyst. In addition, bicarbonates and polymers with amine functional groups accelerate the reaction and can be added to the AKD emulsion.[9] The efficiency of AKD sizing is determined by many factors, including particle retention, particle distribution on fiber surfaces, and the degree of chemical reaction of the sizing. The hydrophobicity of paper is influenced by different forms of AKD in the pulp.[10,11] The sizing of an AKD is usually presented as a three-step process: (a) AKD particle adsorption/retention by fibers and fine cellulosic components; (b) AKD movement to cellulosic surface; (c) AKD molecular reaction and reorientation.[5]

Emulsified AKD is the most commonly used as a sizing agent for neutral papermaking. Although AKD is solid at room temperature, the term 'emulsion' is used here because the material melts just above its melting temperature when disseminated into an aqueous suspension, which must include some type of stabilizer.[12,13] Current AKD production is mainly focused on emulsion-type AKD, which has a multitude of challenges, including the fact that it hydrolyzes quickly and has a limited shelf life, as well as transportation costs and other disadvantages.[14-16] The application of AKD to starch particles tended to impart some barrier properties to the particles, resulting in starch water contact angles of about 85° and 5° for the coated and blended AKD particles, respectively. It is important to understand the influence of reaction conditions on the magnitude of the interaction between AKD and starch.[17]

Many studies on the hydrophobic interaction of AKD on natural fibers have been published.[2,7,9,18–20] In fact, there are significant differences in sizing and swelling ability, mechanical and optical properties, and other aspects between virgin (chemical and mechanical) and recycled fibers. AKD is thought to interact with cellulosic fibers to create a β-ketoester bond that renders paper hydrophobic.[10,18] AKD applied during paper production from pulp made by different methods (chemical, mechanical, recycled) shows different behavior for each fiber type. The effects of AKD sizing on recycled fibers (OCC) have been described in several studies.[9,18] TCF pulps often contain more dissolved chemicals that have an adverse impact on AKD retention, compared to ECF pulps.[21,22] This represents an important issue to investigate, as more research is needed to determine the impact of different fiber types on AKD sizing performance and to compare them to each other.

In this study, the effect of AKD sizing on the properties of bleached kraft, unbleached kraft and chemithermomechanical fibers was observed. The influencing factors in this study, such as surface contact angle and water absorbency (Cobb value), and some mechanical and optical properties of AKD sized papers were investigated. The effects of the starch content used in preparing the AKD emulsion on sizing performance were also studied.

EXPERIMENTAL

Preparation of AKD emulsions

AKD (Wilmar AKD-1840) in pellet form and cationic starch in powder form were purchased from the market. The specifications of the AKD and cationic starch used in this study are given in Table 1.

In preparation for sonication, 10 g of AKD wax was converted from solid form to liquid form by heating to 55±5 °C. The starch was dissolved in deionized water to give concentrations of 1%, 2% and 3%. It was then heated in a water bath at 93±1 °C for 35-40 minutes, as recommended by the manufacturer. This heated starch sample was poured into the melted AKD in a 100 mL flask. A Hielscher ultrasonicator (UP200Ht, Hielscher Ultrasonics Inc) was used for all emulsifications. This device operates at a frequency of 26 kHz (200 watts). The sonicator's 10 mm titanium horn was immersed into the liquid. The composition of this emulsion is shown in Table 2, which indicates the dispersion of mg AKD/mL solutions.

Table 1
AKD and cationic starch specifications used in the study

AKD		Cationic starch	
Specifications	Values	Specifications	Values
CAS No	84989-41-3	Starch base	Maize/tapioca starch powders
Content	≥88%	Physical state	Fine white odorless dry powder
Color	Slight yellow	pH 10% w/v dispersion	5.00 to 8.00
Toluene	0%	Moisture	Max. 14%
Form	Pellet	Ash	Max. 1.5-2.0%
Description	C18 about 40%	Fineness (100 mesh)	Min. 99%
Melting point	Min. 47 °C	Degree of substitution	Min. 0.04%
Acid value	Max. 5 mg KOH/g	Nitrogen content	Up to 0.3%
Iodine value	Min. 45 gl^2/100 g	Viscosity 5% at 50□	High (greater than 2200 cps)

Table 2
Components of prepared AKD emulsions

Components	1% Starch-containing AKD emulsion	2% Starch-containing AKD emulsion	3% Starch-containing AKD emulsion
AKD (g)	10	10	10
Starch solution (g)	0.75	1.5	2.25
Starch solution volume (mL)	75	75	75
De-ionized water (mL)	100	100	100
1M HCl (mL)	0.5	0.5	0.5
Total volume (mL)	186.25	187.00	187.75
AKD (mg AKD/mL)	53.7	53.5	53.3

In order to achieve sufficient homogeneity, the material was sonicated four times for 2.5 minutes each. After sonication, the solution was quickly cooled in a steel beaker containing 100 mL of cold deionized water. 1M hydrochloric acid (0.5 mL) was added to lower the pH to about 4-4.2. The samples were kept cool until further examination.

Internal sizing and paper production

Chemithermomechanical (CTMP), bleached kraft (BKP) and unbleached kraft (KP) pulps were used to determine the effects and performance of different ratios of starch-containing AKD emulsions on these pulp types. The pulps were beaten with a laboratory-type Hollander to a freeness level of 35±2 SR° and the ISO 5267-2 standard was used to measure SR° number and drainability. After that, the refined pulps were used to introduce the necessary treatments. The AKD emulsions were mixed into these pulps in four stages (0.0, 0.1, 0.2, 0.3% based on oven dried pulp) at 0.25% pulp consistency using a magnetic stirrer at 750-850 rpm introduced for 90 seconds. As a retention chemical, cationic polyacrylamide (cPAM) was added to the pulp suspension at a rate of 0.01%. The test papers with grammages (basis weight) of 80±2 (g/m^2) were made according to ISO 5269-2 standard using a Rapid Kothen (RK-21) semi-automatic paper machine. The papers were then conditioned in the laboratory at 23±1 °C and 50±1% relative humidity for 24 hours before being used for testing and analysis.

Optical and mechanical measurements

Some measurements were carried out to determine the effects of AKD on the properties of the papers. Sections of the optical, tensile and burst test specimens from the papers are shown in Figure 2 and ten papers were used for each test. Reflectance factor was measured with a Datacolor Elrepho 450x spectrophotometer. The ISO brightness, ISO whiteness and yellowness values of the conditioned papers were

measured using ISO standard methods 11475, 2470 and 17223, respectively.
ISO 1924-2 (tensile strength) and ISO 2759 (burst strength) standards were used to determine the tensile (50 mm/min) and burst indices, which are important indicators of paper strength characteristics.

Water absorptiveness (Cobb), hydrophobicity, SEM and XRD analyses

The amount of water that a 1 m^2 sheet of paper absorbs at a given point in time under acceptable conditions is called the water absorption capacity (Cobb value). Water absorption is influenced by paper properties, such as surface modification, coating and sizing. The Cobb value was measured according to ISO 535 (2014) and calculated according to Equation 1:

$$Cobb\ (g/m^2) = (W_W - W_D)\ x\ 100 \quad (1)$$

where W_W is the wet weight of the papers after the test and W_D corresponds to the dry weight of the papers before the test. A CAM 200 (KSV Instruments Ltd., Germany) meter fitted with a video camera and CAM2008 software was used to measure the contact angle of the papers. The study was performed at room temperature an average of 5 times, with water droplet volumes ranging from 0.95 µL to 1.00 µL for each measurement. Prior to analyses, the paper was placed over the slides to allow equilibration with ambient temperature and humidity. The CAM2008 program was used to examine the contact angle measurement, which recorded the contact angle as a function of time. SEM images of sheets were captured using a ZEIZZ-EVO LS10 microscope, with an acceleration voltage of 0–30 kV. The X-ray diffractometer (XRD) spectra of the papers were obtained using a Philips X'Pert PRO XRD, with Cu K radiation at a wavelength of 1.5406 °. Measurements were performed with a scan rate of 2/min for a wide range of diffraction angles (2ϴ) from 10° to 90°. Using Segal's peak height approach, the crystallinity indices (CI) of the pulps were calculated as described in Equation 2:[23]

$$CI\ (\%) = [(I_{002}-I_{am})/I_{002}]\ x\ 100 \quad (2)$$

where I_{002} is the maximum intensity of the peak at 2ϴ ≈ 22.5°, and I_{am} corresponds to the intensity at 2ϴ ≈ 18°.

