Aging Effects on Paper Dispersibility – A Review

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The aging of paper significantly impacts fiber-water interactions, leading to a decline in dispersibility over time. This deterioration is particularly critical for water-dispersible paper and packaging applications designed to dissolve easily after use, as well as for recycling processes, where reduced dispersibility increases energy consumption and reject content. The aging process is notably faster and more pronounced in unbleached fibers compared to bleached fibers, indicating that lignin plays a crucial role in this phenomenon. A decrease in dispersibility is closely linked to reductions in water retention value (WRV) and increases in paper wet strength, driven by natural aging mechanisms such as hornification, auto-crosslinking, extractives self-sizing, and cellulose recrystallization. These processes reduce fiber swelling capacity and hinder paper disintegration in water. To mitigate the decline in dispersibility due to aging, minimizing moisture cycling and avoiding high temperatures are promising. Also reduction of refining energy and wet-end starch dosage in papermaking are ways to better preserve repulpability. Understanding these aging mechanisms is essential for optimizing paper formulations and ensuring long-term performance in both functional and recyclable paper products.

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INTRODUCTION

Aging of paper is a crucial factor studied across various research domains, *e.g.* preservation of cultural heritage or the yellowing of graphical paper (Kulak *et al.* 2016), or transformer insulation materials (Lundgaard *et al.* 2005; Przybylek 2010). This work is focusing on the mechanisms driving the deterioration of paper dispersibility over time. Understanding the process why paper dispersibility is eventually declining and how this is related to the physical and chemical aging processes in paper is highly relevant to the field of paper recycling. Repulpability is a key property for paper during the recycling process. It is evaluated in all recyclability tests for packaging papers (Kochersperger and Schabel 2024), particularly in the EU Harmonized Recyclability Test for Paper and Board Materials (CEPI 2022).

Also various applications of water-dispersible paper are documented, where the functionality of the product depends on preserving good paper dispersibility over the lifetime of the product. Literature can be found on wrapping material for toilet paper rolls (Saito 1998), seed packets (Caspar *et al.* 2013), pouches for conditioners or shampoos (Green 2021), soap wrappers (Banks 1953), coffee cup sleeves (Naithani *et al.* 2017), and seeding sheets for gardening (Koyama *et al.* 2016). Additionally, research highlights a range of water-soluble and biodegradable packaging materials such as nanocomposites (Kaushik *et al.* 2010), granular plant growth regulators (Devisetty *et al.* 2002), and cellulose acetate (Cao *et al.* 2016). Further applications include pulp-based composites, such as poly paper (Del Curto *et al.* 2016). Beyond packaging, water-dispersible paper is also used in specialized contexts, including the secure disposal of confidential documents (Koyama *et al.* 2016) or in illegal activities where the elimination of physical evidence is desired (Itamiya *et al.* 2021).

It has been found that the dispersibility of paper products tends to decrease over time (Pfennich and Hirn 2025). A similar effect has also been found for wet-wipes (Harter *et al.* 2022), which are wet stored cellulose fiber nonwovens. Apparently, there are natural aging processes taking place in cellulose fiber networks that are deteriorating their ability to disintegrate in water. It is the aim of this work to examine the change of dispersibility over time in the context of paper aging, aiming to provide an overview of possibly related mechanisms.

Aging, whether natural or accelerated, can generally be classified into physical and chemical processes, each with distinct characteristics (Strlic and Kolar 2005; Zervos 2010). The most well-known physical aging mechanism is hornification, which is characterized by the loss of fiber wall swelling and increased fiber stiffening, reducing the ability to form inter-fiber bonds (Scallan and Laivins 2018). Other physical processes include recrystallization (Małachowska *et al.* 2021b) and denaturation (Strlic and Kolar 2005). Chemical aging involves irreversible changes in molecular structure and chemical decomposition, including oxidation, hydrolysis, degradation, chain scission, and auto-crosslinking (Flore *et al.* 2016; Zervos 2010). Natural aging of paper induces long-term changes that significantly affect its fiber-water interactions, mechanical and optical properties, and overall lifespan (Małachowska *et al.* 2021b; Strlic and Kolar 2005). Understanding fiber-water interactions involves clarifying the types of water held by wood fibers, including free water, bound water, and non-freezing bound water (Salmén and Berthold 2018).

Over time, paper becomes transformed from being relatively flexible and tough to becoming brittle (Koura and Krause 1978). The impact of aging on water absorption varies depending on factors such as paper type, environmental conditions, and specific aging mechanisms. As a result, this is especially pertinent to the preservation of historical and archival materials. In contrast, accelerated aging simulates these natural processes within a much shorter timeframe, enabling the rapid assessment of material durability. Accelerated aging is frequently used in material science and preservation research (Havermans 1995; Strlic and Kolar 2005; Zervos 2010; Zou *et al.* 1994). A comprehensive understanding of aging processes is essential for the preservation of cultural heritage in archives and libraries (Area and Cheradame 2011). Notably, much of the degradation in archival materials is attributed to bio-deterioration, especially by fungi (Zotti *et al.* 2008). Key properties typically assessed in aging studies include folding endurance, tensile strength, and the degree of acidic degradation—often evaluated across papers with varying acidity levels to observe differential aging behaviors (Havlínová *et al.* 2009; Strlic and Kolar 2005). Additionally, the depolymerization of cellulose is a critical factor in understanding the long-term stability of paper materials (Strlic and Kolar 2005). One of the most immediately noticeable effects of aging in graphical paper is yellowing and loss of brightness, which is highly dependent on the paper's pH. This discoloration results from oxidation and autohydrolysis processes, both of which accelerate the yellowing over time (Bonham and Rolniczak 2006; Lewin 1997).

Key Terms and Mechanisms of Fiber Water Interaction

Dispersion of paper in water is caused by the water opening the fiber-fiber bonds. Hence, fiber-water interaction is highly relevant in the context of this work. In this section, detailed definitions of key terms and mechanisms are provided to explain the various ways in which water interacts with paper. The goal is to facilitate a deeper understanding of the requirements and behavior necessary for optimal paper dispersibility.

A pulp fiber primarily comprises cellulose, lignin, hemicellulose, and associated materials, the proportions of which vary depending on the type of wood and its location (Blechschmidt *et al.* 2021). The *composition* of fibers and the position of water in the paper are interrelated factors that play a crucial role in determining its performance, durability, and suitability for various applications. It affects its strength, absorbency, and other physical properties (Salmén and Berthold 2018). The fiber composition of paper directly affects its water absorption and retention characteristics. Different fiber types have varying levels of hydrophilicity and absorbency, which can impact how water is distributed within the paper structure (Begum *et al.* 2021; Salmén and Berthold 2018).

The term *water position* in paper refers to the distribution of water within the fiber structure. When paper absorbs water, it undergoes changes in its physical dimensions and properties. Water can be present in various forms within the paper, including (Salmén and Berthold 2018):

- *Free Water*: Water molecules that are not bound to the fibers and can move freely within the paper structure.
- *Bound Water*: Water molecules that are adsorbed to the fiber surface by hydrogen bonding and other molecular interactions. To overcome these bonding effects there has to be an additional energy named heat of sorption. Bound water contributes to the flexibility and swelling behavior of paper fibers (Leuk *et al.* 2016; Łojewski *et al.* 2010; Salmén and Berthold 2018). The amount of bound water reflects the composition of the fibers, particularly the wood polymers they are made of (Salmén and Berthold 2018).
- *Pore or Capillary Water*: Water that is held within the small voids and spaces between fibers due to capillary pressure. Capillary water influences the paper's absorbency and wicking properties. The physical changes of the fiber wall, such as its structure and composition, can affect the presence and behavior of pore water in paper (Salmén and Berthold 2018).

