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Review

Chemical Transformations and Papermaking Potential of Recycled Secondary Cellulose Fibers for Circular Sustainability

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Featured Application

The findings of this study can guide papermakers, process engineers, and researchers in optimizing wet-end chemistry, refining, and de-inking operations within recycling lines. By linking fiber chemistry with operational control, the proposed framework supports the design of stable, high-efficiency papermaking systems under closed-water conditions. Its practical relevance lies in enabling mills to maintain product strength, drainage, and optical quality while reducing chemical and energy consumption, advancing both process profitability and circular sustainability in the paper industry.

Abstract

The papermaking and recycling industries face increasing demands to improve efficiency, product quality, and environmental performance under conditions of water closure and high furnish variability. This study presents a comprehensive assessment of process control and management strategies for optimizing fines behavior, retention and fixation efficiency, de-inking performance, and ash balance in modern papermaking systems. The surface chemistry of fines was found to play a pivotal role in regulating charge distribution, additive demand, and drainage behavior, acting both as carriers and sinks for dissolved and colloidal substances. Results show that light, targeted refining enhances external fibrillation and produces beneficial fines that strengthen fiber bonding, while excessive refining generates detrimental fines and impairs drainage. Sequential retention programs involving polyamines, polyaluminum compounds, and microparticle systems significantly improve fines capture and drainage stability when operated under controlled pH and ionic strength. In recycling operations, optimized flotation conditions coupled with detackifiers and mineral additives such as talc effectively reduce micro-stickies formation and deposition risks. Ash management strategies based on partial purge and coordinated filler make-up maintain bonding, optical properties, and energy efficiency. Overall, the findings emphasize the need for an integrated wet-end management framework combining chemical, mechanical, and operational controls. Perspectives for future development include the application of biodegradable additives, nanocellulose-based reinforcements, and data-driven optimization tools to achieve sustainable, high-performance paper manufacturing.

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1. Introduction

The transition toward a circular bioeconomy increasingly depends on a deep understanding of material chemistry, particularly that of cellulose fibers, which form the structural and functional basis of the paper cycle. The chemistry of cellulose governs its reactivity, bonding potential, and behavior during mechanical, chemical, and enzymatic transformations, determining both the efficiency of virgin pulping and the recoverability of fibers through successive recycling loops. In circular production systems, these molecular and interfacial characteristics influence how fibers interact with additives, contaminants, and water, affecting drainage, retention, and final product quality.

These molecular and interfacial mechanisms determine how fibers behave through successive recycling loops and provide the basis for evaluating the chemical, structural, and functional transformations discussed in the following sections. Although fundamental mechanisms such as hornification, fines generation, and de-inking have been extensively studied, recent developments in fiber chemistry, surface reactivity, enzymatic reactivation, and wet-end process control have not yet been consolidated into a unified framework. The novelty of this review lies in integrating chemical, structural, enzymatic, and operational perspectives to explain how secondary fibers behave within modern circular papermaking systems under water-closure conditions. By combining detailed mechanistic explanations with comparative tables, multi-panel schematic figures, and cross-study analysis, this paper synthesizes dispersed findings from the last few decades and highlights how chemical and enzymatic modification strategies can be aligned with circularity objectives. This integrated, multi-scale approach distinguishes the present review from previous, more narrowly focused surveys and provides a comprehensive foundation for both researchers and practitioners.

1.1. Global Context: Cellulose Fibers as Renewable Resources and the Circular Economy in the Paper Industry

Current sustainability targets require materials that can be repeatedly circulated with minimal loss of functionality. Cellulose fibers meet these criteria due to their renewability, structural robustness, and ability to re-enter papermaking loops multiple times. Within this context, cellulose fibers stand out as one of the most promising renewable biopolymers, offering a unique combination of abundance, biodegradability, and functional versatility. Derived mainly from lignocellulosic biomass, cellulose represents a widely available and renewable resource, yet it is not unlimited in practical terms. Effective recycling remains essential to reduce the demand for virgin biomass, lower environmental burdens, and preserve fiber functionality throughout repeated papermaking cycles [1–3]. Its molecular structure, composed of β-(1→4)-linked glucose units, provides high mechanical strength and adaptability, enabling applications that extend from conventional paper and packaging to textiles, bioplastics, and advanced composites. Moreover, the production and recycling of cellulose-based materials align closely with the principles of circularity by enabling renewable sourcing, repeated reuse, and recovery of materials at the end of their life cycle [4,5]. The paper industry, in particular, demonstrates how natural polymers such as cellulose can sustain a regenerative industrial model, where fibers are continuously recirculated through multiple product life cycles. Major industry players are reflecting this shift: International Paper's 2024 (Memphis, TN, USA) report presents its Global Cellulose

Fibers business as a pivot toward renewable, circular products [6]. As global demand for paper- and fiber-based products continues to grow alongside environmental imperatives to reduce carbon emissions and waste, cellulose fibers have become a cornerstone of sustainable production strategies and an essential element in the transition toward bio-based and circular economies.

The efficiency of circularity in the paper industry depends largely on the properties and chemistry of recycled cellulose fibers (secondary fibers), which determine their performance during repeated processing cycles [7]. Each recycling loop induces physical and chemical transformations, such as fiber shortening, wall densification, hornification, and partial oxidation that progressively alter swelling capacity, bonding potential, and strength. Understanding these changes is therefore essential to maintain fiber quality and extend their usability in closed loops. Advanced characterization of fiber morphology, crystallinity, and surface chemistry provides the basis for optimizing reprocessing conditions, selecting suitable additives, such as enzymatic treatments (e.g., cellulases, xylanases), strength additives (e.g., cationic starch), retention and fixation agents (polyamines, polyaluminum coagulants), or surface-reactive polymers, that support drainage, bonding, and charge balance in recycled furnishes, and reducing energy demands [1,8]. Consequently, the preservation and regeneration of fiber properties through improved recycling technologies represent a key lever for enhancing resource efficiency and achieving true circularity in the cellulose-based industry.

