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# Comparative Study of Thermal Aging Effects on Old Newspaper Pulps Bleached with Different Chemicals

# Komparativna studija utjecaja toplinskog starenja na papirnu pulpu od starih novina izbijeljenu različitim kemikalijama

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**ABSTRACT** • *This study investigates the influence of different bleaching systems on the thermal aging behavior of old newspaper pulps (ONP) under controlled laboratory conditions. Hydrogen peroxide, sodium dithionite, and formamidine sulfinic acid (FAS) were applied at their respective optimum dosages, and the resulting pulps were subjected to accelerated aging at (103 ± 2) °C for up to 240 h. Aging was evaluated as a multidimensional process rather than being limited to brightness changes. Optical properties were assessed together with mechanical strength retention and structural modifications associated with hornification and pore evolution. Brightness, whiteness, yellowness, and color difference (ΔE) were measured alongside breaking length, burst index, Cobb water absorption, and air permeability to characterize the overall response of the fiber network during thermal exposure. Statistical analysis was performed using one-way ANOVA followed by Duncan's multiple range test. Distinct differences were observed among the bleaching systems. Peroxide-treated pulps maintained relatively stable optical and mechanical performance during aging. In contrast, dithionite-bleached samples showed pronounced color reversion and a reduction in strength. FAS-treated pulps exhibited intermediate behavior. The results indicate that initial brightness gain alone is insufficient to predict long-term performance, emphasizing the need to consider durability under thermal conditions when selecting bleaching strategies for recycled paper.*

**KEYWORDS:** *newspaper; aging; bleaching; stability; durability*

**SAŽETAK** • *U studiji je istražen utjecaj različitih sustava izbjeljivanja na toplinsko starenje papirne pulpe od starih novina (ONP) u kontroliranim laboratorijskim uvjetima. Vodikov peroksid, natrijev ditionit i formamidinsulfonska kiselina (FAS) primijenjeni su u optimalnim dozama, a dobivena pulpa podvrgnuta je ubrzanom starenju na 103 ± 2 °C tijekom 240 sati. Evaluacija starenja nije bila ograničena samo na promjenu svjetline nego je ono promatrano kao višedimenzionalni proces. Optička svojstva istražena su usporedno sa zadržavanjem mehaničke čvrstoće i strukturnim modifikacijama povezanima s hornifikacijom i razvojem pora. Mjereni su svjetlina, bjelina, žućenje i razlika u boji (ΔE), kao i duljina loma, indeks pucanja, upijanje vode prema Cobbu i propusnost zraka kako bi se upotpunio ukupni odgovor mreže vlakana tijekom toplinskog izlaganja pulpe. Statistička analiza provedena je primjenom jednosmjerne ANOVA-e, a zatim Duncanova testa višestrukog raspona. Uočene su znatne razlike među sustavima za izbjeljivanje. Naime, pulpe tretirane peroksidom održale su relativno stabilna optička i*

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*mehanička svojstva tijekom starenja. Nasuprot tome, uzorci izbijeljeni ditionitom pokazali su izrazito veliku promjenu boje i smanjenje čvrstoće. FAS-om tretirana pulpa pokazala je srednje promjene svojstava. Rezultati upućuju na to da početno postizanje bjeline nije dovoljno za predviđanje dugoročnih svojstava, što nameće potrebu upoznavanja trajnosti u toplinskim uvjetima izbijeljenoga recikliranog papira.*

**KLJUČNE RIJEČI:** *novine; starenje; izbjeljivanje; stabilnost; trajnost*

## 1 INTRODUCTION
## 1. UVOD

Recycling of waste paper, and especially old newspaper pulp (ONP), plays a major role in today's pulp and paper industry. Increasing pressure to use sustainable raw materials, reduce dependence on virgin fibers, and limit the environmental burden of conventional pulping has strengthened the importance of recovered paper streams (Nestor, 1994; Kumar *et al.,* 2020). Within these streams, ONP represents a considerable fraction. However, its high lignin content, together with residual printing inks and various additives from offset and gravure processes, restricts both optical and mechanical performance (Çiçekler and Tutuş, 2025). Compared with many other recovered grades, ONP-derived pulps are more vulnerable to discoloration and strength loss during storage or thermal exposure. The presence of lignin-derived chromophores and printing-related contaminants contributes to reduced stability over time. For this reason, improving the durability of ONP requires bleaching and stabilization approaches that not only account for initial brightness improvement but also for long-term aging behavior.

Bleaching of recycled fibers follows a different logic than bleaching of virgin chemical pulps. In recycled systems, the goal is generally not extensive delignification. Instead, the focus is on improving brightness and visual appearance by modifying existing chromophoric groups and removing residual ink components, while preserving fiber integrity as much as possible. Maintaining mechanical performance during this process is critical, since recycled fibers are already subjected to previous drying and reprocessing cycles that may have weakened their structure (Aguilar-Rivera, 2021; Zeb *et al.,* 2021; Tofani *et al.,* 2022). In recycled fiber processing, hydrogen peroxide ($H_2O_2$), sodium dithionite ($Na_2S_2O_4$), and formamidine sulfinic acid (FAS) are commonly used bleaching chemicals (Koshitsuka, 2002; Bajpai, 2014; Saad *et al.,* 2020; Sepahvand *et al.,* 2025). Hydrogen peroxide is widely used because of its strong oxidative action and its capacity to permanently modify lignin-derived chromophoric structures. It is also generally considered more environmentally acceptable than many alternative bleaching agents (Asha and Badamali, 2020; Miglbauer *et al.,* 2020; Tofani *et al.,* 2021). However, the efficiency of peroxide bleaching depends strongly on process conditions. Parameters such as pH, temperature, and the presence of transition metal ions must be carefully controlled, since unfavorable conditions can lead to cellulose oxidation or subsequent brightness reversion. (Zeb *et al.,* 2021). Sodium dithionite is a reducing bleaching agent that has been widely used in the deinking and brightness enhancement of ONP. Its continued use is largely related to its relatively low cost and its effectiveness in reducing conjugated chromophoric groups (Carreira *et al.,* 2012; Krishnan *et al.,* 2020). However, several studies have shown that dithionite does not permanently remove chromophoric structures. Instead, it reduces them to colorless forms without destroying the underlying conjugated systems. As a result, the chemical stability of the pulp remains limited, and noticeable brightness reversion may occur during storage or thermal aging (Pemberton *et al.,* 1995; Lennholm and Iversen, 1998). To overcome these limitations, formamidine sulfinic acid (FAS) has been introduced as a more stable reductive bleaching option. Compared with dithionite, FAS is reported to provide better resistance to oxidative reversion and to present a comparatively lower environmental impact (Choi and Kim, 2006; Sepahvand *et al.,* 2025). Earlier studies indicate that FAS can reach brightness values similar to those obtained with dithionite, while preserving acceptable initial strength properties in recycled pulps (Choi and Kim, 2006; Yun and He, 2011; Bajpai, 2014; Zeb *et al.,* 2021). However, most of these studies concentrate primarily on short-term optical results, while the long-term durability of FAS-treated pulps under aging conditions has received comparatively little attention.

In addition to initial bleaching efficiency, the aging behavior of recycled pulps is an important performance parameter. Paper products are often exposed to storage over long periods or to elevated temperatures during use, which can gradually affect their properties. For this reason, thermal aging tests are commonly applied to simulate natural degradation processes. These processes typically involve cellulose depolymerization, oxidation of residual lignin components, and a gradual weakening of inter-fiber bonding within the sheet structure (Małachowska *et al.,* 2021a; Ornaghi *et al.,* 2020; Kaszonyi *et al.,* 2022). The type of bleaching chemistry used can significantly influence these degradation processes, since oxidative and reductive agents alter fiber chemistry through fundamentally different reaction mechanisms (Bajpai, 2014; Li *et al.,* 2020; Pydimalla and Reddy, 2020). Earlier studies have largely addressed aging-related optical variations in bleached recycled pulps. In peroxide-bleached systems, brightness reversion has been linked to residual chromophores and oxidation reactions promoted by trace metal ions (Liu, 2003; Rundlöf *et al.,* 2006; Jiao *et al.,* 2020; Kyene *et al.,* 2019). In contrast, dithionite-bleached pulps tend to lose their initial optical improvement more rapidly under thermal conditions, mainly because the reduced chromophoric structures can be easily re-oxidized (Pemberton *et al.,* 1995; Lennholm and Iversen, 1998; Carreira *et al.,* 2012; Krishnan *et al.,* 2020). While FAS has been reported to improve optical stability compared with dithionite, comprehensive assessments under well-controlled thermal aging conditions remain scarce, and most investigations focus primarily on optical properties without extending to mechanical or physical performance (Choi and Kim, 2006; Sepahvand *et al.,* 2025).