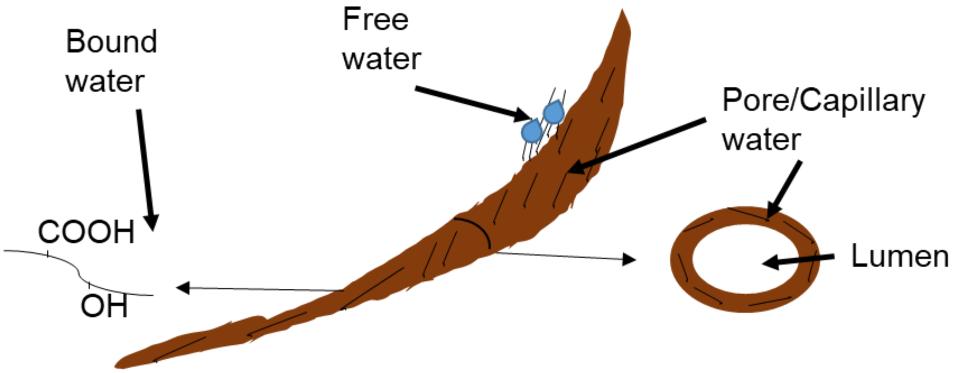

Fig. 1. Forms of water within the paper. This illustration is based on the work of Salmén and Berthold (Gruber 2011; Salmén and Berthold 2018).

Mechanisms Influencing Fiber-Water Interaction

The *disintegration* of water-dispersible paper is primarily driven by its interaction with water. Chemically, this process occurs due to the disruption of fiber-fiber bonding as water penetrates the paper matrix (Cho *et al.* 2009; Nissan 1977). Consequently, the key factors influencing disintegration are water penetration, absorption, and the swelling behavior of the fibers. Understanding the development of paper strength is essential to comprehend how wet strength—and consequently, dispersibility—changes over time. To elucidate the effects of aging on these properties and their impact on disintegration, a brief explanation is provided here.

Paper strength development

Throughout the paper drying process, its strength, stiffness, and hygroexpansion coefficient are increasing (Urstöger *et al.* 2020). An explanatory model outlines the different phases of strength development in paper. In the initial phase, occurring at approximately 25% dryness content, capillary forces emerge, depending on drainage (Belle 2016; Kallmes *et al.* 1977; Kendall 2001; Williams 1983). As further dewatering occurs, the fibers gradually collapse (Belle 2016; Paavilainen 1993a,b; Weise 1998; Weise *et al.* 1996). This collapse results in mechanical interlocking and entanglement of fibers, leading to shape and frictional fitting (Oliveira *et al.* 2008; Tejado and vandeVen 2010; Williams 1983). The second phase occurs between 25% and 60% drying content, where interactions between attractive and repulsive van der Waals forces develop (Derjaguin and Landau 1941; Derjaguin 1954; Israelachvili 2006; Pelton 1993; Wåberg and Annergren 1997). Finally, in the last phase, van der Waals- and hydrogen bonds are forming due to capillary pressure of the remaining water (Persson *et al.* 2013) as the drying process progresses (McKenzie 1984; Nissan and Batten 1990; Wåberg and Annergren 1997).

Inversely, paper stiffness and strength decrease with increasing relative humidity of the paper (Haslach 2000; Salmén and Back 1980). This is due to moisture-induced reduction of the polymer glass transition points in the fibers (Salmén and Back 1977). When unsized paper is wetted, the fiber-fiber bonds are opening and its strength instantly goes down to zero (Lahti *et al.* 2019). This process can be delayed and reduced by hydrophobic sizing (Korpela *et al.* 2021) or crosslinking (Back 1985; Zervos 2010). The accessibility of water to the fibers and fiber-fiber bonds hence is the key factor deteriorating paper strength and thus plays a high role for paper disintegration.

Absorption and capillarity/penetration

Paper fibers have a natural affinity for water due to their hydrophilic nature. The capillary action within paper fibers and between fiber networks plays a significant role in water absorption. Capillary forces draw water into the small spaces and voids between fibers, allowing water to spread and penetrate through the paper structure (Akinli-Kogak 2001; Botková *et al.* 2013). A key characteristic for effective disintegration is strong water penetration (Pfennich *et al.* 2023).

Swelling behavior

The swelling behavior of paper fibers is influenced by factors such as fiber type, morphology, such as fiber length and fiber diameter, chemical composition, and environmental conditions. The fiber type and chemical composition significantly influence dispersibility, with factors such as increased fiber length, unbleached pulp, or higher lignin content resulting in reduced repulpability (Blechschmidt *et al.* 2021; Pfennich *et al.* 2023;

Tervahartiala *et al.* 2018). The environmental factors influencing swelling and aging include heat, humidity, light, oxygen, and pollutants (Erhardt and Mecklenburg 1995; Jajcinovic *et al.* 2018). Variations in swelling among fibers affect the paper's water absorption and retention properties. Upon exposure to water, fibers undergo a diffusion process, absorbing moisture that leads to swelling, thereby increasing the paper's thickness and volume. A portion of the absorbed water is retained within the fiber structure, enhancing the material's retention capacity (Akinli-Kogak 2001; Botková *et al.* 2013). Water absorption influences the strength of paper by causing fiber swelling, which weakens the bonds between fibers and reduces tensile strength (Hoyland 2018).

Drying behavior and aging

The drying process is closely linked to the fiber-water interaction in paper. During drying, water evaporates from the paper, causing the fibers to shrink and the paper to regain its original dimensions, which in turn leads to a severe reduction in its swelling ability. The drying rate, temperature, and humidity conditions influence the drying behavior and final properties of the paper (Salmén and Stevanic 2018). Drying also reduces the amount of bound- and capillary water adsorbed on the fiber; the required desorption energy is commonly referred to as the heat of sorption (Leuk *et al.* 2016).

Aging, both natural and accelerated (here: thermal aging), can be broadly categorized into physical and chemical aging. There is a distinct difference between these two processes. Natural aging occurs over an extended period, with mechanisms progressing slowly and at lower intensities, making it essential for historical and archival purposes. In contrast, accelerated aging simulates the natural aging process within a significantly shorter timeframe. The idea of accelerating aging by elevated temperature is that the reaction kinetics of paper ageing is following an Arrhenius-type model (Zou *et al.* 1996) with the reaction rate – and thus paper aging - increasing exponentially with temperature. Accelerated aging is frequently used in material science and preservation research. A standardized method for accelerated, or thermal, aging is specified by ISO 5630-1. Aging can cause changes in the surface characteristics of paper, such as the formation of a patina or surface degradation. These changes can alter the paper's interaction with water, affecting its moisture absorption capacity (Havermans 1995; Strlic and Kolar 2005; Zervos 2010; Zou *et al.* 1994). The aging and degradation processes are influenced by both endogenous and exogenous factors. Key endogenous contributors include metal ions, lignin, certain degradation products, and pH levels. Prominent exogenous factors encompass pollutant gases, humidity, and, as discussed above, heat (Area and Cheradame 2011).

Testing methods for paper aging

To test paper aging, various methods are employed to evaluate mechanical, physical, and chemical changes over time. Key mechanical tests include tensile strength, tear resistance, and folding endurance, which help determine paper's durability (Havlínová *et al.* 2009; Małachowska *et al.* 2021a; Strlic and Kolar 2005). Accelerated aging tests, often based on ASTM and ISO standards (ASTM D6819 and ISO 5630), simulate long-term effects through heat, humidity, or UV exposure. Chemical tests, such as pH measurement, monitor paper acidity and its role in degradation (Strlic and Kolar 2005), and tests for brightness and color stability (Bonham and Rolniczak 2006; Lewin 1997). Fiber-water interactions are indirectly evaluated through water retention value (WRV), disintegration testing, and sorption analysis (Zervos 2010). Advanced exemplary techniques including Gas Chromatography-Mass Spectrometry (GC/MS), Fourier

Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM) provide insights into molecular degradation processes, analyzing both structural and chemical changes in paper over time (Area and Cheradame 2011; Małachowska *et al.* 2021a).

