Evaluation of Fire Resistance, Thermal and Optical Properties of Bleached Kraft Paper Using some Boron Compounds and Soy Protein Binders

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Bleached kraft papers obtained from unbeaten (UB) and beaten (B) pulps were separately treated with zinc borate (ZB) and boric acid (BA) to improve their flame retardancy. The immersion method was chosen for application, and natural soy protein was added as a binder. The combined effect of soy protein (SP) and used boron compounds was observed. To investigate the thermal and fire resistance properties of the bleached kraft papers (BKP), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), limited oxygen index levels (LOI), and UL-94 burning test were performed. The brightness and color parameters (L^*, a^*, b^*, ΔL^*, Δa^*, Δb^*, ΔE^*) were also measured to determine the optical properties. The results showed that the combined effect of ZB and BA used with SP increased the flame resistance of kraft papers. The bleached kraft paper treated with BA had better flame retardancy in terms of LOI and UL-94 burning tests than paper treated with ZB. These results were also consistent with the TGA and DSC findings. Furthermore, the optical properties varied slightly depending on the chemical usage rates. Zinc borate and SP had a more positive effect on the brightness values of the bleached kraft papers compared to BA and SP.

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INTRODUCTION

As one of the most abundant natural polymers, cellulose offers great potential for the development of a wide range of materials with diverse applications. It is attracting considerable interest due to its renewability and biodegradability (Murigi *et al.* 2014). Paper production is the most important application area of cellulosic materials. For this, wood fibers are first converted into pulp by mechanical or chemical modification (Figueiredo *et al.* 2010). Kraft pulping is the most widely used method due to the superior strength properties of the resulting paper compared to those produced by other chemical pulping methods (Vaaler and Moe 2001).

Cellulosic paper serves as an important renewable resource and is widely used in various applications such as construction, packaging, interior decoration and daily consumer goods due to its light weight and cost effectiveness (Xu *et al.* 2019). Paper produced from cellulosic fibers is highly flammable (Lewin and Basch 1978). This natural property poses a safety issue and limits its range of applications (Upadhyay *et al.* 2023).

Therefore, improving the flame-retardant properties of cellulosic papers is crucial to reduce fire incidents and expand their application areas (Xu *et al.* 2019). Flame retardant papers are commonly used in various application areas, especially for the long-term preservation of valuable materials such as archival documents, books and other specialized items (Zhu 2021).

Flame retardants are substances added to delay the ignition of a flammable material when exposed to flame or to reduce the spread of the resulting flame (Levchik 2007; Ali *et al.* 2018; Mohd Sabee *et al.* 2022). They increase the fire resistance of biocomposite materials, wood and textiles, thereby expanding their application areas (Madyaratri *et al.* 2022). Flame retardants are generally classified as halogenated organic, nitrogen-containing, phosphorous-containing and inorganic (Birnbaum and Staskal 2004). While certain flame retardants have beneficial properties, they also have health and environmental drawbacks (Shaw 2010).

Boron-containing flame retardants have exceptional flame resistance and effective smoke suppression properties, particularly for cellulose-based materials such as cotton, wood, and paper (Armitage *et al.* 1996; Mostashari and Fayyaz 2008; Fang *et al.* 2016). Zinc borate (ZB) is a boron-containing flame retardant and smoke suppressant compound (Polat and Sayan 2020). It is widely used to obtain flame retardant polymer composites and acts as an afterglow suppressant (Ipek 2021; Shen *et al*. 2008). Boric acid (BA) is an inorganic compound known for its flame-retardant properties in wood, paper, and cotton (Shen *et al*. 2019). It prevents the spread of flames during combustion when added to cellulose-based insulation materials (Ohlemiller 1990). Boron derivatives are known as non-durable flame retardants for cellulosic fibers because they can be washed away with water. It is therefore advisable to use them in combination with a binder, which creates a synergy and increases the durability of the fibers (Cakal *et al.* 2011). The coating is a layer of material, which can be in liquid, gaseous, or solid form, applied to the surface of an object (Howarth and Manock 1997; Mohd Sabee *et al.* 2022). The application of fire retardant coatings to improve the fire resistance of materials has emerged as a promising option due to its effectiveness, efficiency, and economic advantages (Zheng *et al.* 2019).

Additives are any substance added to the coating material in small quantities to enhance specific properties of the final coating during its storage, transportation, or application (Bieleman 2008). Biopolymers used as paper surface coatings can replace existing synthetic coating materials. As a renewable resource, biopolymers offer many environmental benefits such as biodegradability, improved recyclability, non-toxicity, and biocompatibility (Rastogi and Samyn 2015). The use of renewable biodegradable polymers as additives has become a promising research topic. According to Andersson (2008) and Khwaldia *et al.* (2010), various biopolymers, including polysaccharides, proteins, lipids, and polyesters, have been utilized for coating paper and paperboard. Proteins derived from plants and animals exhibit remarkable film-forming abilities (Rastogi and Samyn 2015). In particular, Park *et al.* (2000) found that isolated soy protein (ISP) has exceptional film-forming properties. Plant proteins have also been used as binders (Fahmy *et al*. 2010). In addition, proteins are of great interest in flame retardant applications due to their non-toxic nature, safe, environmentally friendly properties and high nitrogen content. In recent years, proteins derived from sources such as soy, whey, keratin and casein have been particularly used for this (Dong *et al.* 2023). The renewable nature and functional properties of soy protein isolate (SPI) make it a valuable material for a wide range of applications in some industries such as food, agriculture, bioscience and biotechnology (Song *et al.* 2011).