1.1.1. Cellulose Fibers as Renewable Biomaterials

Cellulose is the most abundant natural polymer on Earth, constituting the primary structural component of plant cell walls. Its ubiquity across terrestrial biomass, from trees and grasses to agricultural residues and non-wood sources, provides a broad and sustainable feedstock base. Because cellulose is produced by photosynthesis, its carbon content is drawn from atmospheric CO_2, giving cellulose-based materials the potential to act as low-carbon materials if managed properly. Importantly, cellulose fibers exhibit desirable mechanical, chemical, and thermal properties that make them suitable for a wide array of applications, from paper and textiles to composites, packaging, and advanced functional materials [9,10]. Advances in nanocellulose (cellulose nanofibrils, cellulose nanocrystals) have expanded these applications further, leveraging the renewability of the base material while pushing performance limits [11]. Process-side advances also help preserve recycled-fiber performance. Enzymatic pretreatments (cellulase/xylanase) have improved drainage, reduced refining energy, and recovered bonding after hornification in pilot and mill settings [12].

However, in a purely "virgin resource → product → waste" model, the full potential of cellulose is not realized. The generation of waste, either from production processes or end-of-life disposal, leads to loss of the embedded carbon and materials value unless circular strategies are put in place.

1.1.2. The Paper Industry and the Circular Economy

The pulp and paper sector exemplifies circular-material use because cellulose fibers can be recovered and reprocessed multiple times, allowing a significant share of raw materials to originate from recycled streams. High recovery rates, combined with advances in de-inking, screening, and design-for-recyclability, sustain material flows and reduce demand for virgin pulp [13–16].

Another important feature of the industry is its high recycling rates, which surpass those of many other materials. In the United States, the recycling rate of corrugated board has reached approximately 93.6%, while the overall recycling rate for all paper grades

stands near 67.9%. In comparison, the European Union reports even higher levels of circularity, with an average paper and board recycling rate of about 71–73% in recent years and corrugated packaging often exceeding 85–90%, reflecting the maturity and efficiency of EU-wide collection and recycling systems [17]. Validated 2024–2025 recycling data have not yet been published in final form by CEPI, EPRC, FAO, or national associations. Preliminary figures exist but are subject to revision; therefore, the present work relies on the most recent consolidated statistics (up to 2023). The EU Packaging and Packaging Waste Regulation (PPWR), adopted in late 2024, introduces new collection, recyclability, and recycled-content targets that will progressively influence fiber flows from 2025 onwards. As PPWR defines regulatory obligations rather than reporting updated 2024 statistics, its implications are discussed qualitatively rather than through numerical values [18–20].

China's strengthened waste-import restrictions (2021–2024), including the strict control of mixed-paper and old corrugated containers (OCCs) entries, continue to reshape global recovered paper trade patterns. These measures affect the availability and quality of secondary fibers on international markets but do not yet provide consolidated post-2022 statistical datasets [21,22].

By integrating 2023 validated data and contextualizing regulatory shifts introduced between 2024 and 2025, the present review reflects both the current state of global fiber recovery and the evolving policy framework shaping future circularity trajectories.

A further advantage is resource substitution and waste avoidance, since the use of recycled fibers directly decreases the demand for virgin wood pulp. This not only mitigates the pressure on forests but also leads to considerable reductions in energy and water consumption during pulping and papermaking processes [14].

Finally, the growing integration of design for circularity reinforces the sustainability of the paper cycle. Increasing attention is being paid to upstream design factors, such as the compatibility of inks, adhesives, and coatings, as well as product de-inkability, to ensure that paper products remain recyclable throughout their lifecycle [14].

Together, these elements exemplify how the paper industry not only aligns with but actively advances circular economy practices through efficient resource use, closed-loop material flows, and conscious product design. To clarify the scope of this review and the specific mechanisms examined in the following sections, Figure 1 illustrates the principal chemical and enzymatic pathways currently used to modify cellulose fibers in recycling systems. These strategies include chemical oxidation, cationization, carboxymethylation, and silane-based functionalization, as well as enzymatic approaches such as cellulase- and xylanase-assisted surface modification, enzymatic refining, and laccase-mediated oxidative coupling. Together, these pathways represent the main routes through which fiber structure, surface chemistry, bonding potential, and papermaking performance can be enhanced in multi-cycle recycling operations.

Despite these considerable strengths, several challenges continue to limit circularity within the paper industry. One of the most critical issues is the progressive degradation of fiber quality during repeated recycling, compounded by the fact that the origin, prior processing history, and number of cycles a fiber has undergone are often unknown, which makes it difficult to predict its performance and optimize recycling operations. During repeated processing, cellulose fibers undergo morphological and chemical degradation, including hornification, fiber shortening, and loss of hemicelluloses, which progressively reduces their bonding capacity and overall performance [18,19,23,24]. As a result, paper produced from extensively recycled fibers exhibits diminished mechanical strength and printability, making the periodic addition of virgin fibers unavoidable to maintain product quality.