Most of the available literature addresses aging primarily from an optical standpoint. In contrast, the simultaneous changes in mechanical performance and physical structure during aging have received comparatively less attention (Lennholm and Iversen, 1998; Choi and Kim, 2006; Yun and He, 2011; Carreira *et al.,* 2012; Saad *et al.,* 2020). Aging-related changes such as fiber hornification, rearrangement of pore structure, and reduction of inter-fiber bonding area can directly affect tensile strength, burst resistance, water absorption, and air permeability. However, these structural and mechanical consequences are rarely examined together with the type of bleaching chemistry applied (Youssef *et al.,* 2017; Jiao *et al.,* 2020; Chen *et al.,* 2024; Sepahvand *et al.,* 2025; Sevastyanova *et al.,* 2025). Although many studies have investigated bleaching strategies for recycled fibers (Lennholm and Iversen, 1998; Koshitsuka, 2002; Choi and Kim, 2006; Yun and He, 2011; Bajpai, 2014; Saad *et al.,* 2020; Zeb *et al.,* 2021; Sepahvand *et al.,* 2025), a direct and systematic comparison of hydrogen peroxide, sodium dithionite, and formamidine sulfinic acid (FAS) under the same thermal aging conditions has not been thoroughly addressed. In particular, studies using identical raw material and controlled aging parameters for all three systems remain limited.

The present study aims to fill this gap through a controlled comparison of the thermal aging behavior of ONP bleached with hydrogen peroxide, sodium dithionite, and FAS. All three systems were evaluated under identical conditions in order to allow a direct assessment of their performance. In addition to optical stability parameters such as brightness, whiteness, yellowness, and color difference, mechanical properties including breaking length and burst index were examined. Physical changes related to hornification and pore structure development were also considered through Cobb water absorption and air permeability measurements. By combining these parameters, the study seeks to provide a broader understanding of how bleaching chemistry influences long-term durability. Particular attention is given to the relationship between initial property improvement and subsequent stability during thermal exposure. The findings are expected to contribute to more informed selection of bleaching strategies in recycled newspaper processing and to support the optimization of sustainable paper production practices.

## 2 MATERIALS AND METHODS
## 2. MATERIJALI I METODE

Old newspaper dated January 1 2023 was used as the raw material in this study. To ensure consistency among the experimental runs, the same type and number of pages were selected for each trial. Care was taken to avoid variations that could influence bleaching performance. Hydrogen peroxide ($H_2O_2$), sodium dithionite ($Na_2S_2O_4$), and formamidine sulfinic acid (FAS) were used as bleaching agents. Additional chemicals required during bleaching were applied as specified in the experimental design. All reagents were of analytical grade and obtained from MERCK. Deionized water was used throughout the study to prevent possible interference from dissolved ions or impurities.

### 2.1 Recycling and pulping of old newspaper (ONP)
### 2.1. Recikliranje i priprema papirne pulpe od starih novina (ONP)

The old newspapers were manually cut into pieces of approximately 2 cm × 2 cm, following the recommendations of the International Association of the Deinking Industry (INGEDE, Method 11p – 5.5) to maintain uniformity. The prepared samples were placed in sealed polyethylene bags and stored away from light and heat until use.

Pulping was carried out using a Hobart-type laboratory pulper. The ONP samples were pre-soaked at 10 % consistency for 10 minutes and then pulped at 10 % consistency for 22 minutes at speed level 1 – 2. During pulping, the chemical formulation recommended in INGEDE Method 11p – 4.2 was applied. The mixture consisted of 0.6 % sodium hydroxide (NaOH), 0.7 % hydrogen peroxide ($H_2O_2$), 1.8 % sodium silicate ($Na_2SiO_3$), and 0.8 % oleic acid, calculated on an oven-dry pulp basis.

After pulping, the recycled pulp was thoroughly washed and dewatered to a solids content of approximately 20 – 25 %. The pulp was then stored in sealed polyethylene bags at +4 °C until bleaching experiments were conducted.

## 2.2 Bleaching procedure
## 2.2. Postupak izbjeljivanja

The bleaching conditions used in this study are presented in Table 1. All bleaching trials were carried out under controlled and constant conditions. Temperature, reaction time, and pulp consistency were kept the same for all treatments to allow direct comparison between the bleaching systems. When required, auxiliary chemicals such as NaOH, EDTA, $MgSO_4$, and sodium silicate were added to improve process stability and to reduce possible side reactions.

All bleaching experiments were carried out in an electrically heated water bath with a temperature control accuracy of ± 0.5 °C. The recycled ONP and the calculated amounts of chemicals were placed in sealed polyethylene bags. The bags were manually mixed to ensure uniform distribution of the chemicals within the pulp and then immersed in the water bath for the specified reaction time. Each bleaching condition was repeated three times in order to improve reliability and reduce possible experimental variation.

After bleaching, the pulps were diluted to 1 % consistency and formed into standard laboratory handsheets using a Rapid-Köthen RK-21 sheet former in accordance with ISO 5269-2. The target basis weight of the sheets was approximately 70 g/m². For each bleaching condition, ten handsheets were prepared. The sheets were dried under standard laboratory conditions and then conditioned at 23 °C and 50 % relative humidity for 24 hours before testing.

## 2.3 Thermal aging procedure
## 2.3. Postupak toplinskog starenja

The prepared handsheets were subjected to accelerated thermal aging according to ISO 5630-1:1991 to evaluate long-term stability. Only the sheets produced under the optimum bleaching conditions for each chemical were used in the aging tests. Samples were placed in a forced-air oven and aged at (103 ± 2) °C for 72, 120, 168, and 240 hours. During aging, all samples were positioned to allow uniform heat exposure.

At the end of each aging period, the corresponding set of handsheets was removed from the oven and allowed to cool to room temperature. The sheets were then conditioned at 23 °C and 50 % relative humidity before optical and mechanical testing.

## 2.4 Test methods
## 2.4. Ispitne metode

Optical and mechanical properties of the handsheets were measured in accordance with the relevant ISO standards. Brightness was determined according to ISO 2470-1:2016. Whiteness and yellowness indices were measured based on ISO 11475:2017 and ISO 11476:2016, respectively. Opacity was evaluated according to ISO 2471:2008, and CIE $L^*a^*b^*$ color coordinates were determined following ISO 5631-1:2015.

Color changes after thermal aging were assessed using the ΔE parameter, which represents the overall difference between two color measurements. The $\Delta E$ value was calculated using Eq. (1).

$$\Delta E = \sqrt{(L2 - L1)^2 + (a2 - a1)^2 + (b2 - b1)^2} \quad (1)$$

Mechanical properties were evaluated by measuring tensile strength (breaking length) according to ISO 1924-2:2008 and bursting strength in accordance with ISO 2758:2014. Surface wettability was assessed using the Cobb water absorption test (ISO 535:2014), and air permeability was measured following ISO 5636-5:2013 (Gurley method).

All tests were performed under standard laboratory conditions of (23 ± 1) °C and (50 ± 2) % relative humidity, as specified in ISO 187:1990. For each parameter and experimental condition, a minimum of five replicates was tested.

Statistical analysis was conducted using one-way ANOVA, followed by Duncan's multiple range test at a 95 % confidence level. Each bleaching system was analyzed separately to evaluate the effects of chemical dosage and aging time.