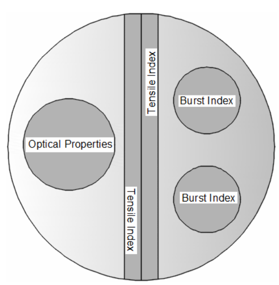

Figure 2: Sections of the papers used in measuring optical and mechanical properties

Statistical analysis

To determine if there is a statistically significant difference between the means of independent groups, a one-way analysis of variance (SPSS for Windows, version 16.0) was performed. The Duncan test was then used to determine the impact of different ratios of starch-containing AKD on paper properties. Pearson's correlation coefficient tests (at the 0.05 significance level) were performed to determine if a linear relationship existed. Taguchi devised an orthogonal array form to construct efficient tests, analyze data, and reduce the number of trials. The result selected is L9 orthogonal array, which has two control parameters: starch content in AKD emulsion and AKD dosage applied to pulps. The identifications demonstrate how parameter and level influence the responses (optical and mechanical properties of papers). The results of the studies are converted into S/N ratios, from which the deviation from typical quality is calculated. There are three choices of S/N ratio, *i.e.*, "Larger is better", "Nominal is the best" and "Smaller is better". In this research, "larger is better" was chosen for whiteness, brightness, tensile index and burst index, expressed by Equation 3, and "smaller is better" –for yellowness and Cobb values, expressed by Equation 4:[24–26]

Larger is better: $10xLog_{10}(sum(1/Y^2)/n)$ (3)

Smaller is better: $10xLog_{10}(sum(Y^2)/n)$ (4)

where Y is the observed data, n is the number of observations.

RESULTS AND DISCUSSION

Effects of AKD sizing on optical and mechanical properties of the papers

Optical properties of papers made from CTMP, KP and BKP sized with different ratios of starch-containing AKD emulsions were presented in Table 3. The sizing of the papers with AKD emulsions caused partial reductions in the whiteness and brightness values of the pulps, with the exception of KP. While the AKD sizing had no statistically significant impact on the CTMP yellowness values, it had on KP and BKP yellowness values.

The optical characteristics of the paper, in particular its brightness, are critical for printing. Sizing treatments required for some applications can affect the appearance of the paper.[27] According to the table, sizing processes led to a decrease in the whiteness and brightness values of the paper. This may occur when one or more of the sizing treatment components have absorbed a substantial quantity of light. These reductions were particularly greater with BKP sizing. BKP pulps consist mainly of cellulose and hemicelluloses, and are obtained by increasing the brightness and whiteness values to the desired level after 5-6 stages of bleaching of unbleached kraft pulps.[28] The reason for these decreases in the optical properties of BKP lies in the better optical properties of BKP, compared to other pulp types (KP and CTMP).

Effects of starch content on optical properties

The relationship between the starch content and optical properties of the papers was evaluated by the Pearson correlation test. Correlation analyses indicated that the starch content significantly affected the brightness (-0.545, $p<0.05$) and whiteness (-0.637, $p<0.05$) of the papers, with the exception of yellowness (-0.237, $p<0.05$) in the sizing of KP. The starch content used in preparing the AKD emulsion had a significant ($p<0.05$) adverse effect on the optical properties of KP papers. Correlation analysis showed an adverse effect for BKP (Brightness: -0.605; Whiteness: -0.686; Yellowness: 0.461, $p<0.05$) and CTMP (Brightness: -0.483; Whiteness: -0.742; Yellowness: -0.104, $p<0.05$) papers. In short, increasing the starch content used to make the AKD emulsion adversely affects the optical properties of the sized paper.

Table 4 shows the effects of sizing parameters on the optical properties of pulps in Taguchi analyses. While the starch content was found to be the most effective parameter for KP (0.68: Max-min S/N ratio) and CTMP (0.06) sizing when preparing the AKD emulsion, it proved to be for BKP (0.04) as less effective. This is believed to be due to the natural color of starch, which is white, compared to the color of KP and CTMP, which is darker.

Effects of AKD dosage on optical properties

The relationship between the optical properties and the AKD dosage used for internal sizing of the pulps was determined with the Pearson correlation test. In internal sizing of KP, the analyses revealed that the AKD dosage only slightly enhanced brightness (0.162, $p<0.05$), whiteness (0.110, $p<0.05$) and yellowness (-0.361, $p<0.05$) of papers.

Table 3
Optical properties of AKD-sized papers

Starch (%)	AKD (%)	Whiteness (ISO%)			Brightness (ISO%)			Yellowness		
		KP	BKP	CTMP	KP	BKP	CTMP	KP	BKP	CTMP
0	0	24.54^{bcd}	71.95^{a}	57.87^{a}	15.27^{abc}	67.17^{a}	41.66^{a}	56.92^{c}	8.95^{a}	38.90^{a}
1	0.1	24.71^{abc}	68.17^{c}	56.57^{b}	15.39^{abc}	61.07^{c}	40.97^{b}	56.53^{c}	14.26^{bc}	37.70^{a}
1	0.2	25.19^{ab}	68.28^{b}	56.42^{bc}	15.71^{ab}	61.06^{c}	40.87^{bc}	56.35^{c}	14.48^{bc}	38.61^{a}
1	0.3	25.45^{a}	69.16^{c}	56.33^{bcd}	15.88^{a}	62.07^{b}	40.89^{bc}	56.17^{bc}	14.02^{b}	38.45^{a}
2	0.1	23.75^{de}	68.49^{c}	55.81^{f}	15.09^{bcd}	61.41^{bc}	40.34^{c}	54.83^{ab}	14.15^{b}	38.74^{a}
2	0.2	22.87^{fg}	68.28^{c}	56.16^{cde}	14.39^{de}	61.08^{c}	40.92^{b}	55.49^{bc}	15.52^{c}	38.15^{a}
2	0.3	24.15^{cde}	68.39^{c}	56.38^{bcd}	15.41^{abc}	61.36^{bc}	41.08^{b}	53.89^{a}	14.16^{b}	37.95^{a}
3	0.1	22.59^{g}	68.02^{c}	55.87^{ef}	14.01^{e}	61.30^{bc}	40.64^{bc}	56.83^{c}	13.69^{b}	38.20^{a}
3	0.2	23.59^{ef}	68.11^{c}	56.10^{cdef}	14.79^{cd}	61.14^{c}	40.72^{bc}	55.64^{bc}	14.07^{b}	38.35^{a}
3	0.3	23.57^{ef}	68.14^{c}	56.04^{def}	14.74^{cd}	61.25^{bc}	40.63^{bc}	55.79^{bc}	13.91^{b}	38.43^{a}
	Sig.	.000	.000	.000	.000	.000	.001	.001	.000	.576

*Mean values with the same lowercase letters are not significantly different at 95% confidence level according to Duncan's mean separation test