This study determined the changes in the combustion, thermal, and optical properties of bleached kraft papers treated with zinc borate and boric acid chemicals, using natural soy protein as a binder, and to compare the performance efficiencies of these chemicals.

EXPERIMENTAL

Materials

In this study, commercially available bleached hardwood (eucalyptus) kraft cellulose was used as the lignocellulosic material for producing paper handsheets. Commercially available soy protein isolate (90% protein, Alphasol) was used as a binder for solution preparation. Zinc borate (Riedel-de Haen Germany) and boric acid (Tekkim Kimya-Türkiye) were used as flame retardants.

Pulp and Handsheet Preparation

In the first stage, the supplied ready-made bleached cellulose (eucalyptus) was first cut into small pieces to prepare kraft pulp. To provide sufficient fiber separation and dispersion, the defibration process was conducted using a laboratory scale disintegrator at 3000 rpm ±25 for 10 minutes. The beating process of pulp was carried out using a laboratory Valley type Hollander beater in accordance with TAPPI T 200 sp-10 (2010). The freeness of these pulp samples was measured according to SCAN-C 19:65 (1964) using a Schopper-Riegler Freeness Tester. After these stages, handsheets of about 60 g/m^2 were prepared from the bleached kraft pulp in two groups, beaten and unbeaten. Ten test papers were produced for each group using a Rapid-Köthen test paper machine according to TAPPI T 205 sp-02 (2006) standard. The resulting handsheets were conditioned for 24 h at 23 ± 1 °C and 50 ± 2% relative humidity according to TAPPI T 402 om-93 (1993). All test papers were produced with low basis weight, particularly to determine their performance for thermal stability and flame resistance. The main reason for this choice was to provide similarity with archival documents and special thin papers, so that the tests better reflect real world applications and provide for a more flammable test environment.

Chemical Preparation and Application Method

Chemical solutions were prepared using zinc borate and boric acid, at concentrations of 3% and 5% (w/v) for each, and soy protein at a concentration of 1.5% (w/v). The experimental parameters are defined in Table 1. The prepared aqueous solutions were applied to dried test paper surfaces for surface sizing by the immersion method (Kalyoncu and Peşman 2022) at ambient temperature until complete surface coverage was achieved. The papers were then passed through rollers to improve the adhesion of the chemicals to the substrate and to remove any excess solution from the paper surfaces. Following this treatment, the samples were dried for 10 minutes in the drying section of a laboratory scale paper testing machine (Rapid Köthen). The test papers were conditioned before analysis and measurements. The weight differences observed after the process in the examples have been calculated to be approximately 1.5%

Table 1. Experimental Parameters

Experimental Parameters
3% ZB
5% ZB
3% BA
5% BA
1.5% SP
3% SP
3% ZB+1.5% SP
5% ZB+3% SP
3% BA+1.5% SP
5% BA+3% SP
C
**ZB: Zinc borate, BA: Boric acid, SP: Soy protein, C: Control*

Thermal Properties

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to determine the thermal properties of the test papers. Differential scanning calorimetry measurements were carried out simultaneously with TGA measurements, and derivative curves of the weight change were recorded. The Perkin Elmer (model STA) 6000 thermogravimetric analyzer was used for TGA and DSC measurements at temperatures ranging from room temperature to 600 °C, under a nitrogen gas flow 20 mL/min, at a heating rate of 10 °C/min. The evaluation of thermal properties was applied only to paper samples produced from unbeaten pulps.

Fire Resistance Properties

Limiting oxygen index (LOI) test

The LOI is the amount of oxygen required for the material to burn in the air and is associated with difficulty of combustion when high and ease of ignition when low. Measurements of test paper samples were made using an oxygen index instrument (Dynisco Limiting Oxygen Index Chamber) in accordance with ASTM D2863-13. The LOI test was performed on paper samples, each measuring 130 mm × 15 mm × 0.18 mm, with five replicates for each group.

Flame test (UL-94)

The flammability test of paper samples was performed using the Vertical UL-94 Burning Test in accordance with ASTM D3801-10. This test represents the tendency of the paper samples to extinguish or spread the flame after being ignited. The flame test was performed with five replicates using paper samples with dimensions of 125 mm × 13 mm × 0.18 mm. The results are determined as measurement (remaining mass) and observation (smoke, ash formation, flame condition, *etc.*). This test is based on the principle that the samples are brought closer to the flame source at 10 second intervals and removed from the flame source after 10 seconds.

Optical Properties

Within the scope of the study, the optical properties of beaten and unbeaten papers were determined. The ISO brightness values of the paper sheets were measured according to the ISO/DIS 2470 (2016) standard. The color values of the paper sheets were calculated using the L^*, a^*, b^* values and the color difference (ΔE^*), as measured with a UV-

spectrophotometer (Konica-Minolta, CM-2600d, Osaka, Japan) using a UV filter (to avoid the interference from residual materials with fluorescence effects) in accordance with TAPPI standard T527 om-13 (2013). Ten test paper samples were used for each measurement.

RESULTS AND DISCUSSION

Thermal Properties

Thermogravimetric analysis measurements

Thermogravimetric analysis curves and derivatives for paper samples treated with boron compounds and soy protein are shown in Figs. 1 and 2, and the analysis results are presented in Table 2.