NATURAL AGING, WET STRENGTH INCREASE and WRV

It has been observed that paper stored under environmental conditions for several months continuously diminishes in its ability to be disintegrated in water (Pfennich and Hirn 2025). This effect is quite moderate for bleached pulp, but it is much stronger for unbleached pulp; furthermore, the effect is increased by refining and the utilization of starch in the wet end (Pfennich and Hirn 2025).

In general, the repulpability, or the ability of paper to disintegrate in water, is reduced by increasing its *wet strength* (Koura and Krause 1978; Siqueira *et al.* 2015; Su *et al.* 2012). Higher wet strength allows paper to maintain its structural integrity when wet, often achieved through additives or treatments that enhance fiber bonding or alter fiber structure (Su *et al.* 2012; Yang *et al.* 2019). When the wet strength of recovered paper is low and subjected to high force, the defibering process is enhanced (Cho *et al.* 2009; Su *et al.* 2012). Also for recovered paper, higher wet strength correlates with increased resistance to defibration (Blechschmidt *et al.* 2021).

In the tissue industry, both accelerated and natural aging processes are employed to maximize wet strength, demonstrating that disintegration is dependent on this property (ISO 12625-17: *Tissue paper and tissue products* 2021). Aging enhances *auto-crosslinking* (the formation of covalent bonds) and *crystallinity*, increasing wet strength and fiber bond strength without changing the bonding area (Dodson 1973; Fellers *et al.* 1989).

Wet strength can increase over time until it peaks and then declines, indicating prolonged aging exacerbates the defibering of paper. The wet tensile strength behavior for various pulps is illustrated in Fig. 2 (Koura and Krause 1978).

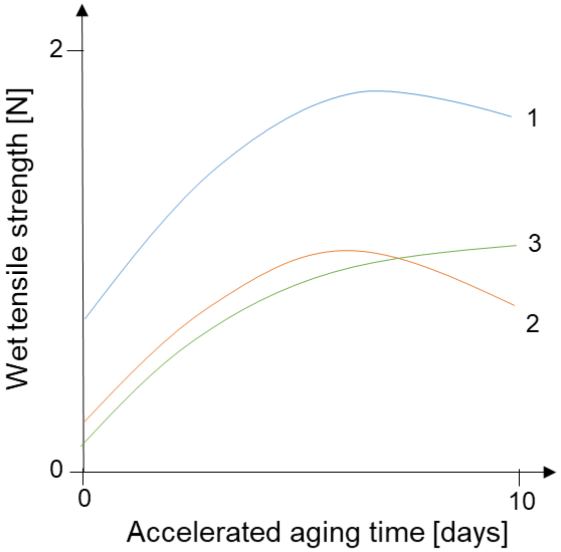

Fig. 2. Wet tensile strength over 10 days accelerated aging time (90 °C and 70 % humidity): 1.) sulfite pulp, 2.) processed sulfite pulp 3.) sulfate pulp: image is based on (Koura and Krause 1978)

Without wet strength agents, the wet strength of recovered paper is influenced by the rate of water penetration. Effective disintegration requires water to infiltrate the fiber to reach the bonding region, which is affected by pore structure and surface hydrophobicity (Cho *et al.* 2009; Su *et al.* 2012).

There is a significant difference between bleached and unbleached pulp fibers in their swelling behavior. Bleached fibers exhibit greater and more rapid swelling due to higher hydroxyl group content, which results from lignin removal during bleaching. Unbleached sulfate or kraft pulp shows diminished swelling and bonding potential during recycling due to decreased strength. Recycled fibers display more hydrophobic behavior compared to original fibers. During recycling, fiber surfaces undergo inactivation, known as irreversible *hornification*, where pore closure in pulp walls prevents re-wetting (Geffert *et al.* 2016; Okayama 2002; Ruvo and Htun 2018; Stone and Scallan 1965). Such effects can give rise to increased *water contact angle* (Geffert *et al.* 2016; Okayama 2002).

When considering water-fiber interaction, it is essential to recognize the significance of the *water retention value* (WRV). Papers stored over several months exhibited reduction in WRV, together with a decrease in dispersibility (Pfennich and Hirn 2025). The WRV measurement reflects the total water content retained by the fiber, encompassing all types of water the fiber can hold (Salmén and Berthold 2018). When fibers undergo drying or aging, a process called *hornification* occurs. This involves the formation of bonds between hydroxyl groups on cellulose surfaces as water is removed, enhancing structural strength, but causing fibers to contract and become more ribbon-like. This contraction reduces the fibers' ability to swell and retain water, leading to a lower WRV (Blechschmidt *et al.* 2021). The decrease in WRV due to repeated drying is particularly relevant for recycled fibers, where the number of recycling cycles and the extent of aging is relevant (Harter *et al.* 2022; Jablonský *et al.* 2014; Kato and Cameron 1999a,b; Šutý *et al.* 2012). Recycled fibers, particularly those made from kraft pulp, exhibit diminished swelling and water-binding potential. The internal fiber surface, especially the lumen, plays a significant role in re-swelling behavior. According to Geffert *et al.* (2016) hornification and lumen contraction are the key factors for reduced WRV of recycled fibers.

Aging exacerbates this issue by closing larger pores within the fiber structure, thereby further reducing re-swelling capacity (Cildir and Howarth 1972). Natural aging, even at moderate temperatures such as 22 °C, acts similarly to drying, inducing irreversible changes such as *auto-crosslinking* and *hydrolytic breakdown of cellulose chains* (Gratton 1991). The bonding within the fiber wall, plays a significant role in this process resulting in stiffer, less conformable fibers that cannot fully regain their water retention capabilities (Wu 1996). The decline in WRV over time is also due to the compaction of the fiber wall structure in non-crystalline regions, a process known as *recrystallization*. The reduction of WRV due to natural ageing for various pulps is shown in Fig. 3 (Koura and Krause 1978).

Another factor to consider in the context of varying disintegration ability is lignin, which significantly contributes to the accelerated deterioration of unbleached paper compared to bleached paper (Pfennich and Hirn 2025). Lignin functions both as an antioxidant and a catalyst for oxidation (Małachowska *et al.* 2020). Additionally, the reduction in disintegration may be attributed to lignin self-sizing, a self-assembly process where lignin molecules organize to expose their hydrophobic regions, thereby increasing the paper's hydrophobicity (Trovagunta *et al.* 2024).

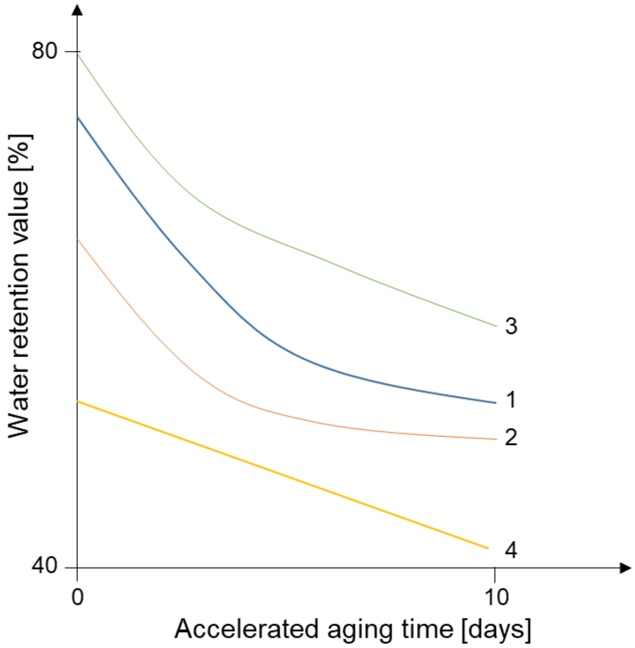

Fig. 3. Water retention value over 10 days accelerated aging time (90 °C and 70 % humidity); 1.) sulfite pulp, 2.) processed sulfite pulp 3.) sulfate pulp 4.) bamboo pulp: image is based on (Koura and Krause 1978)

A potential mechanism for the decline in disintegration over time is self-sizing due to the migration of extractives to the fiber surface (Aspler *et al.* 2018; Hubbe *et al.* 2007; Lindström 2009; Ness and Hodgson 1999). This phenomenon is well-documented in mechanical pulp and unbleached pulp. The higher extractives content in unbleached pulps compared to bleached pulps aligns with the observed faster deterioration of unbleached papers (Pfennich and Hirn 2025).