Table 4
Response mean S/N ratio for optical parameters and significant interaction

Pulp type	Sizing parameter	Mean S/N ratio for optical properties				
		Level 1	Level 2	Level 3	Max-min	Rank
KP	Starch (%)	25.47	25.03	24.79	0.68	1
	AKD (%)	24.97	25.06	25.27	0.30	2
BKP	Starch (%)	36.21	36.20	36.17	0.04	2
	AKD (%)	36.19	36.17	36.23	0.06	1
CTMP	Starch (%)	33.41	33.38	33.35	0.06	1
	AKD (%)	33.36	33.39	33.40	0.04	2

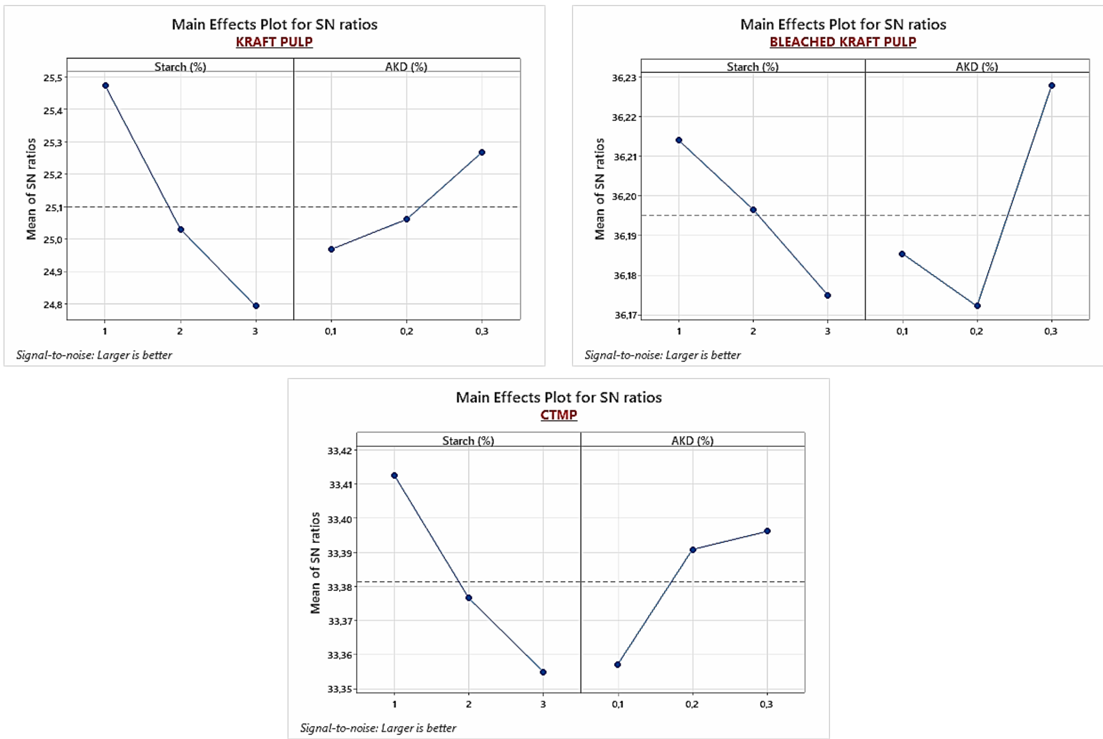

Figure 3: Mean of the single-to-noise (S/N) graph for optical properties

In contrast, increases in AKD dosage had a remarkable effect on the brightness (-0.528, p<0.05), whiteness (-0.480, p<0.05) and yellowness (0.520, p<0.05) of papers in BKP sizing. In CTMP sizing, while it significantly affected whiteness (-0.432, p<0.05), it did not show a significant effect on brightness (-0.193, p<0.05) and yellowness values (-0.108, p<0.05) of the papers. The different effects of AKD dosage on pulp types are due to the different optical properties of the pulps (KP: dark brown, BKP: white, CTMP: yellowish) and AKD (yellowish).

In the Taguchi analyses results (Table 4), it can be seen that AKD is the most effective parameter for optical properties only in the BKP sizing (0.06: max-min S/N ratio), among the parameters applied for the sizing of three different pulps. The effect of AKD dosage used in KP (0.3) and CTMP (0.04) sizing was less than that of the starch content.

Figure 3 depicts the mean of the single-to-noise (S/N) diagram for the optical properties of pulps analyzed using the Taguchi technique. According to this method, the optimal parameters of the sizing process for optical properties were determined as 1% starch content and 0.3 AKD dosages for all pulp types.

Table 5
Mechanical properties of AKD-sized papers

Starch (%)	AKD (%)	Tensile Index (Nm/g) KP	Tensile Index (Nm/g) BKP	Tensile Index (Nm/g) CTMP	Burst Index (kPa m²/gr) KP	Burst Index (kPa m²/gr) BKP	Burst Index (kPa m²/gr) CTMP
0	0	73.14[a]	69.43[a]	24.52[ab]	4.05[a]	4.20[ab]	1.10[a]
1	0.1	72.50[a]	69.11[a]	24.57[ab]	4.07[a]	3.80[b]	1.11[a]
1	0.2	72.95[a]	68.70[a]	26.14[a]	3.64[bc]	3.66[b]	1.07[a]
1	0.3	72.91[a]	72.43[a]	26.03[a]	3.57[c]	4.21[ab]	1.07[a]
2	0.1	72.92[a]	71.44[a]	24.78[ab]	4.00[ab]	4.39[ab]	1.07[a]
2	0.2	71.27[a]	71.97[a]	24.37[ab]	4.00[ab]	4.28[ab]	1.02[ab]
2	0.3	71.24[a]	72.73[a]	22.07[b]	3.65[bc]	3.98[ab]	0.91[c]
3	0.1	71.46[a]	71.56[a]	25.30[ab]	3.54[c]	4.70[ab]	1.07[a]
3	0.2	72.62[a]	71.73[a]	22.78[ab]	3.68[abc]	4.14[a]	0.93[bc]
3	0.3	71.76[a]	72.12[a]	22.98[ab]	3.72[abc]	4.65[a]	1.03[a]
	Sig.	.617	.590	.314	.010	.105	.000

*Mean values with the same lowercase letters are not significantly different at 95% confidence level according to Duncan's mean separation test

Table 6
Response mean S/N ratio for mechanical parameters and significant interaction

Pulp type	Sizing parameter	Mean S/N ratio for mechanical properties Level 1	Level 2	Level 3	Max-min	Rank
KP	Starch (%)	14.38	14.74	14.17	0.57	2
	AKD (%)	14.69	14.49	14.10	0.59	1
BKP	Starch (%)	14.68	15.21	15.78	1.10	1
	AKD (%)	15.53	14.69	15.44	0.84	2
CTMP	Starch (%)	3.647	2.918	3.042	0.729	1
	AKD (%)	3.631	3.017	2.959	0.672	2

From Table 5, it can be seen that there is no statistically significant effect of AKD sizing on the tensile indices of KP, BKP and CTMP, while it has a significant effect on the burst indices of KP and CTMP.

The beta-keto ester linkages are formed when the four-sided lactone ring in AKD interacts with the hydroxyl groups of cellulose and hemicelluloses.[9,18] This process renders the hydroxyl groups in cellulose and hemicelluloses unavailable to form hydrogen bonds with one another, resulting in a decrease in fiber-to-fiber bonding and strength properties. Although it is widely recognized that sizing has a negative impact on the strength properties of paper, still there is some disagreement in this matter.[1] Starch, used as a dry strength agent in the paper industry,[29,30] eliminates the strength losses caused by AKD. Sizing of KP and CTMP with AKD had no significant effect, although there were strength losses. However, increases in strength of 3-4% were observed with BKP sizing, compared to AKD-free papers.