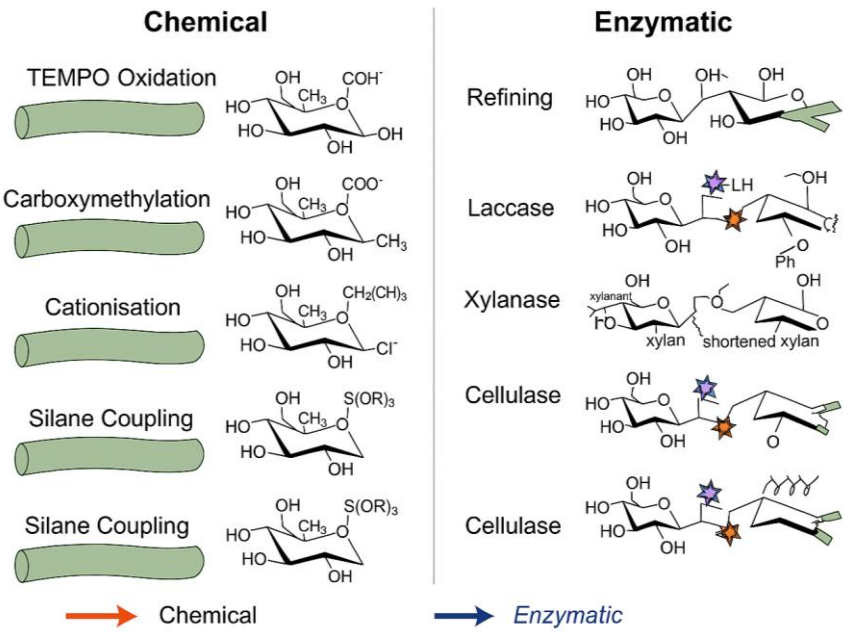


Figure 1. Schematic representation of the main chemical (**left**) and enzymatic (**right**) modification pathways relevant for recycled fibers in circular papermaking. Chemical routes include TEMPO-mediated oxidation, carboxymethylation, cationization and silane coupling, which alter fiber charge, hydrophilicity and bonding capacity. Enzymatic routes include refining-assisting cellulases and xylanases and laccase-based systems, which selectively modify fiber surfaces and fines, influencing flexibility, fibrillation and interfiber adhesion.

Another major constraint arises from material loss and process inefficiencies. Not all used paper is collected, nor is all collected paper suitable for recycling. Contamination with inks, adhesives, coatings, and non-cellulosic materials, along with inefficiencies in sorting and fiber recovery, leads to unavoidable losses during processing and decreases the effective reuse rate across the value chain [20,21,25,26]. Furthermore, the principle of diminishing returns imposes a practical limit on how many times fibers can be recycled before they lose functional integrity. After multiple reuse cycles, fibers become too short and stiff to form strong inter-fiber bonds, ultimately restricting their papermaking potential. In practice, it is estimated that papermaking fibers can typically be recycled between five and seven times before their structural quality drops below acceptable thresholds [22,27]. Thus, while the paper sector is arguably one of the leading industrial domains in circular materials management, its success hinges on technical, economic, and systemic innovations to offset material degradation and losses.

1.2. Significance of Recycling Waste Paper for Sustainability

Recycling reduces demand for virgin fiber, lowers energy and water use relative to primary pulping, and limits landfill-related emissions. These advantages explain its essential role in resource conservation and climate strategies [21–23,26–28].

From an energy and emissions perspective, recycling often demands significantly less energy than producing paper from virgin fibers. According to the U.S. EPA, recycling one ton of paper saves energy and cuts greenhouse gas emissions by reducing the need for new pulp and avoiding methane emissions from landfill decomposition [24,29]. In many accounts, recycling paper can consume 60–70% less energy and water compared to virgin fiber production [25,30]. A life cycle assessment of a recycled-fiber packaging mill in Italy highlighted that energy consumption is a major environmental hotspot, but the presence of cogeneration (combined heat and power) systems can substantially improve environmental performance over conventional energy supply routes [16,26,31]. Recycling

also helps avoid landfill disposal and related impacts. When paper is sent to landfills, anaerobic decomposition emits methane, a potent greenhouse gas; diverting paper from waste streams thus reduces this emission pathway [27,32]. Furthermore, limiting landfilling preserves space and reduces the burden on municipal waste management systems.

In economic and social terms, paper recycling contributes to cost savings, revenue generation, and job creation in collection, sorting, and reprocessing sectors. The substitution of expensive virgin raw material with recycled fiber can reduce operational costs and improve the economics of pulp and paper operations. In developing contexts, small-scale recycling enterprises may provide employment and income opportunities while promoting resource efficiency [28,33]. Finally, the practice of recycling waste paper aligns strongly with global sustainability agendas and the circular economy paradigm. Because paper recycling closes material loops and extends the lifespan of biobased resources, it embodies principles of resource efficiency, waste minimization, and decoupling of consumption from raw material extraction.

Many national and international strategies consider enhanced recycling as a lever to achieve climate, resource, and waste targets. Europe's second-largest recovered-fiber paper mill, Kemsley Paper Mill, operated by DS Smith in the UK, focuses on using 100% recycled fiber in its production of ~830,000 t/y capacity. Cardboard collected from the retailer's distribution centers is segregated to keep fiber quality high, returned to Kemsley, and remade into new corrugated packaging—an example of packaging-to-packaging closed loop [29,34]. In Southern Italy, an LCA of a packaging-paper mill found that the presence of cogeneration systems, also known as combined heat and power (CHP), can substantially improve environmental performance. Mill case studies (India, USA) show that optimized deinking/furnish control and integrated recycled-newsprint lines deliver stable brightness and fiber recovery, translating the theoretical sustainability gains of recycling into operational practice [26,31].