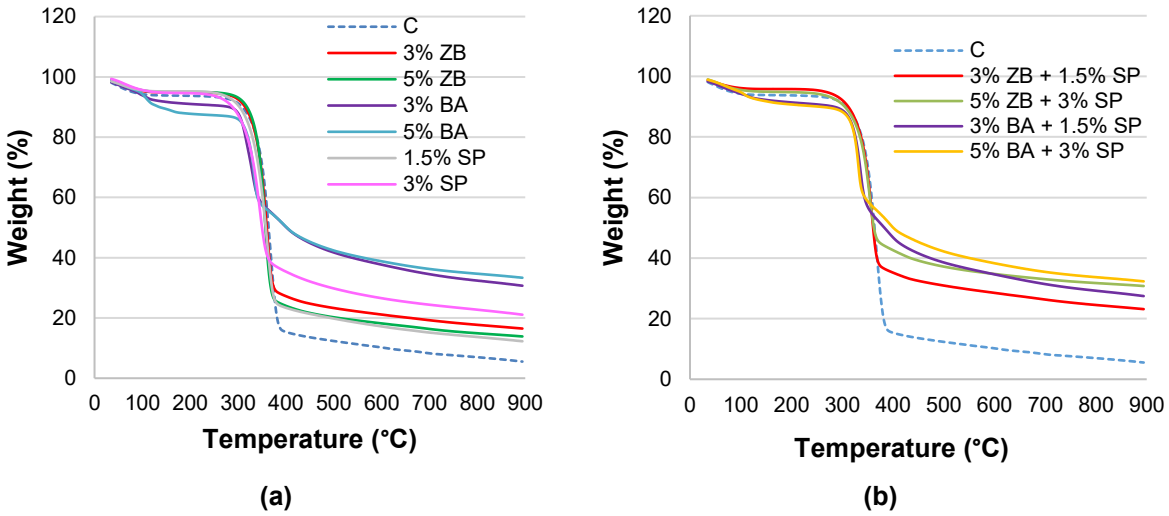


Fig. 1. Thermogravimetric analysis curves of samples

The weight loss diagrams as a function of temperature for the paper samples are shown in Fig. 1. The first step and the first small mass change for all samples is between 35 and 120 °C. The main reason for this initial change is the evaporation of moisture in the test paper samples. The other decomposition step occurred between temperatures of approximately 290 and 400 °C. This step can be described as the pyrolysis stage where the thermal decomposition of the samples begins. According to the graphs, it was observed that BA-applied papers ignited earlier than control paper and ZB-applied papers, and thus, weight loss due to the increasing temperature was first completed in the BA-applied papers.

Residual mass

The residual mass ratio of BA-applied papers at 800 °C was higher than the other groups. Thermogravimetric analysis (TGA) results indicate that the samples with a higher residual mass compared to the control have an increased amount of non-volatile matter. This is associated with an increased tendency for char formation during thermal decomposition. The resulting char layer acts as a physical protective barrier, reducing heat transfer and limiting the diffusion of oxygen to the underlying material. As a result, ignition of the sample is delayed, and its thermal stability is improved.

Boron compounds remove water molecules from cellulose before it reaches the ignition temperature and prevent the combustion from progressing by forming a glassy, protective layer on the cellulose surface through charring during combustion (Lu and Hamerton 2002; Shen *et al*. 2008).

In addition, as shown in Table 2, the observation of a lower onset temperature, inflection point and endset temperature for all treated test papers compared to the control sample indicates that degradation occurred at lower temperatures and within a narrower temperature range.

SP-treated papers showed improved flame resistance, demonstrating a protective effect against combustion. These samples showed reduced mass loss, and an increase in SP concentration led to a higher residual mass ratio. Paper samples treated with BA + SP tended to ignite earlier than both the control group and those treated with ZB + SP. The most favorable result was observed in the sample treated with 5% BA + 3% SP, which showed the lowest mass loss. The addition of SP contributed to a better preservation of mass during combustion.

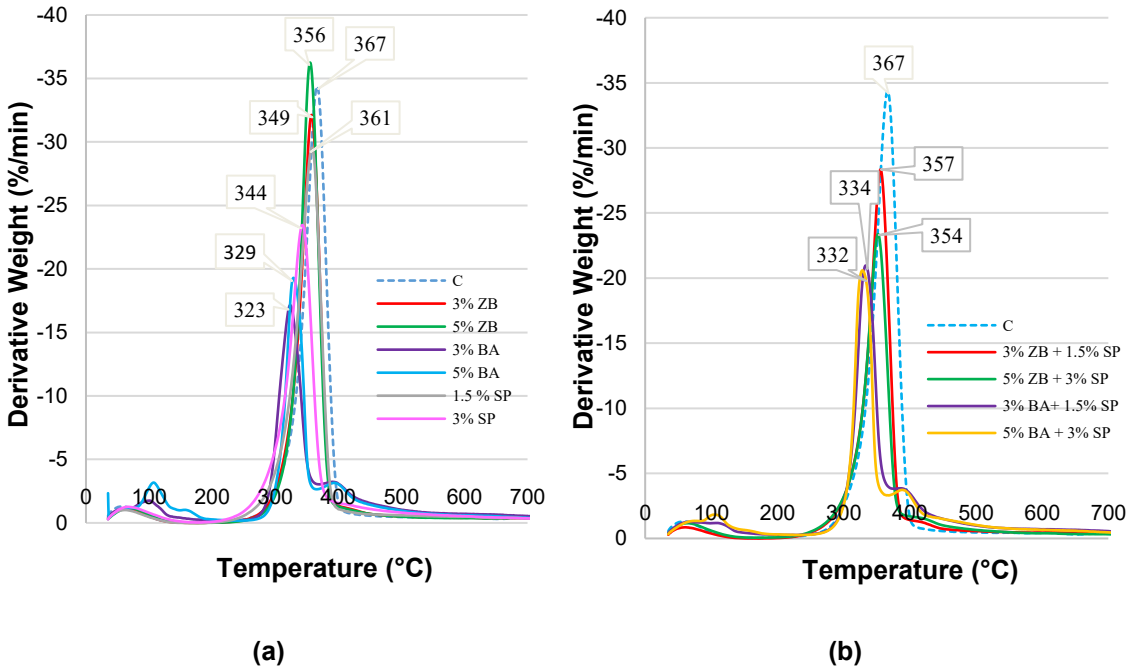


Fig. 2. The derivative weight changes and corresponding peak points in BA- and ZB-treated samples