Effects of starch content on mechanical properties

Correlation analyses (Pearson) revealed that the starch content had a significant adverse effect on the tensile (-0.721, $p<0.05$) and burst (-0.484, $p<0.05$) indices of the papers in the KP sizing. While starch content did not have a critical impact on the tensile (-0.180, $p<0.05$) and burst (-0.389, $p<0.05$) indices of the CTMP sizing, it showed a positive effect especially on tensile strength (0.782, $p<0.05$) in the sizing of BKP.

Among the factors that could affect the sizing of three different pulps, the results of the Taguchi analysis in Table 6 show that the starch content in the AKD emulsion is the most efficient parameter for the strength properties in the BKP (1.10: max-min -S/N ratio) and CTMP (0.729) sizing. The influence of starch content was less than that of AKD dosage in KP sizing (0.57).

Effects of AKD dosage on mechanical properties

According to Pearson correlation analyses, AKD dosage used in KP sizing showed a moderate decrease in tensile index (-0.497, $p<0.05$), while it showed little adverse effect on burst index (-0.155, p<0.05). The AKD dosage has a minimal negative effect on paper tensile (-0.180, p<0.05) and burst (-0.389, p<0.05) indices in CTMP sizing. Contrary to KP and CTMP sizing, the AKD dosage used in BKP sizing has a significantly positive effect on the tensile (0.782, p<0.05) and burst (0.424, p<0.05) strengths of the paper.

The effects of starch content in emulsion and AKD dosage applied to the pulps during sizing on mechanical properties of papers were determined by the Taguchi analysis method and the results were presented in Table 6. As can be seen from the table, the AKD dosage is more effective in (0.59: max-min S/N ratio) sizing of KP than starch. It is less effective in BKP (0.84) and CTMP (0.672) sizing processes.

The mean of the single-to-noise (S/N) diagram for the mechanical characteristics of pulps evaluated by the Taguchi method is shown in Figure 4. The ideal internal sizing process parameters for mechanical properties are 1% starch content and 0.1% AKD dosage for KP and CTMP, and 3% starch content and 0.3% AKD dosage for BKP, based on the Taguchi method.

Schematic representations of three-dimensional response surfaces and two-dimensional contour plots, showing the effects of starch content and AKD dosage on whiteness and brightness, as well as mechanical properties, are presented in Figures 5 and 6.

The varied forms of the contour plots indicate diverse interactions between factors. The correlations between the associated variables are insignificant in circular contour graphs. The elliptical contour indicated a wide range of interactions between the related variables.[31,32]