Therefore, recycling waste paper is not merely a waste management solution but a key enabler of sustainable development. By conserving land, water, and energy resources while reducing carbon emissions and fostering economic and social value, paper recycling exemplifies the transition of industrial systems toward circular and low-impact production models. In this context, the review provides an integrated analysis of the chemical, structural, and functional transformations that secondary cellulose fibers undergo during recycling and examines their implications for papermaking performance and circular sustainability. It synthesizes current understanding of how recycling-induced chemical changes, such as cellulose oxidation, hemicellulose loss, hornification, and surface inactivation, affect fiber reactivity, swelling capacity, and bonding potential. Also, it is analyzed how the progressive deterioration of cellulose fibers during successive recycling cycles arises from a series of structural, physicochemical, and morphological changes that reduce swelling ability, bonding capacity, and overall papermaking performance. These transformations include fiber-wall stiffening, pore collapse, hornification, loss of external fibrillation, and increased generation of fines. Fresh fibers exhibit intact hydrogen bonding, open pore structure, high flexibility, and greater fiber length, while recycled fibers show hornification, pore formation and collapse, fiber-wall stiffening, reduced swelling, and fiber shortening. These cumulative transformations decrease bonding potential and limit the recyclability of fibers in circular papermaking systems. Figure 2 summarizes the main degradation pathways affecting fiber structure during recycling and highlights their cumulative impact on fiber quality.

The paper also identifies and discusses chemical and physicochemical strategies designed to restore or enhance fiber properties, including enzymatic reactivation, surface modification, and optimized wet-end chemistry.

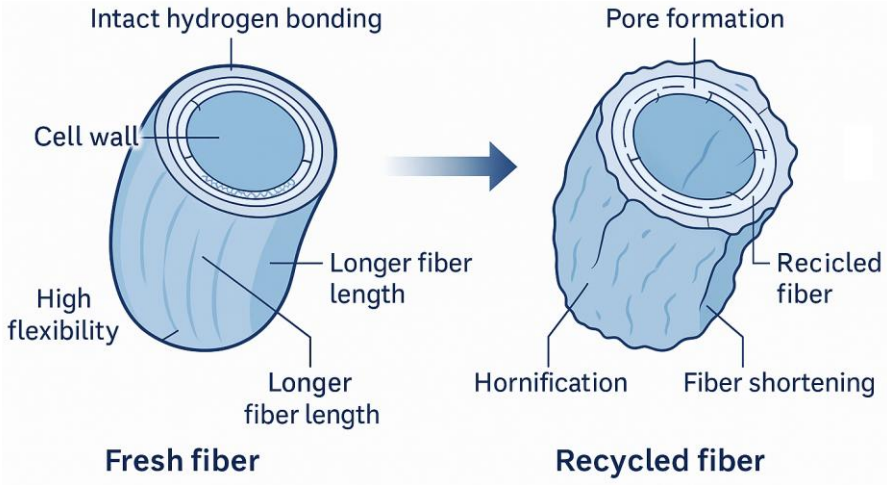


Figure 2. Comparison of fresh and recycled cellulose fibers illustrating the principal structural changes induced by repeated recycling.

2. Sources and Properties of Secondary Cellulose Fiber

2.1. Overview of Primary vs. Secondary Fibers

Cellulose fibers used in papermaking originate from two main categories: primary (virgin) fibers and secondary (recycled) fibers. The distinction between them lies in their source, processing history, and degree of structural integrity, all of which determine their suitability for specific paper grades and recycling applications.

Primary fibers are obtained directly from lignocellulosic raw materials such as wood, agricultural residues, or non-wood plants (e.g., bamboo, bagasse, hemp, and straw). They are produced through chemical pulping (kraft, sulfite) or mechanical pulping processes that separate cellulose from lignin and other components. These fibers retain their full length, flexibility, and bonding potential, providing excellent mechanical properties, brightness, and surface quality. Consequently, they are typically used for high-strength or high-quality papers, including printing, writing, and packaging grades. However, their production requires substantial energy and water inputs and generates chemical effluents, making the process resource-intensive and environmentally demanding [30,35].

In contrast, secondary fibers, often referred to as recovered, recycled, or wastepaper fibers, are obtained from post-consumer or post-industrial paper products collected through recycling systems. They are reprocessed through pulping, cleaning, and de-inking stages to remove inks, fillers, and contaminants before reuse in new paper production [31,36]. Secondary fibers represent the cornerstone of sustainable papermaking, as they reduce the demand for virgin pulp, conserve forest resources, and lower the energy and water footprint of the industry [14].

Despite these environmental advantages, secondary fibers differ from primary ones in their morphological and chemical characteristics. Repeated recycling and drying cause changes in fiber structure, such as shortening, hornification (loss of swelling and bonding ability), and decreased flexibility, which affect their ability to form strong inter-fiber bonds [3,10]. As a result, recycled fibers are often blended with a proportion of virgin fibers to restore paper strength and maintain quality standards.

In modern circular manufacturing systems, both primary and secondary fibers play complementary roles: virgin fibers ensure durability and quality, while recycled fibers enhance sustainability and resource efficiency. The balance between these two fiber sources is essential to achieving environmental and economic optimization in the pulp and paper sector.

2.2. Main Waste Paper Sources

Secondary cellulose fibers originate from a variety of paper products that have completed their initial service life and are recovered through industrial or municipal collection systems [15,32,33,37,38]. The main waste sources include office paper, corrugated packaging, and mixed paper, each characterized by distinct fiber compositions, additives, and degrees of contamination that influence their recycling potential and final paper quality. Recovered paper streams exhibit substantial variability in fiber morphology, which directly influences their behavior during reprocessing and their suitability for different paper grades. Figure 3 classifies the main types of recovered fibers based on key quality parameters such as mean fiber length, fines content, lumen condition, and coarseness. The diagram distinguishes long-fiber recovered papers, short-fiber recovered papers, mixed recovered fibers, and contaminated or complex grades, using mean fiber length and fines/coarseness content as principal axes. Representative morphological features, such as lumen collapse, fines generation, and fiber stiffness, are illustrated for each category to highlight their differing behavior during recycling and papermaking. This fiber-quality-oriented perspective highlights why different recovered paper categories contribute differently to sheet consolidation, strength development, drainage behavior and overall recyclability, thereby providing an essential framework for understanding the upgrading strategies discussed in the following sections.