Figure 2 shows the peaks associated with weight change and the weight losses that occur at these peaks. Chemical-dependent degradation generally starts at low temperatures. As shown in Fig. 2a, degradation started at low temperatures, especially with BA and SP additives, and the peak height decreases according to control. Although degradation started at lower temperatures with ZB compared to the control, the amount of derivative weight, especially with 5% ZB, resulted in a slightly higher peak than the control sample. The papers treated with 3% ZB and 5% ZB decomposed at the highest temperatures, while the papers treated with 3% BA and 5% BA decomposed at the lowest temperatures. Due to its ability to maintain its hydration up to 290 to 300 °C, zinc borate is suitable for use in the production of polymers requiring high-temperature resistance (Eltepe 2004). The lowest

peak height observed in 3% BA is associated with a small amount of decomposition product. Boric acid effectively protects the material from oxygen and heat by forming a glassy B_2O_3 layer on its surface under the influence of heat (Visakh *et al*. 2016; Xu *et al.* 2018).

Figure 2b shows the peak points associated with the change in weight of samples treated with BA + SP and ZB + SP mixtures. The peak height decreased as the ZB ratio increases, while the increase in the BA ratio does not cause a significant difference. In addition, the BA + SP treated papers had a lower peak height compared to the others.

Compared to the control, the degradation temperature at 3% SP decreased from 367 to 344 °C (Fig. 2a). As the SP ratio increased, the peak height and degradation rate decreased. When comparing ZB and BA, the papers treated with BA show lower peak heights and lower calorific values.

As shown in Table 2, the onset temperatures ranged from 305.61 to 341.23 °C. The onset temperatures of all test papers treated with only BA or containing BA were lower than those of the others, including the control. The highest onset temperature was recorded for the 5% ZB group, and the lowest for the 3% BA group. The inflection point temperature was 368.53 °C for the control, 330.71 °C for the %3 BA treated, 333.26 °C for the %5 BA treated, 336.49 °C for the 3% BA + 1.5% SP treated, and 332.70 °C for the 5% BA + 3% SP treated paper samples.

Table 2. TGA Results of Paper Samples

Sample Groups	Onset °C	Inflection Point °C	Endset °C	ΔY (%)	Residual Mass at 800 °C (%)
3% ZB	337.67	361.59	373.18	68.391	17.715
5% ZB	338.83	358.34	370.09	71.030	14.922
3% BA	305.61	330.71	356.00	46.062	32.395
5%BA	319.83	333.26	350.01	42.648	34.672
1.5% SP	320.52	362.05	375.34	72.103	13.686
3% SP	316.22	345.52	362.33	60.235	22.737
3% ZB+1.5% SP	335.09	360.08	370.52	60.429	24.518
5% ZB+3% SP	329.01	354.75	368.21	53.200	31.764
3% BA+1.5% SP	321.61	336.49	355.29	47.326	29.230
5% BA+3% SP	322.02	332.70	347.00	46.309	33.706
C	341.23	368.53	382.14	78.779	6.975
**ZB: Zinc borate, BA: Boric acid, SP: Soy protein, C: Control*					

In addition, the residual mass rate at 800 °C was higher for all papers treated with BA compared to other samples, including the control. All paper samples treated with BA started to degrade at low temperatures, completed the process early and produced the highest residue rate. These results show that BA led to a greater resistance to high temperatures. The turning point temperature was reached in the shortest time with samples containing 5% BA + 3% SP. The retention of BA increased with the addition of SP. The highest residue (34.7%), and therefore, the lowest degradation rate-Delta Y (42.6%) were obtained with samples treated with 5% BA. The time to reach the turning point temperature from the start was extended with the addition of SP to ZB. The application of SP with BA showed a more compatible effect. However, the residual mass of the paper samples treated with BA and SP (at 800 °C) was significantly higher, especially for 5% BA (34.7%) and

5% BA + 3% SP (33.7%), together with an increased carbonization degree. According to TGA results, while a high residual mass fraction was beneficial in maintaining the structural integrity of the test papers, it may also restrict the general usability of the paper in conventional applications. However, in specialized applications where enhanced flame retardancy is critical, this property may offer a significant advantage that contributes to improved fire resistance and safety standards.

DSC measurements

Differential Scanning Calorimetry (DSC) analysis curves of paper samples treated boron compounds and soy protein are displayed in Fig. 3. It measures heat flow and provides information about sample behavior of depending on temperature changes. Papers treated with BA produced fewer calories and had lower degradation peak heights compared to others (Fig. 3a). Similarly, samples treated with BA + SP and ZB + SP blends produced lower peak heights and therefore lower heat amounts than control samples (Fig. 3b). When compared in terms of fire retardancy and thermal resistance, the BA + SP application gave more effective results than the ZB + SP application, and heat formation decreased with SP supplementation.