AGING PROCESSES

In this section the different aging processes taking place in paper, and their implications on water interaction and paper dispersibility, are being discussed.

Physical Aging

Hornification

The concept of hornification was first introduced in 1944 by Jayme, who used the designation "Irreversible Verhornung" (Lindström and Ström 2022; Weise *et al.* 1996). This phenomenon denotes an irreversible change (Sjöstrand *et al.* 2023) of fibers and water-holding capacity mostly resulting from drying, but also from water removal in general and wet pressing (Fernandes Diniz *et al.* 2004; Luo *et al.* 2011; Maloney *et al.* 1997; Scallan and Laivins 2018). Notably, hornification also occurs at room temperature (Kato and Cameron 1999b; Fernandes Diniz *et al.* 2004; Scallan and Laivins 2018). The hornification process comprises four stages: the initial crystallization period, which occurs at moisture levels above 70%; the cocrystallization period, spanning moisture content between 70% and 31%; the hemicellulose control period, ranging from 31% to 11% moisture content; and the second crystallization period, occurring at the lowest moisture content of 11% to 0%. During the cocrystallization and second crystallization stages, there is a reduction in water retention value, indicating the occurrence of hornification (Mo *et al.* 2022).

This state of hornification can be quantified by calculating the decrease in water retention value using Eq. 1 (Jayme 1944),

$$Hornification\ status\ [\%] = \frac{WRV_0 - WRV_1}{WRV_0}\ x\ 100 \tag{1}$$

where WRV_0 is the water retention value before- and WRV_1 after hornification. Already Jayme and Hunger (1956), proposed a mechanism of closing of pores due to hard-to-reverse bonding among individualized microfibrils. In essence, this process generates bonded regions between cellulose microfibrils, manifested as *irreversible* (Lindström 1986) intra-fiber hydrogen bonding connections (Fernandes Diniz *et al.* 2004; Kato and Cameron 1999b; Mo *et al.* 2022; Salmén and Stevanic 2018). The pores in the fibers collapse, which imparts resistance to swelling forces upon rewetting (Köhnke *et al.* 2010; Salmén and Stevanic 2018; Scallan and Laivins 2018). These irreversible changes post-drying also include increased brittleness and reduced fiber flexibility (Kato and Cameron 1999b).

Recrystallization

Recrystallization is a physical degradation process that can occur in cellulose fibers within paper. It involves the reorganization of cellulose molecules into a more ordered structure (Koura and Krause 1978), often as a response to changes in environmental conditions such as temperature and humidity, or to mechanical load, such as during milling (Ling *et al.* 2019). While recrystallization can interact with- and influence both, hydrolysis and oxidation, which are chemical degradation processes (Małachowska *et al.* 2021b). Water plays a significant role in promoting recrystallization due to its ability to form hydrogen bonds with cellulose molecules. Additionally, water's high surface tension can facilitate the organization of cellulose molecules into a more ordered crystalline structure (Bertran and Dale 1985).

Self-sizing

Self-sizing is a vital process in wood-containing papers or those with high extractive content. It involves the redistribution of resins and extractives with low softening points on the fiber material through surface diffusion. This thermodynamically favorable process allows resins in parenchyma cells to form a monomolecular layer at the interface between air and fiber surface, transforming a high-energy surface (cellulose) into a low-energy surface. The reorientation of amphiphilic molecules at the boundary surface can also play a role in self-sizing (Lindström 2009). However, self-sizing can lead to increased resistance to wetting, which may impede the reception of aqueous glues or spilled materials. This issue is often due to the presence of fatty and resin acids on fiber surfaces, which can migrate during paper formation, drying, or storage. If aluminum species are present, they can act as mordants, binding to the carboxylate groups of wood resins and orienting hydrophobic groups outward (Hubbe *et al.* 2007). To counteract the effects of self-sizing, surfactants can be added (Hubbe *et al.* 2007; Aspler *et al.* 2018), or extractive materials can be removed from the pulp to eliminate their negative impact on paper properties (Ness and Hodgson 1999).

Additionally, lignin self-sizing is another important factor to consider. This self-assembly process involves lignin molecules organizing in a way that exposes their hydrophobic regions (Trovagunta *et al.* 2024).

Chemical Aging

The chemistry of pulp aging is considered in relation to the degradation of the paper and cellulose. Chemical aging can involve different reactions, such as oxidation, hydrolysis and chain scission, and auto-crosslinking. The main degradation products that originate from the oxidation and hydrolysis of the paper, are sugars, oligomers, organic acids, volatile organic compounds and phenolic products of lignin degradation (Zervos 2010). In considering the lignin content in paper, it is noted that lignin is more susceptible to oxidation by air compared to cellulose. Consequently, paper containing lignin, hemicellulose, or other additives is more prone to oxidation, hydrolysis, and various other degradation processes (Małachowska *et al.* 2020).

Hydrolysis and chain scission

For the natural and accelerated aging, the main reaction for the degradation of cellulose is the acid hydrolysis of the glycosidic bonds (Fellers *et al.* 1989; Zervos 2010; Zou *et al.* 1994).

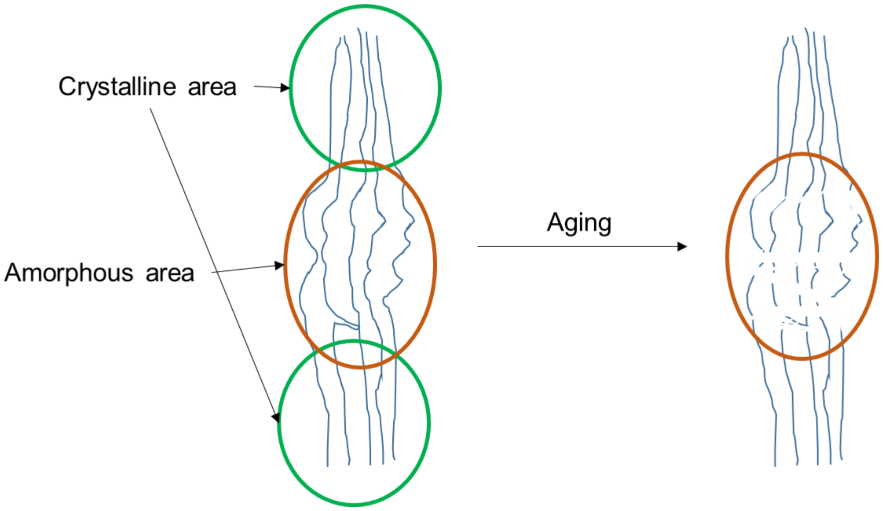

Fig. 4. Effect of aging on the supermolecular structure of cellulose: image is based on (Koura and Krause 1978)

Hydrolysis is a fundamental chemical process wherein water molecules, along with acidic or alkaline agents, catalyze the breakdown of chemical bonds within the cellulose. In the realm of paper aging, hydrolysis predominantly targets the β-acetal oxygen bridge in cellulose under acidic conditions. This hydrolysis leads to the cleavage of bonds between the glucose molecules, resulting in chain scission and eventual degradation of paper fibers (Carter 1996; Seery 2013). The degradation primarily occurs in the amorphous regions, resulting in an increase in the degree of crystallization (Anders *et al.* 1995). Consequently, the paper becomes rigid, brittle, and less flexible, thereby facilitating its disintegration. Moreover, the hydrolysis of cellulose reduces the degree of polymerization, leading to the formation of shorter chains, which further weakens the paper's strength (Carter 1996; Seery 2013).