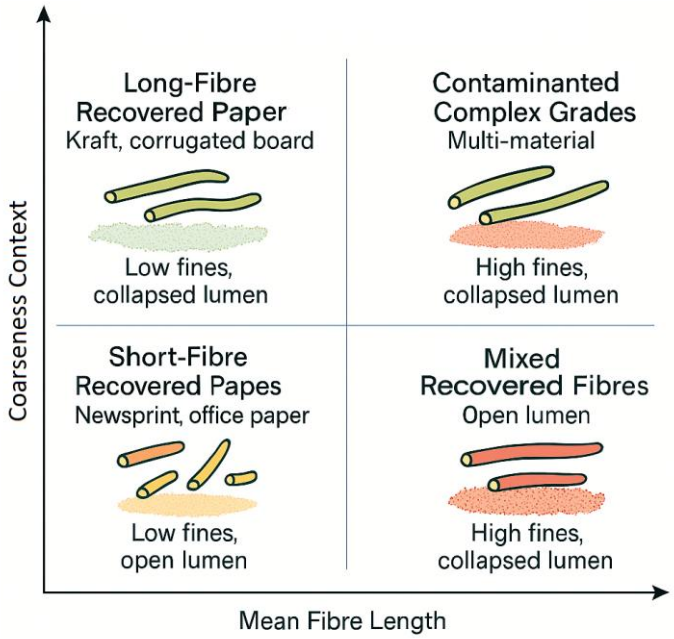


Figure 3. Classification of recovered paper based on key fiber-quality parameters.

Office paper represents one of the most valuable grades of recovered paper due to its high cellulose purity and low lignin content. It is typically composed of chemically pulped fibers derived from hardwood and softwood species, yielding long, flexible fibers with excellent bonding capacity and brightness [34,39]. Office waste includes printed and unprinted copier paper, writing paper, and forms from administrative and educational institutions. Because this category generally contains limited amounts of fillers, coatings, or inks, it is considered a high-grade recyclable material (grade 1.11 in the EN 643 European List of Standard Grades of Recovered Paper and Board). However, contamination from synthetic adhesives, colored inks, and polymer-based coatings may complicate de-inking processes and affect the optical quality of recycled products [35,40]. Recovered office paper

is often used in the production of recycled printing and writing papers, tissue, and de-inked pulp for high-quality applications.

Corrugated packaging, which includes corrugated boxes, cartons, and board materials is the largest contributor to global recovered paper streams. It consists mainly of unbleached kraft fibers with a relatively high lignin content, derived from softwoods such as pine and spruce. The structure of corrugated board comprises linerboard (outer layers) and fluting (inner corrugated layer), contributing to both its high mechanical strength and resilience. These fibers are well suited for multiple recycling cycles due to their robustness, though their dark color and coarse texture limit their use in white or fine papers [36,37,41,42]. Recycled corrugated materials are primarily employed in the manufacture of testliners, fluting media, and other packaging papers. In the EN 643 classification, corrugated board corresponds to grades 1.04 (corrugated cardboard) and 1.05 (used kraft paper and board). Owing to their abundance and ease of collection from retail and logistics sectors, corrugated materials constitute the backbone of large-scale recycling operations [14].

Mixed paper refers to heterogeneous paper waste streams containing a combination of low- and high-quality grades. It typically includes magazines, catalogs, colored office papers, paperboard, and household paper waste. The diversity of fiber sources, coatings, adhesives, and fillers makes mixed paper more challenging to process. High ink content, variable moisture, and the presence of non-paper contaminants such as plastics and metals reduce its uniformity and yield. Nevertheless, due to its wide availability and relatively low cost, mixed paper is often used as a supplementary raw material in the production of lower-grade packaging papers, boxboard, and tissue products after adequate sorting and cleaning [38,43]. In the EN 643 list, mixed paper corresponds mainly to grades 1.02 and 1.03.

Inland Empire Paper Company (Millwood, WA, USA), an integrated paper mill, uses a mixture of de-inked recycled newspaper fibers combined with thermomechanical pulp to produce newsprint and various specialty paper grades. Continuous optimization of flotation deinking and water reuse has enabled more than 350 t day^{-1} of recycled newsprint production while reducing effluent and energy demand [39,44]. Stora Enso Langerbrugge Mill (GhentBelgium, processes 100% recovered paper, mainly high-grade office and printing waste, into newsprint and magazine paper. Annual capacity ≈ 540 000 t is achieved with about 40% CO_2 reduction versus virgin-fiber mills through use of recycled furnish and combined heat and power generation [40,45]. The city of Milan implemented separate collection of mixed paper and cardboard, achieving > 90% purity. The sorted material supplies nearby recycled-paper mills such as Cartiera di Ferrara Ferrara, Italy), which produces packaging grades from this stream. LCA analysis confirmed lower GHG emissions than virgin pulp alternatives [26,31]. Smurfit Kappa (Schipol, Netherlands and Dublin, Ireland) operates on-site baling and back-haul systems for cardboard and paper packaging waste from supermarkets and logistics companies, closing the loop within its own integrated mill network. Material recovery exceeds 90% for corrugated waste [41,46].

Overall, the composition and quality of recovered paper sources significantly influence the efficiency of recycling processes and the properties of recycled fibers. Office papers contribute high-quality fibers suitable for white-grade papers, while corrugated materials provide structural strength for packaging applications. Mixed papers, despite their heterogeneity, support bulk production of recycled materials when properly sorted and treated [38,42,43,47]. A balanced utilization of these waste streams is therefore essential for maintaining both economic feasibility and environmental sustainability in the pulp and paper recycling chain.