As shown in Fig. 3, DSC analysis revealed a distinct exothermic peak at high temperatures for the control sample, indicating a rapid heat release. In contrast, the samples treated with BA and ZB showed broader and less intense thermal transitions, especially in the high-temperature range, indicating a reduction in heat release and an improvement in thermal stability. This effect was more pronounced in the groups containing soy protein (Fig. 3b). Such behavior is probably due to the endothermic nature of soy protein, resulting from dehydration processes and thermal degradation of protein structures. The BA + SP and ZB + SP samples showed lower thermal activity at elevated temperatures, indicating a potential for heat absorption that could delay combustion. In particular, the BA + SP combination showed superior flame retardancy and thermal stability compared to ZB + SP, highlighting the effectiveness of soy protein in reducing heat release.

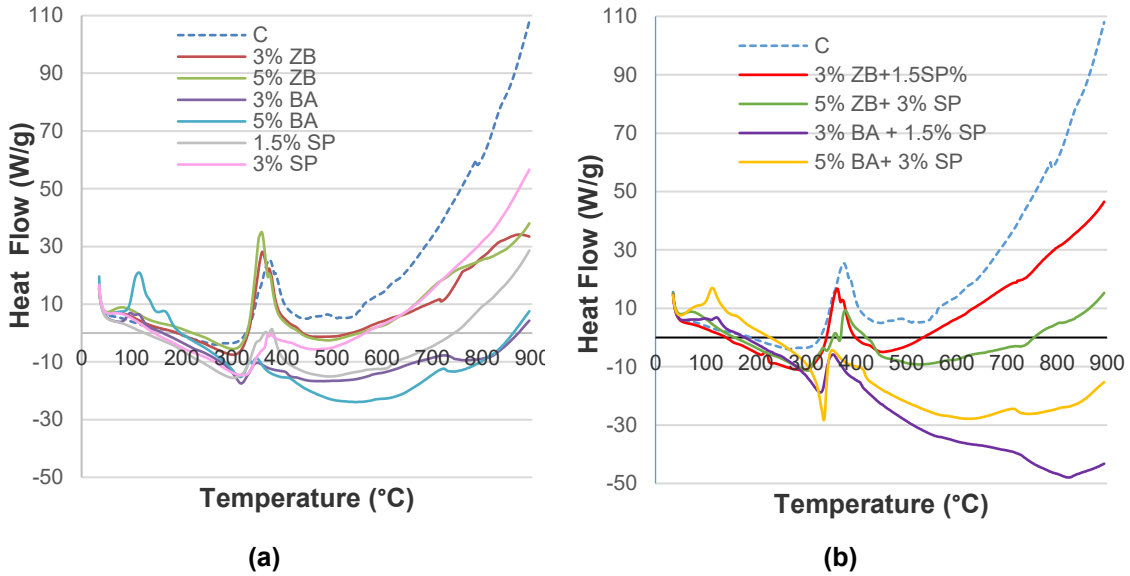


Fig. 3. Differential scanning calorimetry analysis curves of samples

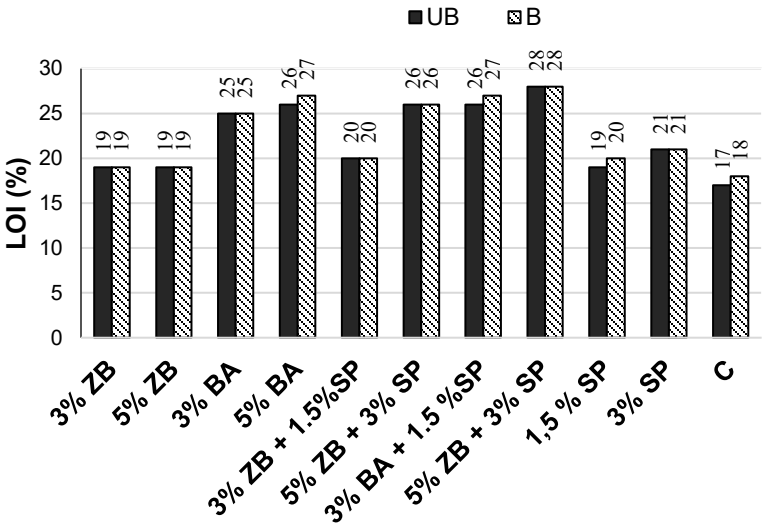
Fire Resistance

To accurately assess the flame retardancy of the test papers, the TGA data was interpreted in conjunction with standardized flammability tests such as the Limiting Oxygen Index (LOI) and UL-94 burning tests.

LOI levels

The test papers were analyzed with an LOI analyzer to determine the amount of oxygen needed to burn the paper. The LOI values of the unbeaten (UB) and beaten (B) test samples as a function of the type of chemical and their application rates are displayed in Fig. 4 as a percentage of oxygen. The LOI value of the control paper (UB: %17, B: %18) increased to 19 with ZB usage at both 3% and 5% rates. The beating status of the papers did not affect the results for ZB applied test papers. Test papers treated with BA showed higher LOI values. For papers treated with 3% BA, both unbeaten and beaten samples had LOI values of 25%, while for papers treated with 5% BA, these values increased to 26% for unbeaten samples and 27% for beaten samples. Higher LOI values indicate reduced flammability and improved flame retardancy (Laoutid *et al*. 2009; Schinazi *et al*. 2022).