**Table 1** Process conditions for bleaching experiments
**Tablica 1.** Parametri procesa izbjeljivanja

| **Parameters** *Parametri* | **Hydrogen peroxide ($H_2O_2$)** *Vodikov peroksid ($H_2O_2$)* | **Sodium dithionite ($Na_2S_2O_4$)** *Natrijev ditionit ($Na_2S_2O_4$)* | **Formamidine sulfinic acid (FAS)** *Formamidinsulfonska kiselina (FAS)* |
|---|---|---|---|
| Reagent charge, % / *udio reagensa,* % | 3 – 5 – 7 | 0.5 – 1.0 – 1.5 | 0.5 – 1.0 – 1.5 |
| NaOH, % | $H_2O_2$/0.75 | – | 0.25 – 0.5 – 0.75 |
| pH | 10.9 | 5.5 | – |
| Temperature, °C / *temperatura,* °C | 70 | 65 | 65 |
| Time, min / *vrijeme,* min | 60 | 60 | 60 |
| Pulp consistency, % / *konzistencija,* % | 12 | 5 | 5 |
| EDTA, % | 0.5 | - | - |
| $MgSO_4$, % | 0.5 | – | – |
| Sodium silicate, % / *natrijev silikat,* % | 2.0 | – | – |

## 3 RESULTS AND DISCUSSION
## 3. REZULTATI I RASPRAVA

### 3.1 Determination of optimum dosages for different bleaching agents
### 3.1. Određivanje optimalnih doza različitih izbjeljivača

To identify the most suitable bleaching dosage for each chemical, the optical and mechanical properties of the handsheets were evaluated statistically. One-way ANOVA was applied, followed by Duncan's multiple range test to compare group means. The analyses were performed separately for hydrogen peroxide, sodium dithionite, and formamidine sulfinic acid (FAS), so that the effect of the dosage could be examined within each bleaching system.

In the Duncan test, mean values sharing the same letter were considered not significantly different at the 95 % confidence level. The average results for all measured parameters, together with their statistical groupings, are given in Table 2.

Among the peroxide treatments, the 3 % dosage provided the highest whiteness (59.50 %) and brightness (47.27 %), and the differences were statistically significant ($p < 0.05$). At this level, mechanical properties were also maintained at acceptable values, with a breaking length of 3.83 km and a burst index of 2.60 kPa·m²/g. Increasing the peroxide dosage to 5 % and 7 % did not lead to a meaningful improvement in brightness. In fact, whiteness decreased slightly, and a noticeable reduction in breaking length was observed at 7 %. When optical results are considered together with mechanical performance, chemical consumption, and process practicality, the 3 % peroxide treatment appears to offer the most balanced outcome.

Sodium dithionite treatment led to moderate increases in optical properties, but tensile strength gradually decreased as the dosage increased. At 1 %, whiteness (43.71 %) and brightness (39.56 %) were significantly higher than those of the unbleached pulp, while the corresponding strength values remained within an acceptable range. Increasing the dosage beyond 1 % resulted in only slight additional improvements in optical properties. However, these limited gains were accompanied by higher chemical usage and a potential increase in effluent load. Considering both performance and process efficiency, the 1 % dosage appears to represent a reasonable balance for dithionite bleaching.

In the case of FAS, optical properties increased gradually with higher dosages. The highest whiteness (48.33 %) and brightness (40.99 %) were obtained at 1.5 %. However, statistical analysis showed that the differences between 1 % and 1.5 % FAS were not significant for several parameters. Although the 1.5 % dosage provided slightly higher optical values, the improvement was limited. Considering the additional chemical consumption and its potential impact on process cost and environmental load, the 1 % dosage appears to provide a more practical balance between optical enhancement and preservation of mechanical properties.

Based on the statistical results, and taking into account economic and environmental aspects, the most suitable dosages were 3 % for hydrogen peroxide, 1 % for sodium dithionite, and 1 % for formamidine sul-

**Table 2** Optical and mechanical properties of ONP bleached with hydrogen peroxide, sodium dithionite, and FAS at different dosages
**Tablica 2.** Optička i mehanička svojstva ONP-a izbijeljenoga različitim dozama vodikova peroksida, natrijeva ditionita i FAS-a

| | % | **Breaking L., km** *Duljina loma,* km | **Burst In., kPa·m²/g** *Indeks loma,* kPa m²/g | **Whiteness (ISO), %** *Bjelina (ISO), %* | **Brightness (ISO), %** *Svjetlina (ISO), %* | **Yellowness (E313)** *Žućenje (E13)* | **Opacity (ISO) %** *Prozirnost (ISO), %* | *L** | *a** | *b** |
|---|---|---|---|---|---|---|---|---|---|---|
| UBP** | 0 | 3.80$^{a*}$ | 2.28$^{b}$ | 42.85$^{c}$ | 38.63$^{b}$ | 14.57$^{a}$ | 99.12$^{a}$ | 71.5$^{b}$ | -0.54c | 6.29$^{a}$ |
| Per | 3 | 3.83$^{a}$ | 2.60$^{a}$ | 59.50$^{a}$ | 47.27$^{a}$ | 19.92$^{b}$ | 98.11$^{ab}$ | 81.6$^{a}$ | -1.47$^{a}$ | 13.9$^{d}$ |
| Per | 5 | 3.92$^{a}$ | 2.36$^{ab}$ | 56.07$^{b}$ | 46.80$^{a}$ | 20.87$^{b}$ | 95.89$^{c}$ | 81.6$^{a}$ | -1.13$^{b}$ | 9.55$^{c}$ |
| Per | 7 | 3.40$^{b}$ | 2.49$^{ab}$ | 54.88$^{b}$ | 46.92$^{a}$ | 15.27$^{a}$ | 96.47$^{bc}$ | 82.1$^{a}$ | -0.54$^{c}$ | 7.43$^{b}$ |
| FAS | 0.5 | 2.94$^{b}$ | 2.42$^{a}$ | 44.19$^{c}$ | 38.73$^{b}$ | 16.98$^{b}$ | 98.90$^{ab}$ | 72.3$^{b}$ | -0.90$^{a}$ | 7.75$^{b}$ |
| FAS | 1 | 2.90$^{b}$ | 2.25$^{a}$ | 46.14$^{b}$ | 39.10$^{b}$ | 19.50$^{c}$ | 98.95$^{ab}$ | 73.2$^{c}$ | -0.61$^{b}$ | 8.85$^{c}$ |
| FAS | 1.5 | 2.73$^{b}$ | 2.22$^{a}$ | 48.33$^{a}$ | 40.99$^{a}$ | 21.14$^{d}$ | 98.35$^{b}$ | 74.3$^{d}$ | -0.50$^{c}$ | 9.33$^{d}$ |
| Dit | 0.5 | 3.00$^{b}$ | 1.85$^{b}$ | 43.43$^{b}$ | 39.20$^{c}$ | 13.78$^{a}$ | 99.10$^{a}$ | 71.9$^{b}$ | -1.01$^{b}$ | 6.29$^{a}$ |
| Dit | 1 | 2.70$^{c}$ | 1.78$^{b}$ | 43.71$^{b}$ | 39.56$^{b}$ | 13.63$^{a}$ | 98.12$^{b}$ | 72.1$^{b}$ | -1.10$^{ab}$ | 6.19$^{a}$ |
| Dit | 1.5 | 2.41$^{d}$ | 1.75$^{b}$ | 45.01$^{a}$ | 40.70$^{a}$ | 14.11$^{ab}$ | 97.61$^{b}$ | 72.9$^{a}$ | -1.18$^{a}$ | 6.54$^{a}$ |

*Mean values with the same lower-case letters are not significantly different at the 95 % confidence level according to Duncan's mean separation test. **UBP refers to unbleached pulp.
*Srednje vrijednosti označene istim malim slovima ne razlikuju se značajno na razini pouzdanosti od 95 % prema Duncanovu testu. **UBP se odnosi na nebijeljenu pulpu.*

finic acid. The final selection was therefore not determined solely by statistical differences. Chemical consumption, possible environmental effects, and practical applicability in industrial conditions were also considered in the evaluation.

### 3.2 Optical stability and color reversion
### 3.2. Optička stabilnost i promjena boje

Changes in optical properties during accelerated thermal aging varied depending on the bleaching agent used (Table 3). Statistical analysis carried out separately for each bleaching system showed that aging time had a significant effect on several optical parameters. However, the magnitude of these changes and their statistical significance differed among the bleaching treatments.