2.3. Quality Parameters and Contaminants Affecting Fiber Chemistry

The quality of secondary cellulose fibers is determined by a combination of intrinsic fiber characteristics and extrinsic factors related to the paper's prior use, collection, and recycling processes. These parameters play a decisive role in the performance of recycled pulp, influencing its bonding potential, mechanical strength, optical properties, and overall suitability for specific papermaking applications. Many laboratory recycling protocols differ from industrial conditions in terms of drying intensity, chemical environment, and cycle duration, which partly explains discrepancies between academic findings and mill-scale performance [43,44,48,49]. The chemistry of recovered fibers is not static but evolves with each recycling cycle, reflecting both the original fiber source and the effects of mechanical, thermal, and chemical treatments.

Figure 4 presents a radar-chart comparison of key quality parameters: fiber length, fines content, surface charge, ash/fillers and coatings, and ink and adhesive contamination, for typical recovered paper grades, shown on a 0–100 scale for old corrugated containers (OCCs), mixed office waste (MOW), old newspapers (ONPs) and mixed paper (MP). The contrasting profiles highlight how different sources of recovered paper exhibit distinct combinations of morphology, surface chemistry and impurity load, which in turn influence refining response, bonding potential and overall recyclability. These parameters are well established as key determinants of fiber behavior during reprocessing, influencing swelling, bonding, drainage, refining energy demand, and sheet consolidation [45,50]. Because no unified dataset simultaneously reports all five parameters for the same set of recovered-paper grades, Figure 4 synthesizes typical ranges from recent literature to illustrate how different recovered-paper streams occupy distinct positions within a multi-parameter quality space. This multidimensional perspective highlights the diverse reprocessing behavior and treatment requirements associated with each grade and underscores the need for more comprehensive, standardized datasets to support future circular-fiber quality assessments [50,51].

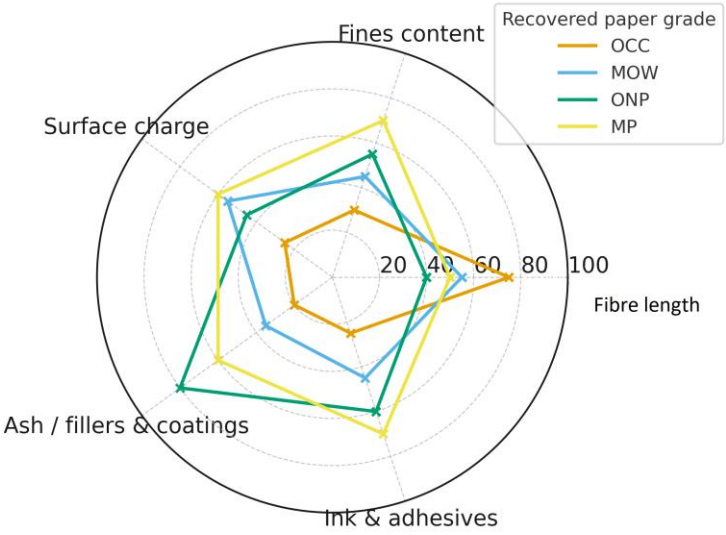


Figure 4. Radar-chart representation of key quality parameters for selected recovered paper grades.

Fiber length is one of the most important intrinsic determinants of bonding potential, with longer fibers contributing to tensile strength and network integrity, whereas shorter fibers offer reduced mechanical reinforcement. Variations in fiber-length distributions across recovered grades are widely reported, with OCC generally exhibiting longer fibers and ONP or MP containing shorter, more mechanically fatigued fibers due to previous printing and deinking steps [45,50].

Fines content also varies considerably between recovered-paper streams. Fines, as small cellulosic particles generated during pulping and repeated recycling, strongly influence drainage, water retention and sheet formation. Their relative abundance increases with recycling severity and is often higher in newsprint- and mixed-paper-derived pulps [52,53].

Surface charge governs fiber–fiber and fiber–additive interactions by modulating electrostatic and colloidal stability conditions. Although comprehensive datasets comparing charge densities across recovered-paper grades remain limited, recent analyses show that charge heterogeneity increases as fibers accumulate contaminants, extractives and degradation products during successive use cycles [54].

Ash, fillers and coating residues represent another decisive quality parameter, especially in graphic-paper-derived recovered fibers such as ONP, which typically carry elevated mineral loads. Recent work examining filler removal and cellulose purification from waste-paper sources reports wide variability in ash levels, reflecting the different coating and printing technologies applied to various recovered-paper grades [55].

Ink, adhesive and sticky contaminants are among the most problematic factors in recycled pulps. Their chemical diversity and complex morphology lead to agglomeration, deposition and sheet defects. Comparative analyses of different recovered-paper grades confirm that stickies and ink residues are particularly prevalent in mixed office waste, newsprint, and mixed-paper streams (Wang et al., 2022; Deshwal et al., 2019) [51,56].

Another key parameter is the water retention value (WRV), which indicates the fibers capacity to reabsorb water after drying. WRV is directly linked to the degree of hornification as the irreversible closure of micropores and hydrogen bonding sites that occurs during drying. A decrease in WRV signifies reduced swelling capacity and flexibility, which in turn limits fiber–fiber bonding [46]. Mo et al., (2022) studied hornification and found that it lowers WRV measurably [57]. In controlled drying/rewetting studies, WRV decreases in distinct stages as crystallinity rises during hornification, evidencing fewer accessible pores/hydroxyls for re-swelling. Lab recycling of wheat-straw and hardwood pulps showed WRV decline alongside hemicellulose depletion and a drop in degree of polymerization early in the cycles, directly tied to reduced swelling and bonding capacity [47,58]. Related to this is fiber swelling and surface charge, both influenced by the presence of carboxylic and hydroxyl groups on the cellulose chain. Recycling reduces surface charge due to the loss of hemicelluloses and extractives, leading to diminished interfiber bonding and lower reactivity toward chemical additives.