The limiting oxygen index values increased significantly as the SP concentration increased from 1.5% to 3%. The use of ZB and BA in combination with SP reinforcement provided a moderate increase in the LOI values of the paper samples, enabling them to achieve higher fire resistance. The optimum combination was found to be 5% BA + 3% SP. The highest values, reaching 28%, were obtained for both UB and B papers treated with this combination. The main reason for this positive effect is the improved adhesion of both BA and ZB to the paper surfaces with the reinforcement of SP. In addition, there were no instances of smoke formation observed in the paper sample groups during LOI measurements. Observations during the test revealed that samples treated with BA exhibited green flames, whereas the other groups showed minimal to no smoke formation.



**Due to the minimal variation in standard deviations (±0.1 - ±0.3), standard deviations are not included in the chart.*

Fig. 4. The changes on the LOI levels of paper samples (UB: unbeaten, B: Beaten)

Flame test (UL-94)

The UL-94 test evaluated the flame retardancy of paper samples treated with BA and ZB. For all samples, the combustion process was completed within the first 10 second period. As can be seen in Fig. 5, the residual parts after combustion were significantly higher in samples treated with BA and ZB boron compounds than in the control group. Figure 5 also shows that the addition of SP improves UL-94 ratings across all concentrations of ZB and BA. Due to the adhesive properties of soy protein, positive results were obtained with samples treated with soy reinforcing boron compounds. The highest values were obtained from paper samples treated with 5% BA + 3% SP.

As shown in Fig. 6, the control samples burned completely, leaving ash behind. The boron compounds maintained the integrity of the sample during combustion, resulting in improved combustion resistance compared to the control group. The combustion performance of samples treated solely with soy protein was similar to that of the control; these samples burned quickly with minimal ash formation. However, the combination of soy protein with BA and ZB had a positive effect and gave good yield results. In particular, the combination of soy protein with BA achieved the highest burn resistance efficiency and the highest residual mass ratio. When BA, ZB, BA + SP, and ZB + SP were applied to the paper surface, the amount of paper remaining intact after burning was higher than the control.

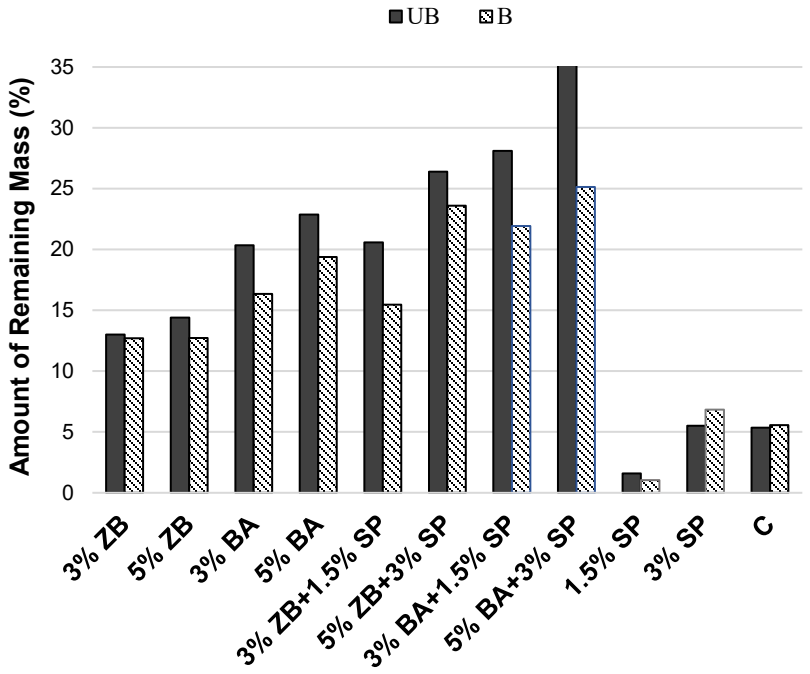


Fig. 5. Remaining mass of paper samples after UL-94 tests (UB: unbeaten, B: Beaten)

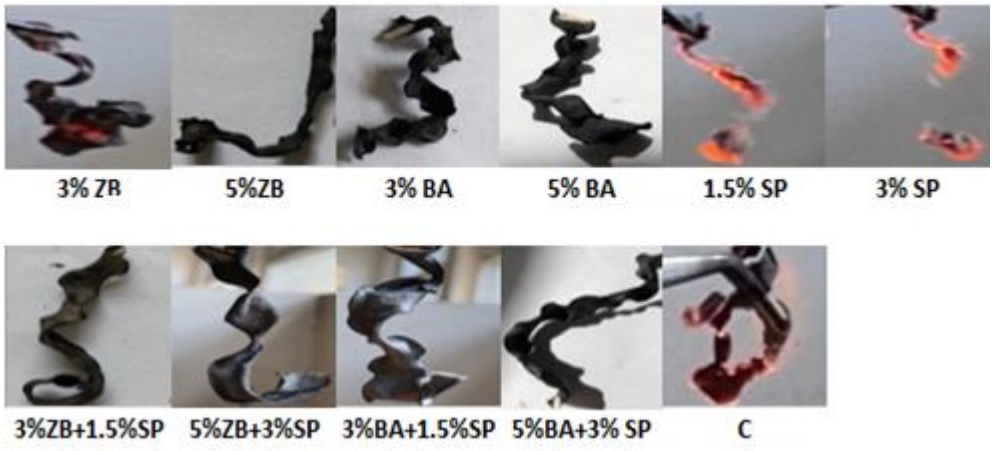


Fig. 6. Paper samples after UL-94 test

Optical Properties of Papers

The brightness values, the color coordinates (L^*, a^*, and b^*) and the color differences (ΔL^*, Δa^*, and Δb^*) of the test papers are presented in Tables 3, 4 and 5, respectively. The brightness values showed different trends depending on the experimental parameters. Beating effects reduced the brightness values for all test samples.