The phenomenon of recrystallization significantly impacts the rate of hydrolysis by regulating the accessibility of cellulose molecules to water molecules. Upon undergoing recrystallization, the penetration of water molecules is impeded, thus obstructing the initiation of hydrolytic reactions (Tan *et al.* 2023). Conversely, instances where recrystallization exposes a larger surface area of cellulose molecules to water may accelerate the hydrolysis process (Area and Cheradame 2011; Battista 1950; Bertran and Dale 1985; Małachowska *et al.* 2021b; Tumkur *et al.* 2020).

Chain scission in this context is a more general term for breaking of polysaccharide chains due to various mechanisms including chemical degradation reactions such as hydrolysis, oxidation, and exposure to radiation (such as UV light). In the context of paper aging, chain scission often occurs concurrently with hydrolysis (Kato and Cameron 1999b; Koura and Krause 1978; Zervos 2010). After hydrolysis and chain scission, an increase in crystalline regions is observed as a result of the degradation of amorphous areas (Fellers *et al.* 1989; Zou *et al.* 1994).

Oxidation

The oxidation of paper is a chemical process that occurs when paper is exposed to oxygen in the air over time. This process can lead to various changes in the properties of the paper, often resulting in deterioration and degradation (Area and Cheradame 2011).

The degree of oxidation is influenced by temperature, consequently resulting in comparatively lower degradation from oxidation at room temperature, as opposed to the degradation induced by acid hydrolysis (Małachowska *et al.* 2021b).

During the process of oxidation, hydroxyl groups present on the anhydroglucose units are converted into carbonyl groups and carboxylic groups (Carter 1996). The cellulose experiences a decrease in its degree of polymerization, concomitant with the formation of carboxyl groups (Fellers *et al.* 1989). The oxidized cellulose exhibits accelerated degradation compared to untreated cellulose (Zervos 2010). It can be asserted that the natural aging process of paper leads to the development of oxidized groups bonded to the cellulose matrix (Kyujin 2013). Lignin in paper plays a crucial role in the degradation of cellulose, acting either as an antioxidant or as a catalyst for oxidation (Małachowska *et al.* 2020).

Auto-crosslinking

Both accelerated and natural aging processes can induce auto-crosslinking phenomena taking place within the fiber, but also in fiber-fiber bonds. This manifests as a reduction in wet elongation, heightened wet strength, limitation of water absorption-induced swelling, and an elevation in the brittleness of paper (Back 1967; Graminski 1970; Ruffini G. 1966; Wilson; and Parks 1979; Zervos 2010). This all suggests the oxidative generation of carbonyl groups along neighboring cellulose chains, leading to the formation of either hemiacetal bonds between them or ester linkages between carboxyl groups on one chain and hydroxyl groups on an adjacent chain. It is worth noting that auto-crosslinking and chain scission are competitive processes, leading to an initial peak and subsequent decline in tensile strength (Back 1967; Graminski 1970; Robertson 1976; Ruffini 1966; Zervos 2010).

CONCLUSIONS

1. Repulpability (dispersibility) is a key aspect of all recyclability tests for paper-based packaging materials. Thus it is highly relevant to understand why and how the dispersibility of paper is deteriorating over time.
2. This deterioration is considerably faster and more pronounced for unbleached fibers compared to bleached fibers, indicating that lignin and/or extractives content are playing a key role in the process.
3. A decrease in dispersibility goes hand in hand with a decrease in water retention value and an increase in paper wet strength. Hornification, auto-crosslinking, cellulose recrystallisation and self-sizing due to the presence of extractives are well known natural aging phenomena in paper which are well able to explain the observed changes in dispersibility, water retention value (WRV) and increased wet strength.
4. In order to slow down or prevent the aging of paper and the associated decline in dispersibility, it is crucial to explore methods to delay hornification, auto-crosslinking and diffusion (self-sizing), *e.g.* by preventing moisture cycling and high temperatures of storage. Reducing refining and wet end starch in papermaking was also found to mitigate declining dispersibility due to paper aging.

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REFERENCES CITED

Ahn, K. (2013). *Sustainability of Mass Deacidification of Library Objects*, PhD Dissertation, University of Vienna, pages 80.

Akinli-Kogak, S. (2001). *The Influence of Fiber Swelling on Paper Wetting*, Master's Thesis, University of Maine, pages 144.

Anders, M., Bartsch, P., Bredereck, K., and Haberditzl, A. (1995). “Zur chemischen Festigung von Papier in Zusammenhang mit der Papierentsäuerung,” *IADA Prepr.*, 81-85.

Area, M. C., and Cheradame, H. (2011). “Paper aging and degradation: Recent findings and research methods,” *BioResources* 6(4), 5307-5337. DOI: 10.15376/biores.6.4.5307-5337

Aspler, J. S., Chauret, N., and Lyne, M. B. (2018). “Mechanism of self-sizing of paper,” in: *Papermak. Raw Mater.*, pp. 707-727. https://doi.org/10.15376/frc.1985.2.707.MECHANISM

Derjaguin, B. (1954). “A theory of the heterocoagulation, interaction and adhesion of dissimilar particles in solutions of electrolytes,” *Discuss Faraday Soc*. 18, 85-98.

Derjaguin, B., and Landau, L. (1941). “The theory of stability of highly charged lyophobic sols and coalescence of highly charged particles in electrolyte solutions,” *Acta Phys Chim USSR*, 14, 331-354.

Back, E. L. (1985). “The relative moisture sensitivity of compression as compared to tensile strength,” in: *Papermaking Raw Materials*, Trans. of the VIIIth Fund. Res. Symp. Oxford, 497-509. https://doi.org/10.15376/frc.1985.2.497

Back, E. L. (1967). “Thermal auto-crosslinking in cellulose material,” *Pulp Pap. Mag. Canada* 68(4), 165-171.

Banks, M. S. (1953). “Water disintegratable soap package,” Patent No. US2539395A.

Battista, O. A. (1950). “Hydrolysis and crystallization of cellulose,” *Ind. Eng. Chem.* 42(3), 502-507. https://doi.org/10.1021/ie50483a029

Begum, H. A., Tanni, T. R., and Shahid, M. A. (2021). “Analysis of water absorption of different natural fibers,” *J. Text. Sci. Technol.* 07(04), 152-160. https://doi.org/10.4236/jtst.2021.74013

Belle, J. (2016). *Gewichtung von Einflussfaktoren auf die initiale Nassfestigkeit von Papier*, PhD Dissertation, University of Hamburg, pages 267.

Bertran, M. S., and Dale, B. E. (1985). “Enzymatic hydrolysis and recrystallization behavior of initially amorphous cellulose,” *Biotechnol. Bioeng.* 27(2), 177-181. https://doi.org/10.1002/bit.260270212

Blechschmidt, J., Dobschall, E., Blechschmidt, J., Heinemann, S., Fischer, K., Bäurich, C., Naujock, V. P. H., Gliese, T., Kleemann, S., Naujock, H., Holik, H., Svenka, V. P., Sangl, R., Wilken, R., Kappen, V. J., Pollex, I., Rochner, F., Dau, O., Jung, H., Pracht, D., Hrsg, J. B. (仁佐藤）, Blechschmidt, J., and Naujock, H. (2021). *Taschenbuch der Papiertechnik. Taschenb. der Pap.*

Bonham, J., and Rolniczak, B. (2006). “Accelerated ageing of copy papers containing recycled fibre,” *Appita J.* 59(5), 365-369.

Botková, M., Sutý, Š., Jablonský, M., Kucerkova, L., and Vrška, M. (2013). “Monitoring of kraft pulps swelling in water,” *Cellul. Chem. Technol.* 47 (1–2), 95-102.

CEPI (2022). "Harmonised European laboratory test method to generate parameters enabling the assessment of the recyclability of paper and board products in standard paper and board recycling mills," CEPI, Brussels, Belgium.