Crystallinity also plays a key role in fiber chemistry. During recycling, the amorphous regions of cellulose, responsible for water absorption and flexibility, tend to collapse, while crystalline domains increase. According to Yılmaz et al. (2021), repeated recycling caused a progressive decrease in fiber size and a marked rise in the proportion of fines, which reached about 44% of the total pulp after the third recycling cycle [48,59]. The authors observed that shorter and thinner fibers accumulated mainly on the 100–200 mesh sieves, while long fibers became scarce. This morphological degradation was accompanied by a continuous decline in tensile, tear, and burst indices reductions of roughly 9%, 10%, and 16%, respectively, after three recycling runs, and a pronounced increase in air permeability. These physical changes were associated with structural modifications in cellulose, including higher crystallinity and crystallite width, leading to reduced swelling capacity and weaker hydrogen bonding within the fiber network. This change enhances stiffness but reduces rehydration and bonding potential. Consequently, recycled fibers often exhibit higher crystallinity indices, which correlate with lower tensile and burst strength of recycled-containing paper. The chemical composition of fibers, particularly the ratio of cellulose to hemicelluloses and lignin, further determines the behavior of recycled pulps. Fibers with higher hemicellulose

content tend to re-swell more easily and maintain better bonding, whereas lignin-rich fibers display reduced bonding potential but greater resistance to mechanical stress.

Beyond the intrinsic fiber characteristics, the presence of contaminants exerts a significant influence on fiber chemistry and pulp processing. Common contaminants include inks, adhesives, coatings, fillers, plastics, and non-fibrous materials introduced during paper use or printing. Ink particles and pigments alter fiber surface, requiring de-inking processes based on flotation, washing, or enzymatic treatment. Recent studies confirm that hydrophobic ink residues and polymeric adhesives remain major obstacles to fiber recycling efficiency [34,39,49,60], while surveys highlight widespread industrial concern over coating and stickies contamination [38,43,50,61]. Inadequate de-inking can leave hydrophobic residues on the fiber surface, impeding fiber hydration and bonding. Adhesives and pressure-sensitive labels, collectively referred to as "main stickies generators" pose one of the most persistent challenges in recycling. These thermoplastic materials, often derived from synthetic polymers, can agglomerate under heat and pressure, forming deposits that disrupt paper formation, reduce surface quality, and contaminate process water.

Fillers and coating pigments such as calcium carbonate, kaolin, and titanium dioxide, while essential in the production of high-quality printing papers, accumulate in recycled fibers and modify their surface chemistry. They reduce fiber–fiber contact, hinder hydrogen bonding, and alter zeta potential, which affects retention and drainage during papermaking. Furthermore, repeated recycling increases the concentration of these inorganic materials, resulting in ash build-up that decreases fiber yield and complicates sludge management. Recent studies confirm that the accumulation of inorganic fillers such as calcium carbonate, kaolin, and titanium dioxide alters fiber surface charge and bonding capacity, while their persistence in closed-loop systems increases ash content and hinders drainage and retention [51–54,62–65].

Residual sizing agents (e.g., alkyl ketene dimer, rosin, or synthetic substitutes) may also interfere with wetting and fiber swelling, diminishing the efficiency of subsequent bonding [55,56,66,67].

In addition to these chemical contaminants, biological and environmental impurities can degrade fiber quality. Microbial growth in stored wastepaper and recycled pulp can lead to the formation of biofilms, odors, and enzymatic degradation of cellulose. Dust, sand, and metallic particles introduced during collection and transportation also contribute to mechanical wear in pulping and screening equipment, while affecting optical cleanliness [57,58,68,69].

Overall, the interplay between quality parameters and contaminants defines the recyclability and functional performance of secondary fibers. Maintaining high-quality recovered paper requires stringent sorting, cleaning, and de-inking to minimize chemical interference and preserve the natural bonding potential of cellulose. Advanced analytical techniques, including fiber fractionation, zeta potential analysis, and spectroscopic methods (FTIR, XRD), are increasingly applied to assess changes in fiber chemistry [43,48,53,64]. Optimizing these parameters not only enhances paper quality but also supports the broader goals of resource efficiency and circular economy in the pulp and paper industry.

3. Chemical and Structural Effects of Fiber Recycling

3.1. Dimensional and Morphological Changes

The recycling of cellulose fibers induces a complex set of dimensional and morphological transformations that progressively alter their structural integrity, bonding potential, and papermaking performance. These changes are primarily caused by the mechanical, thermal, and chemical stresses to which fibers are subjected during the stages of collection, repulping, screening, de-inking, and drying. Recent investigations confirm that the

combined mechanical, thermal, and chemical stresses encountered during recycling stages as repulping, de-inking, and drying lead to irreversible dimensional and morphological deterioration of cellulose fibers [43–45,48,50]. As fibers undergo multiple recycling cycles, their geometry, surface topography, and flexibility evolve in ways that directly influence both the microstructure of the paper sheet and its macroscopic mechanical behavior. At the heart of these transformations is the reduction in fiber length and width. Mechanical treatments such as repulping and refining fragment fibers and fibrils, leading to a steady reduction in the average fiber length and an increase in the proportion of fines, tiny cell wall fragments and fibrillar debris. Studies have shown that each recycling loop may reduce mean fiber length by 10–25%, depending on the type of pulping and refining conditions applied [59,70]. Industrially relevant trials reported average fiber length falling from ~1.22 mm (virgin) to ~0.73 mm by the 3rd recycle, with fines content increasing, degrading formation and consolidation. Classic comparative work found ~50% strength loss in kraft pulps after four recycles (largest losses in the first two), while mechanical pulps showed smaller changes, linking chemistry/morphology to macroscopic strength [43,48,60,71].