The peroxide-treated samples showed the most stable optical behavior during aging. Whiteness decreased slightly from 61.90 % ISO to 61.16 % ISO after 240 h. Although this change was statistically significant ($p$ = 0.0079), the difference was small in practical terms. Duncan's test indicated considerable overlap between aging periods, suggesting a gradual change rather than a sharp decline. Brightness and yellowness were more affected by thermal exposure. Both parameters changed significantly over time ($p$ = 0.0000 and $p$ = 0.0003, respectively). However, even in these cases, the overall variation remained relatively moderate compared with the other bleaching systems.

The total color difference ($\Delta E^*$) increased gradually from 0.94 at 72 h to 2.14 at 240 h. Despite this upward trend, the effect of aging time on $\Delta E$ within the peroxide group was not statistically significant ($p$ = 0.8512). This suggests that color change occurred in a steady manner rather than through distinct stages. The relatively low $\Delta E^*$ values observed for peroxide-treated samples indicate a higher resistance to thermally induced color reversion compared with the other bleaching systems.

These results can be explained by the oxidative mechanism of hydrogen peroxide. Peroxide is known to break down conjugated chromophoric structures, especially those associated with lignin-derived functional groups (Liu, 2003; Rundlöf *et al.,* 2006; Jiao *et al.,* 2020; Li *et al.,* 2020). In contrast to reductive bleaching systems, peroxide modifies or removes these chromophores rather than simply converting them into temporarily colorless forms. As a result, the fiber structure tends to remain more chemically stable, which may contribute to the lower degree of brightness reversion observed during thermal aging (Chen *et al.,* 2015).

By contrast, dithionite-treated samples showed a more pronounced decline in optical stability during thermal aging. Aging time did not significantly affect whiteness ($p$ = 0.5941), but clear changes were observed in brightness and yellowness ($p$ = 0.0003 and $p$ = 0.0000, respectively). In particular, yellowness increased from 10.24 at the beginning of the test to 17.80 after 240 h, which corresponds to an increase of nearly 95 %. Duncan's test separated the longer aging periods into distinct statistical groups, indicating that optical deterioration became more evident with extended exposure.

**Table 3** Optical properties of bleached pulps during thermal aging
**Tablica 3.** Optička svojstva izbijeljene pulpe tijekom toplinskog starenja

| **Group** *Grupa* | **Duration, h** *Trajanje,* h | **Whiteness (ISO), %** *Bjelina (ISO),* % | **Brightness (ISO), %** *Svjetlina (ISO),* % | **Yellowness (E313)** *Žućenje (E13)* | **$\Delta E$** |
|---|---|---|---|---|---|
| Peroxide | 0 | 61.90$^{ab*}$ | 50.86$^{c}$ | 26.74$^{c}$ | 0.00$^{c}$ |
| | 72 | 62.76$^{b}$ | 50.04$^{bc}$ | 27.22$^{bc}$ | 0.94$^{bc}$ |
| | 120 | 62.88$^{b}$ | 50.20$^{bc}$ | 27.82$^{bc}$ | 0.96$^{bc}$ |
| | 168 | 62.08$^{ab}$ | 49.04$^{ab}$ | 28.64$^{ab}$ | 1.30$^{ab}$ |
| | 240 | 61.16$^{a}$ | 47.92$^{a}$ | 29.80$^{a}$ | 2.14$^{a}$ |
| | p values | 0.0079 | 0.0000 | 0.0003 | 0.8512 |
| FAS | 0 | 56.20$^{ab}$ | 48.54$^{a}$ | 18.88$^{d}$ | 0.00$^{e}$ |
| | 72 | 55.98$^{b}$ | 47.98$^{ab}$ | 20.32$^{c}$ | 1.04$^{d}$ |
| | 120 | 56.84$^{a}$ | 48.22$^{a}$ | 20.94$^{c}$ | 1.38$^{c}$ |
| | 168 | 56.42$^{ab}$ | 46.92$^{bc}$ | 22.78$^{b}$ | 2.08$^{b}$ |
| | 240 | 56.44$^{ab}$ | 46.20$^{c}$ | 24.46$^{a}$ | 3.00$^{a}$ |
| | p values | 0.5430 | 0.0004 | 0.0000 | 0.8505 |
| Dithionite | 0 | 50.76$^{ab}$ | 47.14$^{a}$ | 10.24$^{e}$ | 0.00$^{e}$ |
| | 72 | 50.92$^{a}$ | 46.50$^{ab}$ | 12.36$^{d}$ | 1.10$^{d}$ |
| | 120 | 50.34$^{b}$ | 45.48$^{bc}$ | 13.80$^{c}$ | 1.56$^{c}$ |
| | 168 | 50.50$^{ab}$ | 44.70$^{cd}$ | 15.32$^{b}$ | 2.72$^{b}$ |
| | 240 | 50.44$^{ab}$ | 44.06$^{d}$ | 17.80$^{a}$ | 3.52$^{a}$ |
| | p values | 0.5941 | 0.0003 | 0.0000 | 0.3254 |

*Mean values followed by the same lowercase letter within the same column are not significantly different at the 95 % confidence level according to one-way ANOVA and Duncan's multiple range test
**Srednje vrijednosti označene istim malim slovom unutar istog stupca ne razlikuju se značajno na razini pouzdanosti od 95 % prema jednosmjernoj ANOVA-i i Duncanovu testu višestrukih raspona.*

The ΔE values also increased noticeably during aging, reaching an average of 3.52 at 240 h. In some cases, individual measurements were as high as 4.40. Although the differences between aging periods were not statistically significant ($p = 0.3254$), the overall $\Delta E$ values were clearly higher than those measured for peroxide- and FAS-treated samples. This higher color difference suggests that dithionite-bleached pulps experienced more pronounced optical changes during thermal exposure.

The observed trend is consistent with the chemical action of sodium dithionite. As a reducing agent, dithionite converts chromophoric groups into colorless forms but does not eliminate the underlying conjugated structures (Carreira *et al.,* 2012; Krishnan *et al.,* 2020). These reduced structures can be unstable under thermal or oxidative conditions and may revert to their original-colored state. This explains the rapid increase in yellowness and color difference during aging. Similar patterns have been described in earlier studies on dithionite-bleached mechanical and recycled pulps, where low initial yellowness was followed by pronounced thermal yellowing and brightness reversion (Friman *et al.,* 2004; Boeva and Radeva, 2014; El-Sakhawy *et al.,* 2021; Vaysi and Ebadi, 2021).

FAS-treated samples showed optical behavior that fell between peroxide and dithionite systems. Aging time did not have a significant effect on whiteness ($p = 0.5430$), suggesting that overall perceived whiteness remained relatively stable throughout the aging period. However, brightness and yellowness were affected by thermal exposure ($p = 0.0004$ and $p = 0.0000$, respectively). The changes were gradual, and although deterioration was evident over time, it was less pronounced than in the dithionite-treated samples.

The $\Delta E$ values increased from 1.04 at 72 h to 3.00 at 240 h. As observed in the other bleaching systems, aging time did not lead to statistically significant differences among ΔE values ($p = 0.8505$). Nevertheless, the overall ΔE levels measured for the FAS-treated samples were consistently lower than those of the dithionite group. This suggests that FAS provides better resistance to thermal color reversion compared with conventional dithionite bleaching.

This trend is consistent with previous reports suggesting that FAS behaves as a more stable reducing agent than dithionite. Earlier studies have indicated that FAS can delay oxidative reversion while still providing the benefits associated with reductive bleaching systems (El-Sakhawy, 2002; Yun and He, 2011; Fišerová *et al.,* 2018; Paranjape and Athalye, 2024).

Although one-way ANOVA did not show statistically significant differences in $\Delta E$ values over time within each bleaching group ($p > 0.05$), this does not contradict the general optical trends observed. The $\Delta E$ parameter represents the combined change in $L^*$, $a^*$, and $b^*$ values. When color variation progresses gradually and continuously, it may not produce clearly separated statistical groups, even though a steady shift is present. Similar observations have been reported in other accelerated aging studies, where $\Delta E$ increased over time without distinct statistical separation.