Cao, J., Sun, X., Lu, C., Zhou, Z., Zhang, X., and Yuan, G. (2016). “Water-soluble cellulose acetate from waste cotton fabrics and the aqueous processing of all-cellulose composites,” *Carbohydr. Polym.* 149, 60-67. https://doi.org/10.1016/j.carbpol.2016.04.086

Carter, H. A. (1996). “The chemistry of paper preservation: Part 1. The aging of paper and conservation techniques,” *J. Chem. Educ.* 73(5), 417-420. https://doi.org/10.1021/ed073p417

Caspar, T., Gaspareto, D., Gaultney, D., Ross, G., Hallahan, B., Hallahan, D., Johnson, B. H., Jones, P., Kratz, K., Lakshmanan, K., Mahajan, S., Mather, B. D., Morris, B. A., Nunhez, M. L., and Xu, J. (2013). “Plant artificial seeds and methods for the production thereof,” Australian patent AU 2012358929B2.;2(12):57

Cho, B. U., Ryu, J. Y., and Song, B. K. (2009). “Factors influencing deflaking kinetics in repulping to produce molded pulp,” *J. Ind. Eng. Chem.* 15(1), 119-123. https://doi.org/10.1016/j.jiec.2008.08.003

Cildir, H., and Howarth, P. (1972). “The effect of re-use on paper strength,” *Pap. Technol.* 13(10), article 333.

Del Curto, B., Barelli, N., Profaizer, M., Farè, S., Tanzi, M. C., Cigada, A., Ognibene, G., Recca, G., and Cicala, G. (2016). “Poly-paper: A sustainable material for packaging, based on recycled paper and recyclable with paper,” *J. Appl. Biomater. Funct.*

Mater. 14(4), e490-e495. https://doi.org/10.5301/jabfm.5000335

Devisetty, B., Beach, R., Menendez, R., and Warrior, P. (2002). "A concentrated, water-soluble, granular plant growth regulator formulation and methods for use of same," US Patent 9,388,532 B2.;2(12).

Dodson, C. T. J. (1973). "A survey of paper mechanics in fundamental terms," in: *The Fundamental Properties of Paper Related to its Uses*, Trans. of the Vth Fund. Res. Symp. Cambridge, 202-226. DOI: 10.15376/frc.1973.1.202.A

Erhardt, D., and Mecklenburg, M. F. (1995). "Accelerated vs natural aging: Effect of aging conditions on the aging process of cellulose," *Mat. Res. Soc. Symp. Proc.*, 352, 247-270.

Fellers, C., Iversen, T., Lindstrom, T., Nilsson, T., and Rigdahl, M. (1989). "Ageing/degradation of paper, a literature survey," *FoU- Proj. Papperskonservering* (1), 139.

Fernandes Diniz, J. M. B., Gil, M. H., and Castro, J. A. A. M. (2004). "Hornification - Its origin and interpretation in wood pulps," *Wood Sci. Technol.* 37(6), 489-494. https://doi.org/10.1007/s00226-003-0216-2

Flore, D., Wegener, K., Seel, D., Oetting, C. C., and Bublat, T. (2016). "Investigation of chemical ageing and its effect on static and fatigue strength of continuous fibre reinforced plastics," *Compos. Part A Appl. Sci. Manuf.* 90, 359-370. https://doi.org/10.1016/j.compositesa.2016.08.001

Geffert, A., Geffertova, J., Stevulova, N., and Seman, B. (2016). "The change of swelling of pulp fibres under recycling," *Solid State Phenom.* 244 (February 2016), 161-167. https://doi.org/10.4028/www.scientific.net/SSP.244.161

Graminski, E. (1970). "The stress-strain behavior of accelerated and naturally aged papers," *Tappi* 53(3), 406-410.

Gratton, M. F. (1991). "The recycling potential of calendared newsprint fibers," *Proc. 1991 CPPA Recycl. Forum, CPPA Press*, 65. Montreal.

Green, B. (2021). "Water-dispersible and biodegradable films for the packaging of liquids and moisture-sensitive materials," Patent No. US20210032002A1.

Gruber, E. (2011). "Papier- und Polymerchemie," *Vor. zum Lehrgang „Papiertechnik" an der Dualen Hochschule Karlsruhe*.

Harter, T., Steiner, H., and Hirn, U. (2022). "Investigating mechanisms deteriorating the dispersibility of biodegradable and flushable wet wipes," *Cellulose* 29(16), 8827-8842. https://doi.org/10.1007/s10570-022-04816-y

Haslach, H. W. (2000). "Moisture and rate-dependent mechanical properties of paper: A review," *Mech. Time-Dependent Mater.* 4(3), 169-210. https://doi.org/10.1023/A:1009833415827

Havermans, J. (1995). *Environmental Influences on the Deterioration of Paper*, Rotterdam.

Havlínová, B., Katuščák, S., Petrovičová, M., Maková, A., and Brezová, V. (2009). "A study of mechanical properties of papers exposed to various methods of accelerated ageing. Part I. The effect of heat and humidity on original wood-pulp papers," *J. Cult. Herit.* 10(2), 222-231. https://doi.org/10.1016/j.culher.2008.07.009

Hoyland, R. W. (2018). "Swelling during the penetration of aqueous liquids into paper," 557-577. https://doi.org/10.15376/frc.1977.1.557

Hubbe, M. A., R. A. Venditti, and O. J. Rojas. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review." *BioResources* 2(4), 739-788. https://doi.org/10.15376/biores.2.4.739-788

Israelachvili, J. (2006). “Electrostatic forces between surfaces in liquid,” in: *Intermol. Surf. Forces*. pp. 213-259, Academic Press, Amsterdam.

Itamiya, H., Shimoda, O., Hirakawa, J., Sawada, H., Hibino, K., and Sugita, R. (2021). “Analysis of water-soluble paper for forensic discrimination,” *Forensic Sci. Int.* 321, article 110719. https://doi.org/10.1016/j.forsciint.2021.110719

Jablonský, M., Botková, M., Šutý, Š., Šmatko, L., and Šima, J. (2014). “Accelerated ageing of newsprint paper: Changes in swelling ability, WRV and electrokinetic properties of fibres,” *Fibres Text. East. Eur.* 104(2), 108-113.

Jajcinovic, M., Fischer, W. J., Mautner, A., Bauer, W., and Hirn, U. (2018). “Influence of relative humidity on the strength of hardwood and softwood pulp fibres and fibre to fibre joints,” *Cellulose* 25(4), 2681-2690. https://doi.org/10.1007/s10570-018-1720-8

Jayme, G. (1944). “Micro-swelling measurement in cellulosic pulp,” *Pap. Pap.* 6(72), 187-194.

Jayme, G., and Hunger, G. (1956). “Verhornungserscheinungen an Cellulosefaser-strukturen in elektronenoptischer Sicht,” *Monatshefte für Chemie* 87(1), 8-23. https://doi.org/10.1007/BF00903586

Kallmes, O., Bernier, G., and Perez, M. (1977). “Mechanistic theory of the load - elongation properties of paper - 2. The characteristics of fibres taken into account,” *Pap. Technol. Ind*. 18(8), 243-245.

Kato, K. L., and Cameron, R. E. (1999a). “Structure-property relationships in thermally aged cellulose fibers and paper,” *J. Appl. Polym. Sci.* 74(6), 1465-1477. https://doi.org/10.1002/(SICI)1097-4628(19991107)74:6<1465::AID-APP20>3.0.CO;2-3.

Kato, K. L., and Cameron, R. E. (1999b). “A review of the relationship between thermally-accelerated ageing of paper and hornification,” *Cellulose* 6(1), 23-40. https://doi.org/10.1023/A:1009292120151

Kaushik, A., Singh, M., and Verma, G. (2010). “Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw,” *Carbohydr. Polym.* 82(2), 337-345. https://doi.org/10.1016/j.carbpol.2010.04.063.

Kendall, K. (2001). *Molecular Adhesion and its Applications: The Sticky Universe*. *Mol. Adhes. its Appl.* Kluwer Academic Publishers, New York.