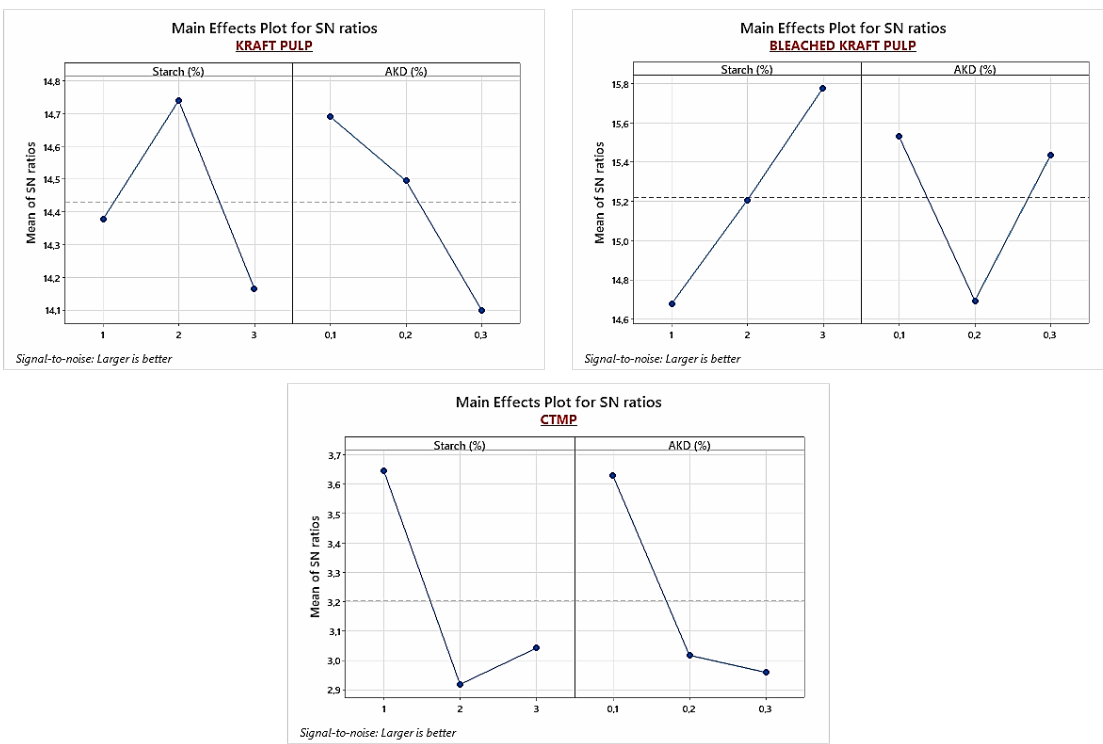

Figure 4: Mean of the single-to-noise (S/N) graph for mechanical properties

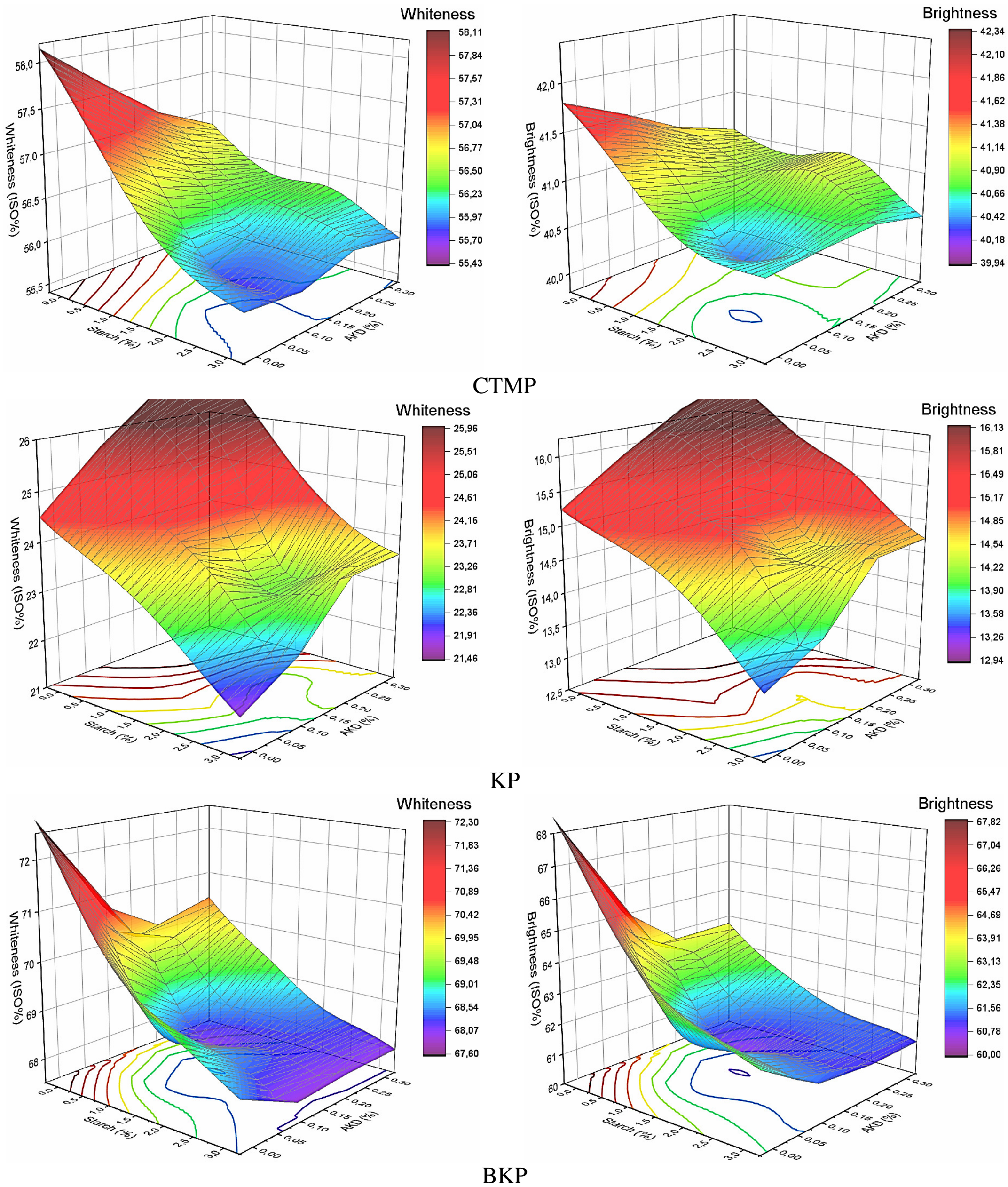

Figure 5: Response surface (3D) with (2D) contour plots presenting the interaction effects of starch content and AKD dosage on optical parameters of AKD-sized papers

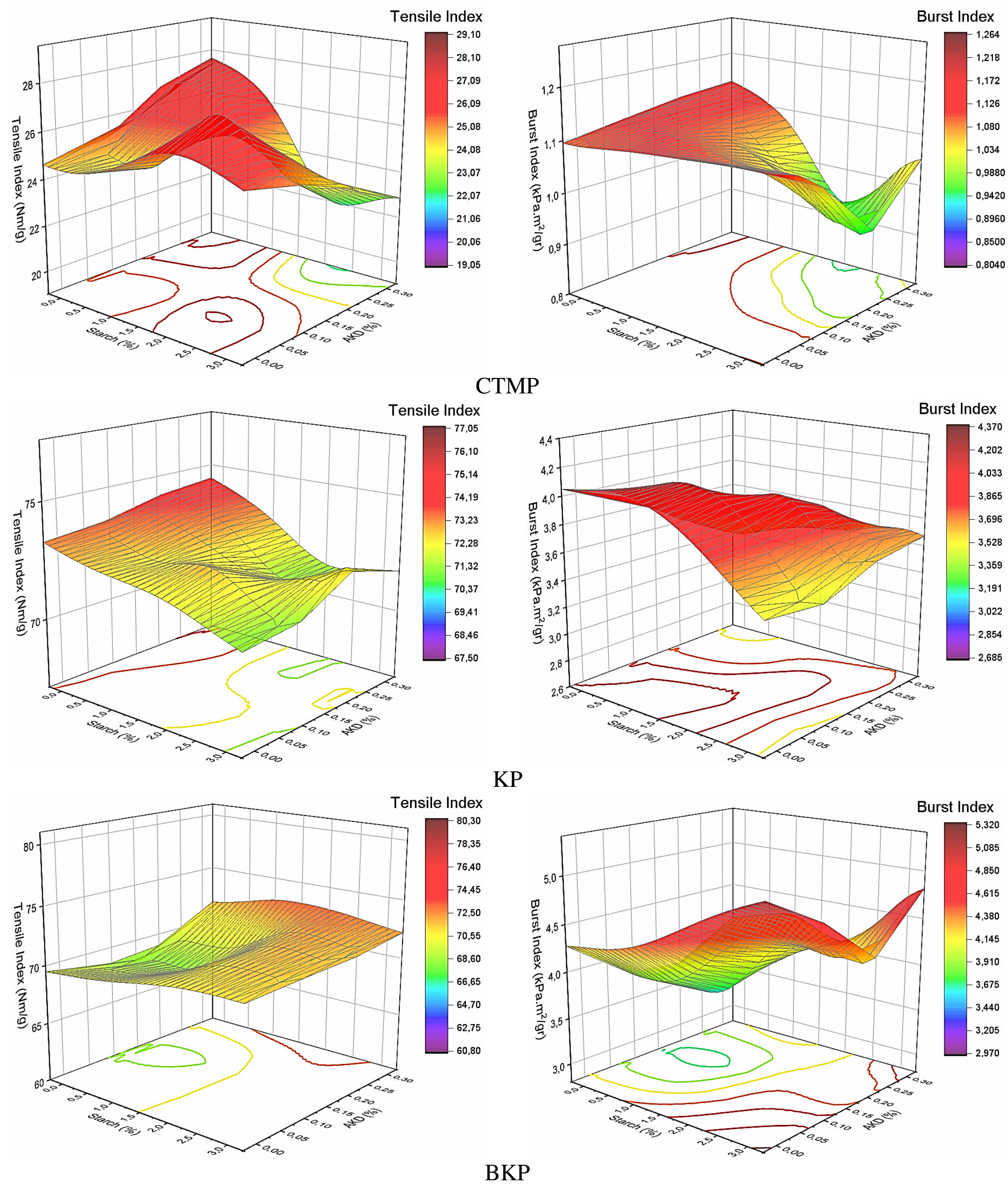

Figure 6: Response surface (3D) with (2D) contour plots presenting the interaction effects of starch content and AKD dosage on mechanical parameters of AKD-sized papers

Effects of AKD sizing on Cobb values and contact angles

The Cobb values of the various papers sized with different ratios of starch-containing AKD are presented in Table 7. The table shows that AKD sizing has a significant impact on the Cobb values of the papers. Water vapor transmission rate is the most important parameter for packaging materials. This rate must be increased to maintain the freshness of the food and protect it from the development of bacteria.[33] Innovative studies have been carried out to increase this parameter with coatings other than sizing. In coating processes, materials that provide water resistance, such as chitosan,[33,34] cellulose nanocrystals[35] and polyaniline,[36] are used. However, the coating with these materials did not form a uniform film on the paper surface. As can be seen from the table, AKD sizing has reduced the Cobb values of the papers to 20 g/m^2.

The minimum Cobb values of the KP, BKP and CTMP papers were determined to be 24.3, 22.4, and 19.9 g/m^2, respectively. AKD was most effective in sizing CTMP pulp, reducing the Cobb value by 90.9%. However, different ratios of starch-containing AKD emulsion led to irregularities in the sizing of CTMP, compared to KP and BKP. This is because CTMP pulps contain more lignin and extractives than KP and BKP. Simultaneously, the hydrophobic groups (phenylpropane and C14–C20) can stretch and orient outwards, forming a continuous film layer that is water-repellent.[33,34,39] It is also explained that the Cobb values of CTMP papers decreased more than those of the other papers.

Effects of starch content and AKD dosage on Cobb values

As a result of the Pearson correlation analyses on the data, the starch content (-0.630, $p<0.05$) in AKD emulsion significantly decreased the Cobb values in sizing of KP, while the AKD dosage (0.112, $p<0.05$) used did not show much effect. In BKP and CTMP sizing, both starch content (BKP: -0.686; CTMP: -0.624, $p<0.05$) and AKD dosage (BKP: -0.478; CTMP: -0.666, $p<0.05$) significantly decreased Cobb values. The correlation analyses show that the starch content in preparation of the AKD emulsion is highly effective on the water absorptiveness (Cobb) in the sizing of different pulp types. The addition of cationic starch to the AKD emulsion increases the sizing effect with AKD and aids in the neutralization of tiny anionic fractions.[40] Increasing the starch content when preparing the AKD emulsion reduced the Cobb values of papers and increased internal sizing efficiency.