For unbeaten paper samples, the 3% ZB treatment gave higher brightness values than the 3% BA treatment. However, the 5% ZB treatments showed slightly lower brightness values than the 5% BA treatments. The addition of SP as an additive to the ZB process led to a further increase in brightness values, whereas its addition to the BA process caused a decrease in brightness values. This phenomenon can be attributed to the more pronounced effect of the natural yellowish hue of soy protein on the BA matrix.

Table 3. ISO Brightness Values of Paper Samples (UB: unbeaten, B: Beaten)

	ISO Brightness (%)	
	UB	B
3% ZB	82.09	71.64
5% ZB	79.00	67.41
3% BA	80.78	67.74
5% BA	80.63	61.83
1.5% SP	73.09	43.05
3% SP	61.08	52.93
3% ZB+1.5% SP	82.11	68.9
5% ZB+ 3% SP	81.29	69.39
3% BA+ 1.5% SP	79.57	62.88
5% BA+ 3% SP	79.53	60.77
Control	79.72	67.94

The CIE $L^*a^*b^*$ color space is a three-dimensional system that represents the spectrum of human color perception. The CIE L^* value in this color system indicates the lightness level and provides values similar to brightness, ranging from 0 to 100, with L^* 0 indicating black and L^* 100 indicating white. The CIE a^* value represents the color position along the red (+ a^*) to green (- a^*) axis, while the CIE b^* value represents the color position along the yellow (+ b^*) to blue (- b^*) axis (Altay *et al.* 2023; Hubbe *et al.* 2008).

Although CIE *L** values of all samples were close to each other, ZB was more effective than BA. As with the brightness values, the *L** values of the UB samples are higher than those of the B samples. The CIE *a** values of the papers treated with 5% ZB decreased to -0.02, changing the color of the paper to greenish. In addition, negative CIE *a** values indicated greenish color formation in unbeaten bleached kraft papers (UB-BKP) treated with ZB + SP and BA + SP. The CIE *a** values of the beaten bleached kraft papers(B-BKP) were measured to be 0.41 with 3% BA + 1.5% SP and 0.62 with 5% BA + 3% SP. This indicates that the reddish color of the papers increased slightly with the higher concentrations of BA and SP. When evaluating the CIE *b** color values, it was observed that SP contributed to a dominant yellow color, and the yellowness value increased with higher SP concentrations.

Table 4. CIE *L***a***b** Values of the Paper Samples (UB: unbeaten, B: Beaten)

		*L**		*a**		*b**	
		UB	B	UB	B	UB	B
3% ZB	Mean value	94.86	89.93	0.09	0.47	3.24	7.49
	Std. dev.	0.20	0.26	0.00	0.01	0.11	0.19
5% ZB	Mean value	93.57	88.89	-0.02	0.43	4.68	7.23
	Std. dev.	0.36	0.28	0.06	0.12	0.35	1.18
3% BA	Mean value	94,09	89.28	0.09	0.54	3.76	6.47
	Std. dev.	0.05	0.22	0.07	0.14	0.23	0.58
5% BA	Mean value	93,66	87.79	0.08	0.97	3.66	6.57
	Std. dev.	0.20	0.49	0.05	0.35	0.06	0.70
1.5% SP	Mean value	92.54	87.86	0.03	0.89	6.76	9.51
	Std. dev.	0,43	0.51	0.03	0.14	0.91	0.63
3% SP	Mean value	88.8	82,44	0.37	1.12	11.33	12.15
	Std. dev.	0.93	0.87	0.18	0.13	0.66	0.62
3% ZB + 1.5% SP	Mean value	94.6	90.09	-0.10	0.19	3.68	6.11
	Std. dev.	0.70	0.06	0.11	0.18	1.15	0.39
5% ZB + 3% SP	Mean value	94.97	90.97	-0.01	0.14	5.40	7.03
	Std. dev.	0.10	0.05	0.04	0.14	0.38	1.42
3% BA + 1.5% SP	Mean value	93.86	87.62	-0.11	0.41	4.48	7.38
	Std. dev.	0.41	0.43	0,03	0.17	0.37	0.48
5% BA + 3% SP	Mean value	93.36	89.00	-0.15	0.62	5.38	7.69
	Std. dev.	0.72	0.23	0.07	0.19	1.22	0.79
C	Mean value	92.26	88.53	0.00	0.36	3.71	6.95
	Std. dev.	0.01	002	0.00	0.03	0.13	0.01

For UB papers, *b** values increased in paper samples where ZB and BA were used with SP. For B papers, *b** values decreased with the use of ZB with SP, while *b** values increased with the use of BA with SP. Papers treated with 5% ZB + 3% SP among the unbeaten papers exhibit the highest yellowness values (Table 4).

The definitions of Δ*L**, Δ*a**, and Δ*b** are as follows: Δ*L** = difference in lightness (+ indicates the sample is lighter than the reference, - indicates the sample is darker than the reference), Δ*a** = difference on the red/green axis (+ indicates the sample is redder than the reference, - indicates the sample is greener than the reference), Δ*b** = difference on the yellow/blue axis (+ indicates the sample is more yellow than the reference, - indicates the sample is more blue than the reference) (Lange 1999). Whereas Δ*E** represents the measurement of the difference between two colors. The Δ*E** color difference scale is as follows: 0: none, 1: very small, 2: small, 3: medium, 4: large, 5: very large (Özcan 2008).