In the present case, $\Delta E$ is more useful as a comparative indicator between bleaching systems rather than as a precise marker of aging stages. Based on overall $\Delta E^*$ levels, peroxide-treated samples showed the most stable optical behavior, whereas dithionite-treated pulps experienced faster and more pronounced color change. FAS-treated samples displayed intermediate performance, performing better than dithionite but not reaching the stability observed with peroxide treatment.

## 3.3 Mechanical strength and durability
## 3.3. Mehanička čvrstoća i trajnost

Accelerated thermal aging led to a general reduction in the mechanical properties of the bleached pulps. This decline can be related to gradual weakening of inter-fiber bonding and cellulose chain degradation, as reported in previous studies (Hirn and Schennach, 2017; Fišerová *et al.,* 2018; Małachowska *et al.,* 2021b; Paranjape and Athalye, 2024). The extent of this reduction, however, varied depending on the bleaching system used (Table 4). Statistical analysis conducted separately for each group showed that aging time had a significant effect on some mechanical parameters, while others changed more gradually without reaching statistical significance. These patterns suggest a progressive deterioration process rather than a sudden loss of mechanical integrity.

Among the tested systems, peroxide-treated samples showed the most stable mechanical behavior during thermal aging. The breaking length decreased from 3.80 km to 3.33 km after 240 h, which corresponds to a reduction of about 12 %. Although aging time had a statistically significant effect ($p = 0.031$), the overlap observed in Duncan's test suggests that the decline occurred gradually rather than in clearly separated stages.

The burst index followed a similar trend. After 240 h of aging, it decreased slightly from 2.28 to 2.12 kPa·m²/g and remained within the same statistical group as some intermediate aging periods. These results indicate that peroxide bleaching helps maintain fiber bonding and sheet integrity more effectively under thermal exposure compared with the reductive systems.

The mechanical stability observed in peroxide-treated samples can be related to its oxidative action on lignin-derived structures. By irreversibly modifying these chromophoric groups, peroxide reduces the number of thermally reactive sites that may contribute to

**Table 4** Mechanical properties of bleached pulps during thermal aging
**Tablica 4.** Mehanička svojstva izbijeljene pulpe tijekom toplinskog starenja

| **Group** *Grupa* | **Duration, h** *Trajanje,*h | **Breaking length, km** *Duljina loma,* km | **Burst index, kPa·m²/g** *Indeks loma,* kPa·m²/g |
|---|---|---|---|
| Peroxide | 0 | 3.80[a*] | 2.28[a] |
| | 72 | 3.54[ab] | 1.91[b] |
| | 120 | 3.53[b] | 2.20[a] |
| | 168 | 3.25[b] | 2.12[ab] |
| | 240 | 3.33[b] | 2.12[ab] |
| | p-value | 0.031 | 0.018 |
| FAS | 0 | 3.47[a] | 2.39[a] |
| | 72 | 3.27[ab] | 1.77[c] |
| | 120 | 3.39[a] | 1.85[bc] |
| | 168 | 3.49[a] | 1.94[b] |
| | 240 | 3.27[b] | 1.76[c] |
| | p-value | 0.214 | 0.000 |
| Dithionite | 0 | 3.64[a] | 2.30[a] |
| | 72 | 3.45[ab] | 1.75[c] |
| | 120 | 3.54[ab] | 1.71[c] |
| | 168 | 3.53[ab] | 1.86[b] |
| | 240 | 3.42[b] | 1.81[bc] |
| | p-value | 0.047 | 0.000 |

*Mean values followed by the same lowercase letter within the same column are not significantly different at the 95 % confidence level according to one-way ANOVA and Duncan's multiple range test
**Srednje vrijednosti označene istim malim slovom unutar istog stupca ne razlikuju se značajno na razini pouzdanosti od 95 % prema jednosmjernoj ANOVA-i i Duncanovu testu višestrukih raspona.*

further degradation during aging (Chen *et al.,* 2015; Fišerová *et al.,* 2018; Jiao *et al.,* 2020; Zeb *et al.,* 2021). With fewer reactive groups present, secondary reactions during thermal exposure are limited. This may help slow down hornification and preserve inter-fiber bonding, which in turn supports better mechanical retention over time. Similar trends have been described in previous studies on peroxide-treated recycled and mechanical pulps.

FAS-treated samples showed relatively stable tensile behavior during thermal aging. The breaking length decreased only slightly from 3.47 km to 3.27 km after 240 h, and the effect of aging time was not statistically significant ($p = 0.214$). This suggests that FAS bleaching is able to maintain tensile load-bearing capacity to a certain extent under thermal exposure. The burst index, however, responded more sensitively to aging. It declined from 2.39 to 1.76 kPa·m²/g, corresponding to a strength reduction of approximately 26 %, and the effect of aging time was statistically significant ($p < 0.001$). Duncan's test distinguished early and late aging periods, indicating a progressive weakening of inter-fiber bonding. Although FAS is often regarded as more stable than conventional dithionite, the present results indicate that extended thermal exposure still leads to noticeable bonding deterioration. In this respect, FAS appears to offer improved tensile stability compared with dithionite, but it does not match the mechanical retention observed for peroxide-treated samples.

Dithionite-treated pulps showed the most pronounced mechanical decline during aging. The breaking length decreased from 3.64 km to 3.42 km, with a statistically significant effect of aging time ($p = 0.047$). While the tensile reduction remained moderate, the burst index dropped more markedly, from 2.30 to 1.81 kPa·m²/g ($p < 0.001$). The decrease in burst strength points to progressive loss of inter-fiber bonding and sheet integrity. Duncan analysis separated longer aging durations into lower statistical groups, confirming continued mechanical deterioration over time. After 240 h, the burst index of dithionite-treated samples remained clearly lower than that of peroxide-treated pulps under the same conditions.

The mechanical trend observed for dithionite-treated samples can be related to its reductive bleaching mechanism. Dithionite reduces chromophoric groups to colorless forms but does not eliminate the underlying conjugated structures (Pemberton *et al.,* 1995; Lennholm and Iversen, 1998; El-Sakhawy *et al.,* 2021; Vaysi and Ebadi, 2021). Under thermal conditions, these reduced structures may be re-oxidized. Such reactions can generate reactive species that contribute to cellulose chain scission, increased fiber brittleness, and gradual loss of bonding strength. Similar behavior has been described in previous studies on recycled and mechanical pulps, where dithionite bleaching was associated with accelerated mechanical deterioration under thermal or oxidative stress (Małachowska *et al.,* 2021b; Vaysi and Ebadi, 2021; Kaszonyi *et al.,* 2022; Chen *et al.,* 2024; Sevastyanova *et al.,* 2025).

In some cases, particularly for breaking length, aging time did not lead to statistically distinct groups ($p > 0.05$). However, this does not mean that degradation was absent. Thermal aging generally progresses through gradual microstructural changes rather than sudden strength failure. Processes such as hornification, reduced fiber swelling, and a slow decrease in bonding area develop progressively over time (Hirn and Schennach, 2017; Zhao *et al.,* 2022; Sjöstrand *et al.,* 2023; Hashemzehi *et al.,* 2024). As these changes occur continuously, strength values measured at different aging intervals may still overlap statistically, even though a practical decline is present. Therefore, the absence of clear statistical separation should be interpreted cautiously in the context of long-term material performance.

For this reason, the mechanical results in the present study should be evaluated not only in terms of statistical significance but also through direct comparison among bleaching systems. When the overall trends are considered, peroxide-treated samples showed the most stable mechanical behavior during aging. In contrast, dithionite-treated pulps experienced a more pronounced decline in strength properties. FAS-treated samples displayed intermediate performance. Tensile strength was relatively well preserved, whereas burst strength showed greater sensitivity to prolonged thermal exposure. These differences highlight the influence of bleaching chemistry on long-term mechanical stability.

### 3.4 Physical properties and surface characteristics
### 3.4. Fizička svojstva i svojstva površine

Accelerated thermal aging led to noticeable changes in the physical properties of the bleached pulps. These changes are associated with modifications in fiber surface characteristics, pore structure, and inter-fiber contact within the sheet. The degree of variation differed depending on the bleaching system used (Table 5). Statistical analysis conducted separately for each group showed that aging time had a significant effect on Cobb water absorption and air permeability. However, the extent and consistency of these changes were not the same for all bleaching treatments.