Kochersperger, S., and Schabel, S. (2024). "Recyclability of paper-based composites for packaging applications –The role of evaluation methods," *Chemie Ingenieur Technik* 96(7), 891-901.

Köhnke, T., Lund, K., Brelid, H., and Westman, G. (2010). “Kraft pulp hornification: A closer look at the preventive effect gained by glucuronoxylan adsorption,” *Carbohydr. Polym.* 81(2). 226-233. https://doi.org/10.1016/j.carbpol.2010.02.023

Korpela, A., Jaiswal, K., and Asikainen, J. (2021). “Effects of hydrophobic sizing on paper dry and wet-strength properties: A comparative study between AKD sizing of NBSK handsheets and rosin sizing of CTMP handsheets,” *BioResources* 16(3), 5350-5360. https://doi.org/10.15376/biores.16.3.5350-5360

Koura, A., and Krause, T. (1978). “Warum altert Papier ? Die Alterung von Pap. Tl. II. Der Einfluß der Mahlung auf die Alterung Ligninfreier Faserstoffe," *Das Papier* 32(5), 189-194.

Koyama, M., Kishimoto, M., and Ishino, Y. (2016). “Water-dispersible paper,” Patent No. US 9,388,532 B2.

Kulak, M. I., Kyrychok, T. Y., Miadziak, D. M., and Kyrychok, P. O. (2016). “Kinetic model of optical characteristics of banknote paper during artificial aging," *J. Appl. Spectrosc.* 83(4), 669-672. https://doi.org/10.1007/s10812-016-0346-6

Lahti, J., Kouko, J., and Hirn, U. (2019). "Time-dependent mechanical response of paper during web-fed high-speed inkjet printing," *Nord. Pulp Pap. Res. J.* 34(1), 107-116. https://doi.org/10.1515/npprj-2018-0011

Leuk, P., Schneeberger, M., Hirn, U., and Bauer, W. (2016). "Heat of sorption: A comparison between isotherm models and calorimeter measurements of wood pulp," *Dry. Technol.* 34(5), 563-573.

Lewin, M. (1997). "Oxidation and aging of cellulose," *Macromol. Symp.* 118, 715-724. https://doi.org/10.1002/masy.19971180192

Lindström, T. (1986). *The Porous Lamellar Structure of the Cell Wall. Pap. Struct. Prop.* New York: Marcel Dekker.

Lindström, T., and Ström, G. (2022). "Bulking of cellulose fibres - A review," *Nord. Pulp Pap. Res. J.* 37(1), 192-204. https://doi.org/10.1515/npprj-2021-0062

Ling, Z., Makarem, M., Cintrón, M., Cheng, H. N., Kang, X., Bacher, M., Potthast, A., Rosenau, T., King, H., Delhom, C., Nam, S., Edwards, J. V., Kim, S. H., Xu, F., and French, A. (2019). "Effects of ball milling on the structure of cotton cellulose," *Cellulose* 26, 305-328.

Łojewski, T., Miśkowiec, P., Molenda, M., Lubańska, A., and Łojewska, J. (2010). "Artificial versus natural ageing of paper. Water role in degradation mechanisms," *Appl. Phys. A Mater. Sci. Process.* 100(3), 625-633. https://doi.org/10.1007/s00339-010-5645-9

Lundgaard, L. E., Hansen, W., Ingebrigtsen, S., Linhjell, D., and Dahlund, M. (2005). "Aging of kraft paper by acid catalyzed hydrolysis," *2005 IEEE Int. Conf. Dielectr. Liq. ICDL 2005*, (June 2015), pp. 381-384. https://doi.org/10.1109/icdl.2005.1490105

Luo, X. L., Zhu, J. Y., Gleisner, R., and Zhan, H. Y. (2011). "Effects of wet-pressing-induced fiber hornification on enzymatic saccharification of lignocelluloses," *Cellulose* 18(4), 1055-1062. https://doi.org/10.1007/s10570-011-9541-z

Małachowska, E., Dubowik, M., Boruszewski, P., Łojewska, J., and Przybysz, P. (2020). "Influence of lignin content in cellulose pulp on paper durability," *Sci. Rep.* 10(1), 1-12. https://doi.org/10.1038/s41598-020-77101-2

Małachowska, E., Dubowik, M., Boruszewski, P., and Przybysz, P. (2021a). "Accelerated ageing of paper: Effect of lignin content and humidity on tensile properties," *Herit. Sci.* 9(1), 1-8. https://doi.org/10.1186/s40494-021-00611-3

Małachowska, E., Pawcenis, D., Dańczak, J., Paczkowska, J., and Przybysz, K. (2021b). "Paper ageing: The effect of paper chemical composition on hydrolysis and oxidation," *Polymers (Basel).* 13(7), article 1029. https://doi.org/10.3390/polym13071029

Maloney, T. C., Li, T. Q., Weise, U., and Paulapuro, H. (1997). "Intra- and inter-fibre pore closure in wet pressing," *Appita J.* 50(4), 301-x3.

McKenzie, A. (1984). "The structure and properties of paper Part XXI: The diffusion theory of adhesion applied to interfibre bonding," *Appita J.* 37, 580-583.

Mo, W., Chen, K., Yang, X., Kong, F., Liu, J., and Li., B. (2022). "Elucidating the hornification mechanism of cellulosic fibers during the process of thermal drying," *Carbohydr. Polym.* 289(March), 1-7. https://doi.org/10.1016/j.carbpol.2022.119434

Naithani, V., Lucia, L., and Banerjee, S. (2017). "High-bulk water dispersible paper-based composites," *ACS Sustain. Chem. Eng.* 5(12), 11334-11338.

https://doi.org/10.1021/acssuschemeng.7b02337

Nissan, A., and Batten, G. (1990). "On the primacy of the hydrogen bond in paper mechanics," *Tappi* 73, 59-164.

Nissan, A. H. (1977). "Water effects on Young's modulus of hydrogen-bonded solids," 609-629. https://doi.org/10.15376/frc.1977.1.609.WATER

Okayama, T. (2002). "The effects of recycling on pulp and paper properties," *Kami Pa Gikyoshi/Japan Tappi J.* 56(7), 62-68. https://doi.org/10.2524/jtappij.56.986

Oliveira, M. H. de, Maric, M., and van de Ven, T. G. M. (2008). "The role of fiber entanglement in the strength of wetpapers," *Nord. Pulp Pap. Res. J.* 23(4), 426-431. https://doi.org/10.3183/npprj-2008-23-04-p426-431

Paavilainen, L. (1993a). "Conformability, flexibility and collapsi- bility of sulphate pulp fibres," *Pap Puu* 75, 689-691.

Paavilainen, L. (1993b). "Importance of cross-dimensional fibre properties and coarseness for the characterization of softwood sulphate pulp," *Pap. ja Puu* 75(5), 343-351.

Pelton, R. (1993). "A model of the external surface of wood pulp fibers," *Nord. Pulp Pap. Res. J.* 8, 113-119. https://doi.org/10.3183/npprj-1993-08-01-p113-119

Persson, B. N. J., Ganser, C., Schmied, F., Teichert, C., Schennach, R., Gilli, E., and Hirn, U. (2013). "Adhesion of cellulose fibers in paper," *J. Phys. Condens. Matter* 25(4). https://doi.org/10.1088/0953-8984/25/4/045002

Pfennich, A. C., and Hirn, U. (2025). "The deterioration of paper dispersibility over time and how it is related to fiber-water interaction," *Recycling* 10(3), article 92. https://doi.org/10.3390/recycling10030092

Pfennich, A. C., Schoeffmann, E. A., Lammer, H., and Hirn, U. (2023). "Water-soluble paper for packaging applications – Balancing material strength and dispersibility," *Nord. Pulp Pap. Res. J.* 38(4), 521-532. https://doi.org/10.1515/npprj-2023-0048

Przybylek, P. (2010). "The influence of cellulose insulation aging degree on its water sorption properties and bubble evolution," *IEEE Trans. Dielectr. Electr. Insul.* 17(3), 906-912. https://doi.org/10.1109/TDEI.2010.5492265

Robertson, D. D. (1976). "The evaluation of paper permanence and durability," *Tappi* 59(12), 63-69.