Figure 7 depicts the effects of starch and AKD, as well as visual representations of three-dimensional response surfaces and two-dimensional contour plots.

The Taguchi analysis technique was used to investigate the influence of the starch content in emulsion and the AKD dosage given to the pulps during sizing on the Cobb values of the papers shown in Table 8. As shown in the table, AKD dosage is more effective than starch content in KP (1.38: max-min S/N ratio), BKP (1.78: max-min S/N ratio) and CTMP (3.46: max-min S/N ratio) sizing. Figure 8 depicts the mean of the single-to-noise (S/N) plot for Cobb values of papers assessed using the Taguchi technique.

Table 7
Cobb values (g/m^2) of AKD-sized papers

Starch (%)	AKD (%)	KP	BKP	CTMP
0	0	124.0^{c}	112.1^{f}	218.6^{c}
1	0.1	32.7^{b}	26.8^{bcd}	41.2^{b}
1	0.2	24.9^{a}	28.2^{cd}	20.4^{a}
1	0.3	24.7^{a}	22.4^{a}	19.9^{a}
2	0.1	31.5^{b}	25.4^{abc}	26.5^{b}
2	0.2	25.1^{a}	31.8^{e}	22.3^{a}
2	0.3	25.0^{a}	23.5^{a}	21.8^{a}
3	0.1	22.0^{a}	29.9^{de}	28.7^{b}
3	0.2	25.4^{a}	24.3^{ab}	21.8^{a}
3	0.3	24.3^{a}	22.7^{a}	22.0^{a}
Sig.		.000	.000	.000

Table 8
Response mean S/N ratio for Cobb values and significant interaction

Pulp type	Sizing parameter	Mean S/N ratio for Cobb				
		Level 1	Level 2	Level 3	Max-min	Rank
KP	Starch (%)	-28.69	-28.65	-27.73	0.96	2
	AKD (%)	-29.22	-28.01	-27.84	1.38	1
BKP	Starch (%)	-28.21	-28.55	-28.12	0.42	2
	AKD (%)	-28.75	-28.96	-27.17	1.78	1
CTMP	Starch (%)	-28.18	-27.44	-27.59	0.74	2
	AKD (%)	-30.01	-26.65	-26.55	3.46	1

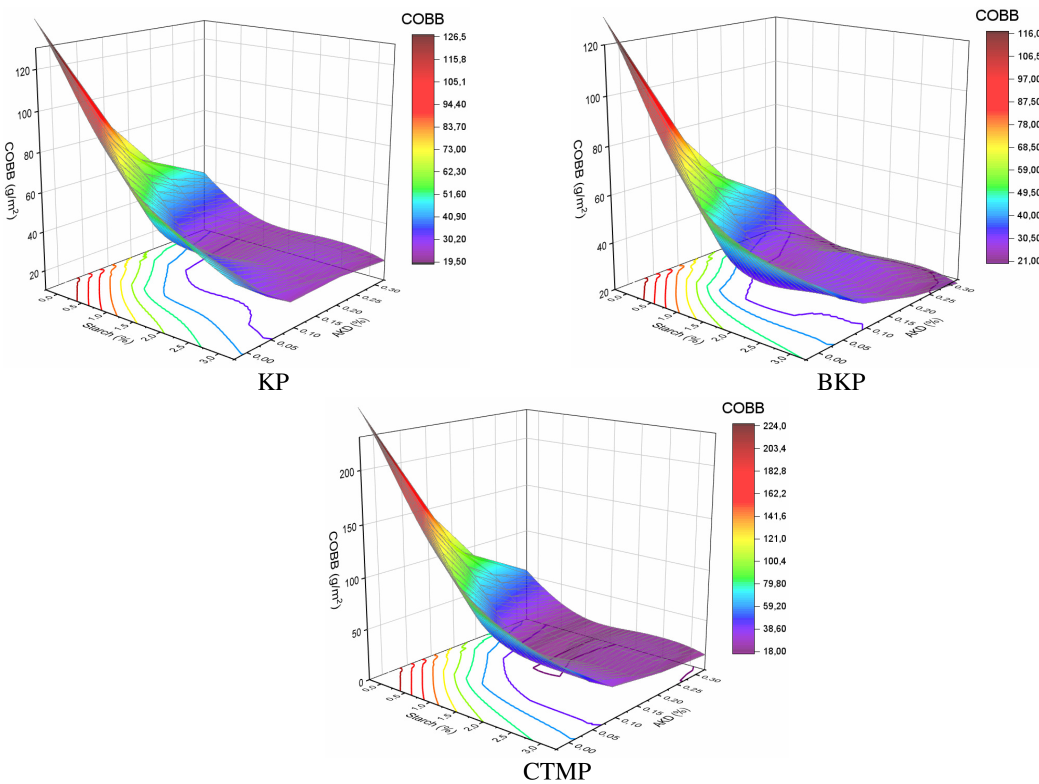

Figure 7: Response surface (3D) with (2D) contour plots presenting the interaction effects for Cobb values of AKD-sized papers

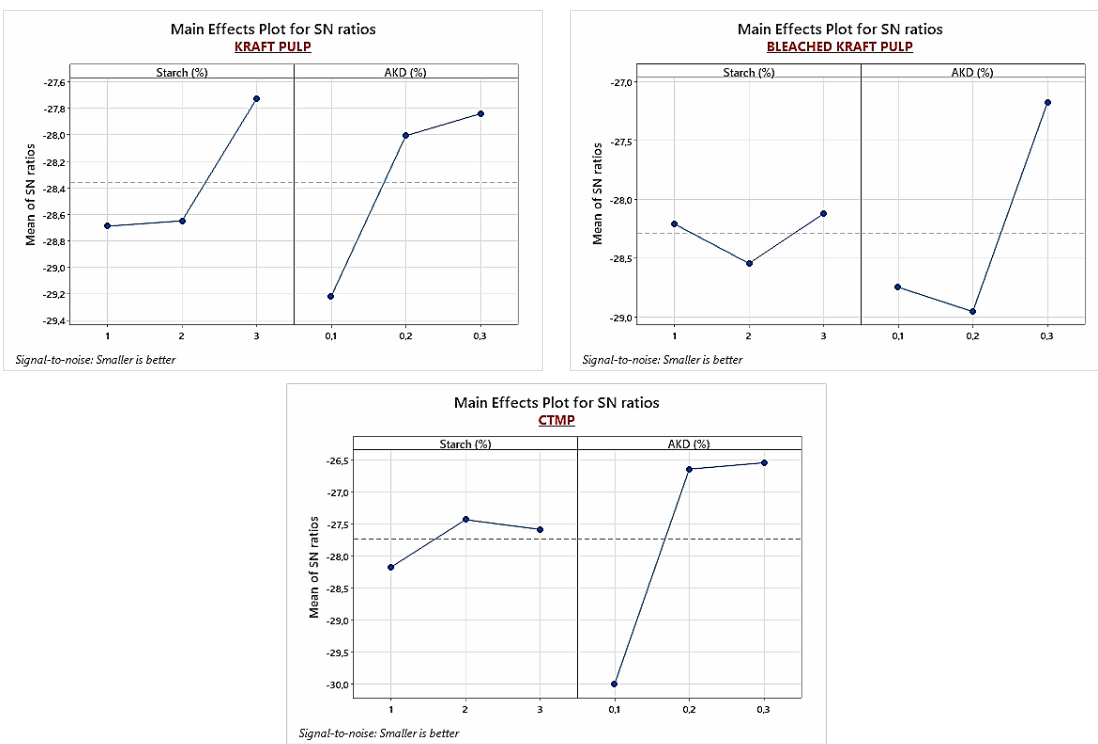

Figure 8: Mean of the single-to-noise (S/N) graph for Cobb values

For Cobb values, the appropriate internal sizing process parameters are 3% starch content and 0.3% AKD dosage for KP and BKP and 2% starch content and 0.3% AKD dosage for CTMP. Samples taken from sizing conditions, where optimum results were obtained in terms of Cobb values, were subjected to other analyses (contact angle, SEM and XRD).