Peroxide-treated samples showed relatively stable physical behavior during thermal aging. Air permeability changed only slightly, decreasing from 21.72 s to 21.46 s after 240 h. Duncan's test grouped early and late aging periods together, indicating that pore structure and overall sheet compactness were largely maintained.

**Table 5** Physical properties of bleached pulps during thermal aging
**Tablica 5.** Fizička svojstva izbijeljene pulpe tijekom toplinskog starenja

| **Group** *Grupa* | **Duration, h** *Trajanje,*h | **Cobb, g/m²** | **Air permeability, s** *Propusnost zraka,* s |
|---|---|---|---|
| Peroxide | 0 | 162.0$^{a*}$ | 21.72$^{a}$ |
| | 72 | 162.2$^{a}$ | 18.94$^{b}$ |
| | 120 | 144.8$^{b}$ | 18.64$^{b}$ |
| | 168 | 145.0$^{b}$ | 20.60$^{ab}$ |
| | 240 | 145.0$^{b}$ | 21.46$^{a}$ |
| | p-value | 0.000 | 0.021 |
| FAS | 0 | 162.8$^{a}$ | 14.70$^{a}$ |
| | 72 | 138.0$^{b}$ | 11.92$^{b}$ |
| | 120 | 128.8$^{c}$ | 12.24$^{b}$ |
| | 168 | 137.2$^{b}$ | 11.50$^{b}$ |
| | 240 | 140.8$^{b}$ | 11.12$^{b}$ |
| | p-value | 0.000 | 0.000 |
| Dithionite | 0 | 161.2$^{a}$ | 15.12$^{a}$ |
| | 72 | 137.2$^{b}$ | 15.02$^{a}$ |
| | 120 | 113.2$^{c}$ | 13.34$^{b}$ |
| | 168 | 109.8$^{c}$ | 11.64$^{c}$ |
| | 240 | 95.2$^{d}$ | 12.00$^{bc}$ |
| | p-value | 0.000 | 0.000 |

*Mean values followed by the same lowercase letter within the same column are not significantly different at the 95 % confidence level according to one-way ANOVA and Duncan's multiple range test
**Srednje vrijednosti uz koje stoji isto malo slovo unutar istog stupca ne razlikuju se značajno na razini pouzdanosti od 95 % prema jednosmjernoj ANOVA-i i Duncanovu testu višestrukih raspona.*

Cobb values decreased from 162.0 g/m² to about 145.0 g/m² ($p < 0.001$). This reduction suggests limited hornification and a moderate decrease in fiber swelling capacity. However, the magnitude of change remained controlled, implying that peroxide treatment helps preserve fiber surface characteristics and pore structure during thermal exposure. Similar observations have been reported in earlier studies, where peroxide bleaching was associated with reduced pore collapse and more stable sheet morphology.

FAS-treated pulps displayed intermediate behavior. Cobb values declined from 162.8 g/m² to 140.8 g/m² ($p < 0.001$), corresponding to roughly a 13 % decrease. Air permeability also decreased from 14.70 s to 11.12 s ($p < 0.001$), indicating changes in pore connectivity and some loss of compactness. Compared with peroxide-treated sheets, FAS samples showed a greater tendency toward structural rearrangement during aging.

Dithionite-treated pulps experienced the most pronounced changes. Cobb values dropped from 161.2 g/m² to 95.2 g/m² after 240 h, and statistical analysis clearly separated aging stages. This substantial reduction points to marked hornification and reduced swelling ability. Air permeability likewise decreased significantly, suggesting progressive alteration of sheet structure under thermal stress.

The lower physical stability observed in dithionite-treated pulps is likely related to its reductive bleaching mechanism. As dithionite does not eliminate lignin-derived structures, certain reactive components remain within the fiber matrix. During thermal aging, these structures may contribute to surface oxidation, pore rearrangement, and gradual fiber embrittlement, which in turn affect both hydrophilicity and porosity. Similar trends have been reported for dithionite-bleached mechanical and recycled pulps exposed to thermal or oxidative conditions (Zhu *et al.,* 2018).

Although all bleaching systems showed statistically significant changes in Cobb and air permeability values ($p < 0.05$), these results should be interpreted in light of the continuous nature of physical aging. Processes such as hornification, pore collapse, and redistribution of surface energy develop progressively rather than abruptly. For this reason, gradual but consistent changes can be practically relevant even when numerical differences appear moderate. When the overall trends are considered, peroxide-treated samples maintained the most stable surface and pore structure during aging. Dithionite-treated pulps exhibited more pronounced physical alteration, while FAS-treated samples showed intermediate behavior under prolonged thermal exposure.

### 3.5 Evaluation of aging performance across bleaching systems

### 3.5. Evaluacija utjecaja starenja u sustavima izbjeljivanja

To strengthen the statistical interpretation of the data, a two-way ANOVA was performed to evaluate the individual and interactive effects of bleaching agent and aging time on optical, mechanical, and physical properties. The analysis revealed that both bleaching agent ($p < 0.05$) and aging time ($p < 0.001$) had significant effects on the evaluated properties. More importantly, a statistically significant interaction between bleaching agent and aging time was observed ($p < 0.05$), indicating that the influence of bleaching treatment varies depending on the duration of thermal aging. This finding confirms that different bleaching chemistries exhibit distinct degradation behaviors across optical, mechanical, and physical performance over time.

Accelerated thermal aging led to noticeable changes in the physical properties of the bleached pulps. These changes are associated with modifications in fiber surface characteristics, pore structure, and inter-fiber interactions. The degree of variation differed depending on the bleaching system used (Figure 1). Statistical analysis conducted separately for each bleaching group showed that aging time had a significant effect on Cobb water absorption and air permeability. However, the extent and consistency of these changes were not the same for all bleaching treatments.

Figure 1 presents an integrated visualization of aging performance by combining optical, mechanical, and physical stability within a unified framework. The radar chart is based on normalized values derived from experimental measurements, enabling direct comparison between bleaching systems despite differences in parameter scales. Rather than replacing statistical analysis, it provides a visual synthesis of multi-parameter behavior and highlights the balance between different performance aspects during aging. This approach demonstrates that bleaching chemistry not only affects individual properties but also their combined contribution to long-term stability, indicating that evaluations based solely on initial optical improvement may be insufficient for selecting appropriate bleaching strategies.

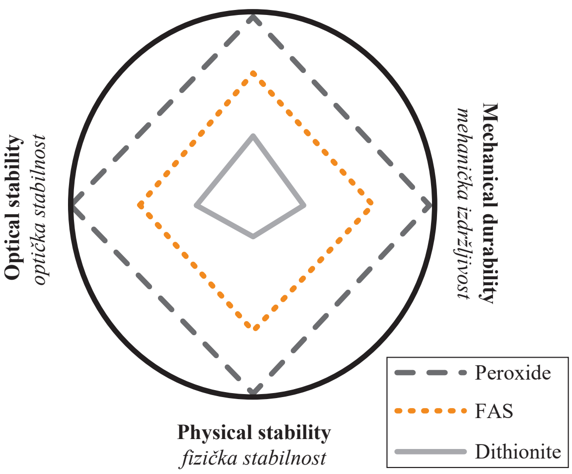


**Figure 1** Aging performance comparison of differently bleached ONP
**Slika 1.** Usporedba utjecaja starenja na različito izbijeljenu papirnu pulpu od starih novina

Peroxide-treated pulps showed stable behavior across the optical, mechanical, and physical parameters evaluated in this study. This trend can be related to the oxidative action of hydrogen peroxide, which modifies lignin-derived chromophoric structures and reduces the number of thermally reactive sites within the fiber matrix (Choi and Kim, 2006; Li *et al.,* 2020; Miglbauer *et al.,* 2020; Zeb *et al.,* 2021). With fewer reactive groups remaining, peroxide-treated fibers tend to display lower brightness reversion, more gradual mechanical decline, and relatively stable surface characteristics during aging. Similar findings have been reported in earlier studies, where peroxide bleaching was associated with improved resistance to thermal and oxidative aging in recycled and mechanical pulps, largely due to the stabilization of residual lignin components (Liu, 2003; Fišerová *et al.,* 2018; Kyene *et al.,* 2019; Jiao *et al.,* 2020; Vaysi and Ebadi, 2021).