Ruffini, G. (1966). "Improvement of bonding in wood pulps by presence of acidic groups," *Sven. Papperstidning-Nordislk Cellul.* 69(3), 72.

Ruvo, A. de, and Htun, M. (1981). "Fundamental and practical aspects of paper-making with recycled fibres," in: *The Role of Fundamental Research in Paper-making*, Trans. of the VIIth Fund. Res. Symp. Cambridge, pp. 195-225. https://doi.org/10.15376/frc.1981.1.195

Saito, K. (1998). "Water-dispersible wrapping paper and wrapping paper," U.S. Patent No. JP3472494B2.

Salmén, L., and Back, E. L. (1977). "Simple stress-strain measurements on dry papers from -25 to 250 °C," Temperature and water induced softening behavior of wood fiber based materials, *Tappi* 60(12), Paper IV, Reprint from Sversk papperStidning no. 6-1977 80 (1977) 178-183.

Salmén, L., and Back, E. L. (1980). "Moisture-dependent thermal softening of paper, evaluated by its elastic modulus," *Tappi* 63(6), 117-120.

Salmén, L., and Berthold, J. (2018). "The swelling ability of pulp fibres," *Fundametals Papermak. Mater.*, pp. 683-701. https://doi.org/10.15376/frc.1997.2.683

Salmén, L., and Stevanic, J. S. (2018). "Effect of drying conditions on cellulose microfibril aggregation and 'hornification'," *Cellulose* 25(11), 6333-6344. https://doi.org/10.1007/s10570-018-2039-1

Scallan, A. M., and Laivins, G. V. (2018). "The mechanism of hornification of wood pulps," *Prod. Papermak.* 12351260. https://doi.org/10.15376/frc.1993.2.1235

Seery, M. (2013). "Paper conservation," *Educ. Chem.*, (March): 1-9.

Siqueira, E. J., Salon, M. C. B., Belgacem, M. N., and Mauret, E. (2015). "Carboxymethylcellulose (CMC) as a model compound of cellulose fibers and polyamideamine epichlorohydrin (PAE)-CMC interactions as a model of PAE-fibers interactions of PAE-based wet strength papers," *J. Appl. Polym. Sci.* 132(26), 1-10. https://doi.org/10.1002/app.42144

Sjöstrand, B., Karlsson, C. A., Barbier, C., and 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

Stankovská, M., Gigac, J., Fišerová, M., and Opálená, E. (2019). "Relationship between structural parameters and water absorption of bleached softwood and hardwood kraft pulps," *Wood Res.* 64(2), 261-272.

Stone, J. E., and Scallan, A. M. (1965). "Influence of drying on the pore structure of the cell wall," *Consol. Pap. Web, Trans. IIIrd Fund. Res. Symp. Cambridge*, 145-166. https://doi.org/10.15376/frc.1965.1.145

Strlic, M., and Kolar, J. (2005). *Ageing and Stabilisation of Paper*, National and University Library.

Su, J., Mosse, W. K. J., Sharman, S., Batchelor, W., and Garnier, G. (2012). "Paper strength development and recyclability with polyamideamine-epichlorohydrin (PAE)," *BioResources* 7(1), 913-924. https://doi.org/10.15376/biores.7.1.913-924

Šutý, Š., Petriláková, K., Katuščák, S., Kirschnerová, S., Jablonský, M., Vizarová, K., and Vrška, M. (2012). "Change in the capability of cellulose fibres to retain water during thermally accelerated ageing of paper," *Cellul. Chem. Technol.* 46 (9–10), 631-635.

Tan, J., Fu, X., Lu, Y., Chen, B., and Ding, Y. (2023). "Investigating the moisture sorption behavior of naturally and artificially aged bamboo paper with multi-analytical techniques," *J. Cult. Herit.* 61, 65-75. https://doi.org/10.1016/j.culher.2023.03.004

Tejado, A., and van de Ven, T. G. M. (2010). "Why does paper get stronger as it dries?" *Mater. Today* 13(9), 42-49. DOI: 10.1016/S1369-7021(10)70164-4

Tervahartiala, T., Hildebrandt, N. C., Piltonen, P., Schabel, S., and Valkama, J. P. (2018). "Potential of all-cellulose composites in corrugated board applications: Comparison of chemical pulp raw materials," *Packag. Technol. Sci.* 31(4), 173-183. https://doi.org/10.1002/pts.2365

Tissue Paper and Tissue Products. 2021. *Int. Organ. Stand.*, 1–5.ISO 12625-17

Trovagunta, R., R. Marquez, L. Tolosa, N. Barrios, F. Zambrano, A. Suarez, L. Pal, R. Gonzalez, and M. A. Hubbe. 2024. "Lignin self-assembly phenomena and valorization strategies for pulping, biorefining, and materials development: Part 1. The physical chemistry of lignin self-assembly," *Adv. Colloid Interface Sci.* 332 (July), article 103247. https://doi.org/10.1016/j.cis.2024.103247

Tumkur, P. P., Bayon, N. N., Gunasekaran, N. K., *et al.* (2020). "Evaluation of cellulose nanoparticles synthesized by acid hydrolysis for safe applications," *J. Nanosci. Res. Reports* 2(4), 1-5. https://doi.org/10.47363/jnsrr/2020(2)114

Urstöger, G., Kulachenko, A., Schennach, R., and Hirn, U. (2020). "Microstructure and mechanical properties of free and restrained dried paper: A comprehensive investigation," *Cellulose* 27(15), 8567-8583. https://doi.org/10.1007/s10570-020-03367-4

Wåberg, L., and Annergren, G. (1997). "Physicochemical characterization of papermaking fibres," *Fundam. Papermak. Mater.* 1, 1-82. https://doi.org/10.15376/frc.1997.1.1

Weise, U. (1998). "Hornification: Mechanisms and terminology," *Pap Puu* 80, 110-115.

Weise, U., Maloney, T., and Paulapuro, H. (1996). "Quantification of water in different states of interaction with wood pulp fibres," *Cellulose* 3(1), 189-202. https://doi.org/10.1007/bf02228801

Williams, D. (1983). "A fiber network model theory for the wet web strength of paper," *Tappi* 66, 159-162.

Wilson;, W., and Parks, E. J. (1979). "An analysis of the aging of paper: Possible reactions and their effects on measurable properties," *Restaur. Int. J. Preserv. Libr. Arch. Mater.* 37-62. https://doi.org/10.1515/rest.1979.3.1-2.37

Wu, Z. (1996). *The Effect of Age and Recycling on Paper Quality*, Master's Thesis, Western Michigan University.

Yang, D., A. Sotra, A., and Pelton, R. H. (2019). "Switching off PAE wet strength," *Nord. Pulp Pap. Res. J.* 34(1), 88-95. https://doi.org/10.1515/npprj-2018-0074

Zervos, S. (2010). "Natural and accelerated ageing of cellulose and paper: A literature review," *Cellul. Struct. Prop. Deriv. Ind. Uses*, 155-203.

Zotti, M., Ferroni, A., and Calvini, P. (2008). "Microfungal biodeterioration of historic paper: preliminary FTIR and microbiological analyses," *Int. Biodeterioration Biodegradation* 62(2), 186-194.

Zou, X., Gurnagul, N., Uesaka, T., and Bouchard, J. (1994). "Accelerated aging of papers of pure cellulose: Mechanism of cellulose degradation and paper embrittlement," *Polym. Degrad. Stab.* 43(3), 393-402. https://doi.org/10.1016/0141-3910(94)90011-6

Zou, X., Uesaka, T., and Gurnagul, N. (1996). "Prediction of paper permanence by accelerated aging. I," *Cellulose* 3(1), 243-267.

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