Average contact angles and ratio of percentage change of water droplets on AKD-free and AKD-sized papers are illustrated in Figure 9.

If the adhesion forces between the drop and the paper surface are stronger than the cohesive forces of the liquid, the liquid will spontaneously spread onto the solid surface. It completely wets the solid surface. Otherwise, it will partially wet the surface and form a contact angle with the surface.[18,37,38] Figure 9 compares unsized and AKD-sized papers at the time of contact (15 s).

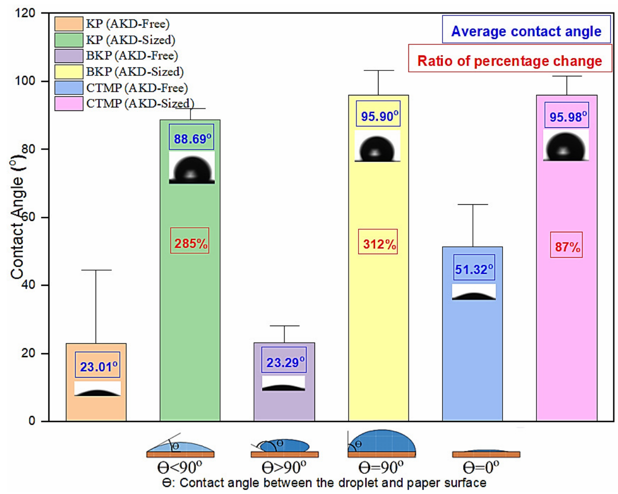

Figure 9: Contact angles and ratio of percentage changes of water droplets on AKD-free and AKD-sized papers

Table 9
Contact angle with increasing time

Contact time (s)	KP-unsized (Θ°)	KP-sized (Θ°)	BKP-unsized (Θ°)	BKP-sized (Θ°)	CTMP-unsized (Θ°)	CTMP-sized (Θ°)
1	44.5	91.2	28.1	103.3	63.8	100.8
2	41.3	92.1	26.5	103.3	63.6	101.6
3	34.7	88.0	24.9	101.6	62.3	96.1
4	32.0	86.4	24.5	100.0	60.1	97.1
5	28.6	88.5	24.2	99.4	58.2	93.4
6	24.0	88.8	23.8	95.8	58.1	94.8
7	21.2	91.1	23.6	95.8	55.1	97.6
8	19.2	87.6	23.3	93.7	53.2	88.2
9	17.6	88.2	23.0	93.6	48.3	96.5
10	16.0	90.3	22.5	93.0	44.7	97.8
11	13.8	84.7	21.9	92.9	43.9	99.9
12	13.8	89.6	21.5	92.9	41.3	97.0
13	13.3	87.5	21.1	91.7	39.8	92.8
14	13.8	89.3	20.6	91.0	39.5	92.3
15	11.5	87.1	20.0	90.6	37.9	94.0

As shown in Table 9, the water contact angle on the surface of unsized papers, except CTMP, approached zero, indicating that unsized KP and BKP fibers showed high surface wettability. However, fibers sized with AKD showed excellent hydrophobic behavior during contact (15 s). The contact angle is proportional to the time it takes for aqueous solutions to come into contact with paper during printing and other applications (contact time in milliseconds), it is important to study the relationship between contact angle and contact time.[18,43]

Table 9 demonstrates that the contact angle of various samples decreased with increasing time. According to the table, the reductions in contact angle were smaller for the sized papers than for the unsized ones. Therefore, sizing the pulps with AKD modified the surface energy of cellulosic fibers and made them hydrophobic.

SEM images and XRD patterns of AKD-sized and AKD-free papers

Figure 10 shows the surface morphology of AKD-free and AKD-sized papers. It has been found that AKD-free papers have smooth image contours and sharp edges.