FAS-treated pulps showed aging behavior that can be described as intermediate between peroxide and dithionite systems. Optical properties remained relatively stable, but mechanical and physical parameters were more sensitive to prolonged thermal exposure. Although FAS is generally considered more stable than sodium dithionite, it still operates through a reductive mechanism and does not completely remove chromophoric structures from the fiber matrix. As aging progresses, gradual oxidative reactions may continue, influencing fiber bonding and pore structure. Similar observations have been reported in earlier studies comparing FAS and dithionite treatments, where FAS was found to slow down aging-related degradation but not fully prevent losses in strength-related properties (Lennholm and Iversen, 1998; Choi and Kim, 2006; Carreira *et al.,* 2012; Hirn and Schennach, 2017; Peşman and Laloğlu, 2018).

Dithionite-treated pulps showed a less stable aging response compared with the other systems. Although the initial optical values were satisfactory, more pronounced changes were observed in mechanical and physical properties during thermal exposure. The reductive action of sodium dithionite converts chromophores into colorless forms but does not eliminate their conjugated structures (Carreira *et al.,* 2012; Vaysi and Ebadi, 2021). As a result, these structures may be re-oxidized during aging, contributing to progressive hornification, pore modification, and weakening of interfiber bonding. This sequence of changes can lead to a gradual decline in both functional and structural paper properties. Similar trends have been reported in previous studies on reductively bleached recycled fibers subjected to thermal or oxidative conditions.

Figure 1 is therefore not only a visual summary but also an interpretive tool that supports the statistical findings by revealing system-level differences in aging behavior. The combined evaluation clearly indicates that peroxide-treated pulps provide the most balanced and stable performance, followed by FAS and dithionite systems.

## 4 CONCLUSIONS
## 4. ZAKLJUČAK

This study compared the optical, mechanical, and physical behavior of ONP bleached with hydrogen peroxide, FAS, and sodium dithionite under accelerated thermal aging at 103 ± 2 °C. The results show that bleaching chemistry has a clear influence on the long-term stability of recycled paper properties. From an optical standpoint, peroxide-treated pulps displayed higher initial brightness and whiteness and maintained these properties relatively well during aging. Dithionite-treated pulps, although characterized by low initial yellowness, exhibited a more pronounced increase in yellowness and color difference over time. This suggests that initial optical improvement alone is not sufficient to predict aging performance. Mechanical and physical results followed a similar pattern. While all samples experienced some reduction in strength and changes in surface-related properties, peroxide-treated sheets showed a more gradual decline. Dithionite-treated pulps were more sensitive to aging, particularly in terms of burst strength and water absorption behavior. FAS-treated pulps showed intermediate performance. Overall, the findings indicate that bleaching agent selection plays an important role in balancing initial quality with long-term durability in recycled paper applications.

### Disclosure of GenAI usage – Izjava o primjeni generativne umjetne inteligencije

The authors confirm that no artificial intelligence (AI) tools were used in the design of the study, data collection, data analysis, interpretation of results, or preparation of scientific conclusions. AI-based language tools were used only for limited language editing and stylistic refinement to improve clarity and readability of the manuscript. All scientific content, interpretations, and final decisions remain the sole responsibility of the authors.

## 5 REFERENCES
## 5. LITERATURA


1. Aguilar-Rivera, N., 2021: Emerging technology for sustainable production of bleached pulp from recovered cardboard. Clean Technologies and Environmental Policy, 23 (9): 2575-2588. https://doi.org/10.1007/s10098-021-02171-3
2. Asha, K.; Badamali, S. K., 2020: Highly efficient photocatalytic degradation of lignin by hydrogen peroxide under visible light. Molecular Catalysis, 497: 111236. https://doi.org/10.1016/j.mcat.2020.111236
3. Bajpai, P., 2014: Bleaching of Secondary Fibres. In: Recycling and Deinking of Recovered Paper, pp. 155-180, Elsevier. https://doi.org/10.1016/B978-0-12-416998-2.00009-X
4. Boeva, R.; Radeva, G., 2014: Kinetic analysis of the effect of bleaching and temperature increase on the ageing of a chemical-mechanical pulp derived from poplar wood. Cellulose Chemistry and Technology, 48 (7-8): 703-711.
5. Carreira, H. J. M.; Loureiro, P. E. G.; Carvalho, M. G. V. S.; Evtuguin, D. V., 2012: Reductive degradation of residual chromophores in kraft pulp with sodium dithionite. TAPPI Journal, 11 (3): 59-67. https://doi.org/10.32964/TJ11.3.59
6. Chen, S.; Zhu, J., Yu, M.; Jin, C.; Huang, C., 2024: Effect of aging and bleaching on the color stability and surface roughness of a recently introduced single-shade composite resin. Journal of Dentistry, 143: 104917. https://doi.org/10.1016/j.jdent.2024.104917
7. Chen, Y.; Wan, J.; Ma, Y.; Dong, X.; Wang, Y.; Huang, M., 2015: Fiber properties of de-inked old newspaper pulp after bleaching with hydrogen peroxide. BioResources, 10 (1): 1857-1868. https://doi.org/10.15376/biores.10.1.1857-1868
8. Choi, W. J.; Kim, H. J., 2006: Studies on the bleaching efficiency in newsprint using formamidine sulfinic acid. In: Proceedings of the Korea Technical Association of the Pulp and Paper Industry Conference, 381-386.
9. Çiçekler, M.; Tutuş, A., 2025: Cellulose nanofibers (cnf) and cellulose nanocrystals (cnc) as high-performance fillers improving the mechanical, optical and surface properties of recycled newspaper. Turkish Journal of Forest Science, 9 (1): 122-140. https://doi.org/10.32328/turkjforsci.1587158
10. El-Sakhawy, M., 2002: Innovative approaches in bleaching of lignocelluloses – A review. Indian Pulp & Paper Technical Association, 14 (2): 69-84.
11. El-Sakhawy, M.; Abd El-Kader, A. H.; Fahmy, T. Y. A.; Abd El-Sayed, E. S.; Kassem, N. F., 2021: Optimization of dithionite bleaching of high yield bagasse pulp. Cellulose Chemistry and Technology, 55 (5-6): 667-673. https://doi.org/10.35812/CelluloseChemTechnol.2021.55.55
12. Fišerová, M.; Opálená, E.; Gigac, J.; Stankovská, M., 2018: Oxidative and reductive bleaching of deinked pulp. Wood Research, 63 (4): 639-654.
13. Friman, L.; Höglund, H.; Agnemo, R., 2004: Tannin-iron impregnated thermomechanical pulp. Part II: Bleachability and brightness reversion. Nordic Pulp & Paper Research Journal, 19 (4): 525-531. https://doi.org/10.3183/npprj-2004-19-04-p525-531
14. Hashemzehi, M.; Sjöstrand, B.; Håkansson, H.; Henriksson, G., 2024: Degrees of hornification in softwood and hardwood kraft pulp during drying from different sol-