As can be seen from Table 5, for both unbeaten and beaten papers, treatment with

ZB and BA solutions resulted in positive ΔL* values, indicating a lighter color compared to the control, which correlates with the brightness values. Table 5 shows that papers produced with the SP application have more negative ΔL* values, indicating that they are darker. When comparing ZB and BA-treated papers among themselves, although the darkness values increased slightly when the usage rate was increased from 3% to 5%, the color lightness values of the papers produced with 5% ZB + 3% SP were significantly improved. This improvement may be due to the increased amount of SP adhering to the paper surface as the ZP ratio increases. This effect was not observed with the beaten samples but instead the color darkness increased with the higher BA and SP ratios used.

Table 5. ΔL^*, Δa^*, Δb^*, ΔE^* Values of Paper Samples (UB: unbeaten, B: Beaten)

		ΔL^*		Δa^*		Δb^*		ΔE^*	
		UB	B	UB	B	UB	B	UB	B
3% ZB	Mean value	2.60	1.41	0.08	1.15	-0.46	0.56	2.64	1.5
	Std. dev.	0.20	0.26	0.001	0.015	0.11	0.02	0.21	0.20
5% ZB	Mean value	1.31	0.37	-0.02	0.10	1,30	0.20	1.63	1.08
	Std. dev.	0.36	0.28	0.06	0.11	1.31	1.18	0.50	0.12
3% BA	Mean value	1.83	0.76	-0.22	0.22	0.06	-0.56	1.84	1.05
	Std. dev.	0.05	0.23	0.60	0.13	0.23	0.58	0.05	0.40
5% BA	Mean value	1.40	-0.73	0.08	0.65	-0.05	0.54	1.41	1.29
	Std. dev.	1.20	0.49	0.05	0.34	0.06	0.70	0.20	0.54
1.5% SP	Mean value	0.28	-0.66	0.03	0.56	3.05	2.48	3.10	2.68
	Std. dev.	0.43	0.50	0.02	0.13	0.91	0.63	0.86	0.54
3% SP	Mean value	-3.46	-6.07	0.37	0.79	7.63	5.12	8.43	7.99
	Std. dev.	0.92	0.89	0.18	0.13	0.64	0.62	1.74	0.91
3% ZB + 1.5% SP	Mean value	2.34	1.50	-0.1	-0.13	-0.02	-0.93	2.56	1.85
	Std. dev.	0.70	0.05	0.10	0.18	1.15	0.40	0.47	0.20
5% ZB + 3% SP	Mean value	2.71	2.44	-0.02	-0.18	1.71	0	3.21	2.71
	Std. dev.	0.10	0.05	0.04	0.14	0.38	1.42	0.28	0.31
3% BA + 1.5% SP	Mean value	1.6	-0.9	-0.12	0.09	0.78	0.35	1.83	1.07
	Std. dev.	0.42	0.43	0.03	0.17	0.36	048	0.24	0.37
5% BA + 3% SP	Mean value	1.10	0.48	-0.15	0.30	1.68	0.66	2.13	1.01
	Std. dev.	0.72	0.23	0.08	0.19	1.22	0.79	1.18	0.62

The color differences in Δa* values were examined and while a color difference determined on the green axis in UB and B papers treated with ZB + SP, a color difference was determined on the green axis in UB papers and on red axis in B papers treated with BA + SP. Similarly, when Δb* values were evaluated, it was seen that color difference occurred in the blue axis only in UB and B papers processed with 3% ZB + 1.5% SP, while color difference occurred in the yellow axis in 5% ZB + 3%SP and all other BA +SP applied papers.

The ΔE* values of all other test papers were generally close to each other, with the exception of the papers produced with the 3% SP application. For unbeaten test papers with 3% SP application, the ΔE* values were 8.43, and for beaten test papers, 7.99, indicating considerably higher color differences than others. Since the ΔE* values of the papers treated with BA + SP are lower than the papers treated with ZB + SP, it can be said that the color change difference obtained with SP enhanced ZB is greater than that with SP enhanced BA.

CONCLUSIONS

1. In terms of flame-retardant and thermal properties, the attributes imparted by boric acid (BA) to bleached kraft paper were more effective than those imparted by zinc borate (ZB). Soy protein (SP) was found to impart a certain degree of flame retardancy to kraft paper. Due to this property of SP and its binding ability, kraft papers treated with SP-enhanced ZB and BA solutions provide more effective flame protection.
2. The highest limiting oxygen index (LOI) value and the highest residual mass after the UL-94 test were obtained by treating the bleached kraft papers with 5% BA + 3% SP. These results were consistent with the thermogravimetric analysis (TGA), differential TGA (DTGA), and differential scanning calorimetry (DSC) data. In addition, there was no significant difference in LOI values for all UB and B samples.
3. The optical properties of the samples, such as brightness and color parameters, changed due to the effect of beating. Negative CIE a^* values indicated greenish color formation in unbeaten bleached kraft papers treated with ZB + SP and BA + SP.
4. Similar to the brightness values, unbeaten paper samples showed higher lightness levels depending on their L^* values. Due to the yellow color specific to SP, SP-additive ZB and BA-treated unbeaten bleached kraft papers show increased yellowness values with positive CIE b^* values.
5. Since SP increased the yellowness value, the highest color change (ΔE^*) was obtained with the papers applied alone especially with 3% SP. Also the highest Δb^* values were determined with 3% SP treated UB and B papers. The Δb^* values decreased for both UB and B papers with the application of SP together with ZB or BA.

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