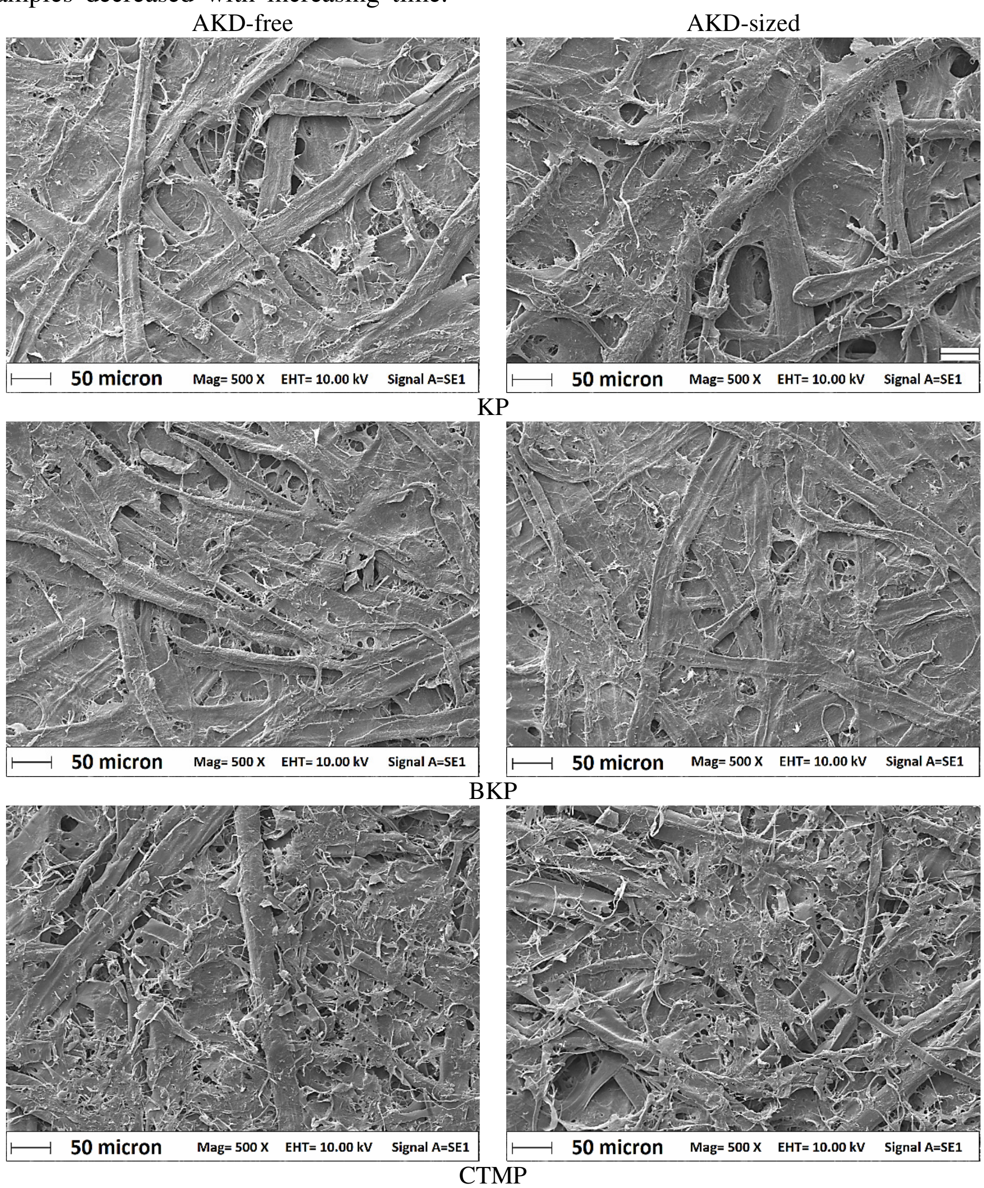

Figure 10: SEM images of AKD-free and AKD-sized papers

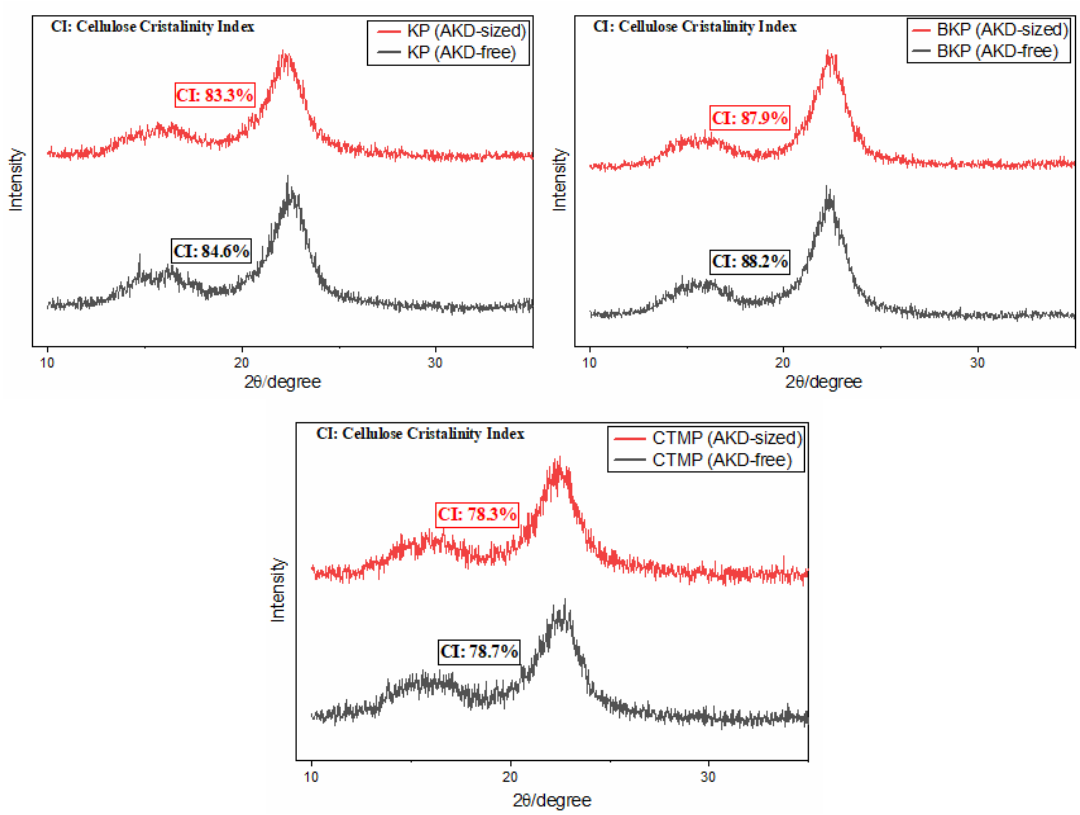

Figure 11: XRD patterns of the KD-sized (bottom) and AKD-free (top) papers

Table 10
Effects of AKD dosage and starch content on some paper properties

Sizing parameters	Increases in AKD dosage			Increases in starch content		
Pulp types / Properties	KP	BKP	CTMP	KP	BKP	CTMP
Tensile index	--	+++	-	---	+++	-
Burst index	-	++	-	--	+	--
Brightness	+	---	-	---	---	--
Whiteness	+	---	--	---	---	---
Yellowness	+	---	-	-	---	-
Cobb value	+	++	+++	+++	+++	+++

*The (+) symbol indicates a positive effect, and the (-) symbol indicates a negative effect. Increasing the number of symbols represents increasing the rate of effect

As a result of AKD sizing, white membrane materials cover most of the surface and interfiber gaps, forming a hydrophobic polymer layer on the paper surface.[18,44] No great morphological variation was found before or after AKD sizing.

Figure 11 shows the XRD patterns of the unsized (bottom) and sized (top) papers. The XRD pattern of the papers did not change much after AKD sizing, as shown in the figure, demonstrating the persistence of the crystalline structure and crystallinity of the cellulose. A comprehensive examination of the AKD sized and unsized paper samples confirms the first impression that AKD has no significant effect on cellulose crystallinity. Using Segal's peak height approach,[23] crystallinity indices of 84.6%, 88.2% and 78.7% were calculated for untreated KP, BKP and CTMP papers, respectively. The respective values for AKD sized papers were found to be 83.3%, 87.9% and 78.7%, respectively. A slight increase in the intensity of the amorphous region for AKD sized papers is due to the amorphous nature of AKD. A slight decrease in the degree of crystallinity of the AKD sized papers, compared to the unsized papers, can be explained in the same way.[45] The preservation of cellulose crystallinity could be viewed as AKD, which only interacts with the surface of the cellulose and does not damage the cellulose crystal structure.[46] These results indicated that the chemical interaction between AKD and different pulps did not modify the crystalline portion of the cellulose, implying that sizing the pulps with AKD only modified the surface energy of cellulose fibers; this is advantageous for the high-quality application of AKD.[47]

A summary showing the effects of AKD dosage used in various pulp sizing processes and starch content in the emulsion on some paper properties is given in Table 10.

CONCLUSION

In this study, different ratios of starch-containing AKD emulsions were prepared and various pulp types were sized with different AKD dosages. The effects of AKD on the properties of KP, BKP and CTMP sized papers were investigated. The influence of the starch content in the AKD emulsion and the AKD dosage added to the pulps on the paper properties was also studied. The findings obtained in the evaluated experimental setups demonstrated that differences in the pulp types used in the sizing process with AKD also had different effects on the paper properties. AKD has caused a deterioration in the optical properties of the papers produced, in particular the sizing of BKP. While AKD sizing causes a significant reduction in CTMP and KP burst strength, it has no significant impact on tensile strength. AKD was most effective in sizing CTMP pulp, reducing the Cobb value by 91%. Increases in starch content in the AKD emulsion adversely affected the mechanical and optical properties of all pulps, except the tensile and burst strengths of BKP. Increases in the AKD dosage applied to the pulps improved the optical properties of KP, but decreased the optical and mechanical properties of the other pulps. When Cobb values were examined, increases in starch content used in preparing the AKD emulsion significantly increased the water resistance of all pulps, while increases in AKD dosage were most effective at Cobb values of CTMP. The water contact angle on the surface of unsized papers, except CTMP, approached zero, indicating that KP and BKP fibers showed high surface wettability. In terms of contact angle, AKD sizing was most effective in BKP, while least effective in CTMP. The chemical interaction between AKD and various pulps did not change the crystalline structure of the cellulose, meaning that sizing the pulps with AKD only changed the surface energy of cellulose fibers. In sum, it has been determined that there are differences in the performance of pulp types in sizing with AKD and that the starch content in the preparation of the AKD emulsion and the AKD dosage applied to the pulps have different effects on each pulp type.

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