vents. Cellulose, 31 (3): 1813-1825. https://doi.org/10.1007/s10570-023-05657-z
15. Hirn, U.; Schennach, R., 2017: Fiber-Fiber Bond Formation and Failure: Mechanisms and Analytical Techniques. In: Trans. of the XVI[th] Fund. Res. Symp. Oxford, 839-863. Fundamental Research Committee (FRC), Manchester. https://doi.org/10.15376/frc.2017.2.839
16. Jiao, J.; Fang, G.; Liang, F.; Deng, Y.; Shen, K.; Tian, Q.; Han, S.; Zhu, B., 2020: Bleachability improvement of eucalypt mechanical pulps using hydrogen peroxide in ethanol-water media. BioResources, 15 (1): 1370-1383. https://doi.org/10.15376/biores.15.1.1370-1383
17. Kaszonyi, A.; Izsák, L.; Králik, M.; Jablonsky, M., 2022: Accelerated and natural aging of cellulose-based paper: Py-GC/MS method. Molecules, 27 (9): 2855. https://doi.org/10.3390/molecules27092855
18. Koshitsuka, T., 2002: Foundation of recycled pulp bleaching technology. Japan Tappi Journal, 56 (7): 963-975. https://doi.org/10.2524/jtappij.56.963
19. Krishnan, J.; Sunil Kumar, S.; & Krishna Prasad, R., 2020: Characterization of kraft pulp delignification using sodium dithionite as bleaching agent. Chemical Engineering Communications, 207 (6): 837-846. https://doi.org/10.1080/00986445.2019.1630391
20. Kumar, V.; Kalra, J. S.; Verma, D.; Gupta, S., 2020: Process and environmental benefit of recycling of waste papers. International Journal of Recent Technology and Engineering, 8 (2S12): 104-106. https://doi.org/10.35940/ijrte.B1020.0982S1219
21. Kyene, S.; Ventorim, G.; Silva Camargo, B.; De Carvalho Araújo, C. K.; Araújo, C. K. D. C.; Ribas De Lima Soares, L.; Almeida Ferraz, A. P., 2019: Ultraviolet resonance Raman spectroscopy analysis of carbonyl groups present after different bleaching stages for various bleach sequences. BioResources, 14 (1): 1915-1927. https://doi.org/10.15376/biores.14.1.1915-1927
22. Lennholm, H.; Iversen, T., 1998: Pulp bleaching with dithionite: Brightening and darkening reactions. Journal of Pulp and Paper Science, 24 (8): 254-259.
23. Li, M.; Yin, J.; Hu, L.; Chen, S.; Min, D.; Wang, S.; Luo, L., 2020: Effect of hydrogen peroxide bleaching on anionic groups and structures of sulfonated chemo-mechanical pulp fibers. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 585: 124068. https://doi.org/10.1016/j.colsurfa.2019.124068
24. Liu, S., 2003: Chemical kinetics of alkaline peroxide brightening of mechanical pulps. Chemical Engineering Science, 58 (11): 2229-2244. https://doi.org/10.1016/S0009-2509(03)00089-7
25. Małachowska, E.; Dubowik, M.; Boruszewski, P.; Przybysz, P., 2021a: Accelerated ageing of paper: Effect of lignin content and humidity on tensile properties. Heritage Science, 9 (1): 132. https://doi.org/10.1186/s40494-021-00611-3
26. Małachowska, E.; Pawcenis, D.; Dańczak, J.; Paczkowska, J.; Przybysz, K., 2021b: Paper ageing: The effect of paper chemical composition on hydrolysis and oxidation. Polymers, 13 (7): 1029. https://doi.org/10.3390/polym13071029
27. Miglbauer, E.; Gryszel, M.; Głowacki, E. D., 2020: Photochemical evolution of hydrogen peroxide on lignins. Green Chemistry, 22 (3): 673-677. https://doi.org/10.1039/C9GC04324A
28. Nestor, D. V., 1994: Issues in the design of recycling policy: The case of old newspapers. Journal of Environmental Management, 40 (3): 245-256. https://doi.org/10.1006/jema.1994.1018
29. Ornaghi, H. L.; Ornaghi, F. G.; Neves, R. M.; Monticeli, F.; Bianchi, O., 2020: Mechanisms involved in thermal degradation of lignocellulosic fibers: A survey based on chemical composition. Cellulose, 27 (9): 4949-4961. https://doi.org/10.1007/s10570-020-03132-7
30. Paranjape, M.; Athalye, A., 2024: Eco-friendly polyester reduction clearing: Examining cutting-edge approaches. Advance Research in Textile Engineering, 9 (3): 1103.
31. Pemberton, R. S.; Depew, M. C.; Heitner, C.; Wan, J. K. S., 1995: Some mechanistic insights into a model bleaching process of quinones by bisulfite and dithionite: An ESR-CIDEP study. Journal of Wood Chemistry and Technology, 15 (1): 65-83. https://doi.org/10.1080/02773819508009500
32. Peşman, E.; Laloğlu, S., 2018: Recycling of colored office paper. Part I: Pre-bleaching with formamidine sulfinic acid at pulper. BioResources, 13 (2): 3949-3957. https://doi.org/10.15376/biores.13.2.3949-3957
33. Pydimalla, M.; Reddy, K., 2020: Effect of pulping, bleaching and refining process on fibers for paper making – A review. International Journal of Engineering Research & Technology, 9 (12): 310-316. https://doi.org/10.17577/IJERTV9IS120143
34. Rundlöf, E. S.; Zhang, E.; Zhang, L.; Gellerstedt, G., 2006: The behavior of chromophoric structures in softwood mechanical pulp on bleaching with alkaline hydrogen peroxide. Nordic Pulp & Paper Research Journal, 21 (3): 359-364. https://doi.org/10.3183/npprj-2006-21-03-p359-364
35. Saad, A.; Owda, M.; Ibrahim, A.; Bassiouni, M., 2020: Effect of deinking and peroxide bleaching on the physical properties of recycled newspapers. Al-Azhar Bulletin of Science, 31 (2): 9-18. https://doi.org/10.21608/absb.2020.35942.1070
36. Sepahvand, S.; Akbarpour, I.; Ashori, A., 2025: Optimizing mixed waste paper properties through formamidine sulfinic acid bleaching and cationic additive treatments. Journal of Polymers and the Environment, 33 (1): 29-50. https://doi.org/10.1007/s10924-024-03411-5
37. Sevastyanova, Y.; Shcherbak, N.; Konshina, K.; Potashev, A.; Palchikova, E.; Makarov, I.; Kalimanova, D.; Sakipova, L.; Kareshova, Z.; Balabekova, S.; Shambilova, G.; Vinogradov, M.; Novikov, E., 2025: Study of the change in properties by artificial aging of eco-papers. Processes, 13 (6): 1750. https://doi.org/10.3390/pr13061750
38. Sjöstrand, B.; Karlsson, C.-A.; Barbier, C.; Henriksson, G., 2023: Hornification in commercial chemical pulps: Dependence on water removal and hornification mechanisms. BioResources, 18 (2): 3856-3869. https://doi.org/10.15376/biores.18.2.3856-3869
39. Tofani, G.; Cornet, I.; Tavernier, S., 2021: Estimation of hydrogen peroxide effectivity during bleaching using the Kappa number. Chemical Papers, 75 (11): 5749-5758. https://doi.org/10.1007/s11696-021-01756-y
40. Tofani, G.; Cornet, I.; Tavernier, S., 2022: Multiple linear regression to predict the brightness of waste fibres mixtures before bleaching. Chemical Papers, 76 (7): 4351-4365. https://doi.org/10.1007/s11696-022-02181-5
41. Vaysi, R.; Ebadi, S. E., 2021: Thermal yellowing of hornbeam chemi-mechanical pulps bleached with hydrogen peroxide and sodium dithionite. BioResources, 16 (4): 7635-7647. https://doi.org/10.15376/biores.16.4.7635-7647

42. Youssef, A.; Rushdy, A.; Noshy, W., 2017: Influence of bleaching materials on mechanical and morphological properties for paper conservation. Egyptian Journal of Chemistry, 60 (5): 893-903. https://doi.org/10.21608/ejchem.2017.1288.1073
43. Yun, N.; He, B. H., 2011: Study on bleaching of de-inked pulp. Advanced Materials Research, 236-238: 1224-1228. https://doi.org/10.4028/www.scientific.net/AMR.236-238.1224
44. Zeb, H.; Hussain, M. A.; Ahmed, I.; Akram, M. S.; Haider, B.; Haider, R.; Babar, Z. B.; Saleem, R. M.; Ahsan, A.; Aziz, I.; Arif, M., 2021: Study of bleaching of old newsprint recycled paper: Reproduction of newspaper material. Materials Research Express, 8 (8): 085305. https://doi.org/10.1088/2053-1591/ac1ca9
45. Zhao, L.; Jiang, W.; Wang, Y.; Wang, Z.; Wang, Y., 2022: Study on micro topography of thermal aging of insulation pressboard based on image processing. Energies, 15 (17): 6317. https://doi.org/10.3390/en15176317
46. Zhu, M.; Chen, Y.; Gu, C.; Zhu, W.; Ma, X.; Wang, X., 2018: Effect of thermal aging on the properties of insulating paper. In: Proceedings of the 4th Annual International Conference on Material Engineering and Application (ICMEA 2017), pp. 122-124. https://doi.org/10.2991/icmea-17.2018.28

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