Shorter fibers reduce the effective bonding area between adjacent fibers, thereby weakening tensile and tear strength. In parallel, fibers tend to become slightly narrower as external fibrils are stripped away, and their cross-sectional profile becomes more irregular. The fiber length-to-width ratio, a key indicator of bonding potential and drainage behavior, thus diminishes gradually with repeated processing [61,62,72,73].

Another prominent morphological alteration involves the stiffening and collapse of the fiber wall, a phenomenon commonly referred to as hornification. During drying, the capillary water that previously swelled the microfibril network is removed, allowing adjacent cellulose chains to form irreversible hydrogen bonds. This collapse of the cell wall structure results in a significant reduction in fiber swelling and flexibility, which compromises the ability of the fiber to conform to neighboring fibers during sheet formation [63,74]. Hornified fibers appear more rigid and less collapsible under the microscope, displaying a flattened or wrinkled lumen rather than a rounded one. The decrease in flexibility also limits the formation of hydrogen bonds during rewetting, reducing interfiber contact and paper strength [64,65,75,76].

The external fibrillation, meaning the presence of fine fibrils on the fiber surface that increase bonding area, is another critical factor affected by recycling. Mechanical refining in the initial pulping stage generally promotes external fibrillation, enhancing inter-fiber bonding and tensile strength. However, in subsequent recycling cycles, the repeated shear forces tend to strip away these fibrils, leaving smoother surfaces with reduced bonding potential [66,77]. This loss of fibrillar material diminishes surface roughness and increases hydrophobicity, both of which reduce the wetting and bonding ability of fibers in recycled pulp. The internal fibrillation, referring to the delamination of cell wall layers within the secondary wall, also declines as hornification progresses, further limiting fiber swelling and flexibility [17,67,78].

Microscopic and imaging analyses, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM), have revealed distinct morphological markers of fiber degradation. After several recycling cycles, fibers exhibit increased surface smoothness, micro-cracks, and collapsed lumens. The fiber cross-section becomes more compact, with reduced wall porosity and less open fibrillar structure. These structural modifications hinder water penetration and swelling during repulping, contributing to longer pulping times and higher energy consumption [68,79].

In addition to changes in fiber dimensions and wall structure, recycling affects the distribution and composition of fines within the pulp. The accumulation of fines, as cell wall fragments smaller than 200 μm can have dual effects. On one hand, they improve

sheet density and surface smoothness, which is desirable in printing and tissue papers. On the other, excessive fines reduce drainage and air permeability, increase energy demand during dewatering, and lower bulk and tear strength. Therefore, the fines content becomes a crucial parameter for balancing paper properties and process efficiency in recycled pulp systems [43,48,69,80].

The fiber curl and kink indexes are additional morphological attributes significantly influenced by recycling. As fibers are subjected to repeated mechanical stresses in pulping and refining, they develop localized bends (kinks) and overall curvature (curl). These distortions reduce fiber conformability and bonding efficiency but may increase bulk and softness in certain paper grades. Over time, the accumulation of curl and kinks contributes to a more irregular fiber network, influencing sheet formation and optical properties [70,71,81,82].

The combined effect of these morphological and dimensional alterations is a gradual decline in paper performance. Papers produced from extensively recycled fibers show lower tensile, burst, and tear indices, as well as reduced optical brightness and smoothness. The degree of degradation depends on the fiber source (e.g., hardwood vs. softwood), pulping method (chemical vs. mechanical), and recycling conditions. For instance, fibers from chemical pulps typically retain better recyclability due to their higher cellulose purity and flexibility, whereas mechanical pulps, rich in lignin and hemicelluloses, stiffen more rapidly under thermal and mechanical cycling [72,83].

Table 1 summarizes the principal dimensional and morphological changes occurring in cellulose fibers through successive recycling cycles, highlighting their causes, effects on fiber properties, and implications for paper quality and recyclability. Differences in pulping severity, fiber source, and measurement methodology contribute to the contradictory observations reported for fines generation, fiber shortening, and swelling capacity [43,44,48,49,65,68,73–76,79,84–87]. These dimensional and morphological alterations collectively contribute to the gradual deterioration of recycled fiber performance. Understanding and controlling these changes are key to optimizing the recycling process and maintaining paper strength, appearance, and process efficiency over multiple cycles.

Table 1. Dimensional and morphological changes in recycled cellulose fibers.

Parameter/Feature	Description of Change During Recycling	Effect on Fiber Properties	Impact on Paper Quality
Fiber length	Progressive shortening due to mechanical cutting during pulping and refining.	Reduced fiber–fiber contact area; lower bonding potential.	Decreased tensile and tear strength; need for virgin fiber blending.
Fiber width and cross-section	Collapse of cell wall and lumen; irregular cross-sectional shape.	Reduced flexibility and swelling capacity.	Lower bonding and sheet density; poor surface smoothness.
Hornification	Irreversible hydrogen bonding during drying leading to wall stiffening.	Loss of swelling ability and rehydration potential.	Reduced tensile strength and poor rewetting behavior.
External fibrillation	Loss of surface fibrils due to repeated refining and washing.	Smoother surface, reduced bonding sites.	Decreased fiber bonding and sheet strength.
Internal fibrillation	Reduced delamination between cell wall layers.	Limited flexibility and swelling.	Weaker fiber bonding, poorer formation.
Fines content	Accumulation of small fiber fragments and cell wall debris.	Increased density but reduced drainage.	Higher smoothness but lower bulk and tear strength.

Table 1. *Cont.*

Parameter/Feature	Description of Change During Recycling	Effect on Fiber Properties	Impact on Paper Quality
Fiber curl and kink	Increase in fiber distortions with repeated mechanical treatment.	Reduced conformability and orientation in the sheet.	Lower tensile strength, but higher bulk and softness.
Surface roughness	Smoothing of fiber surface due to fibril loss.	Reduced surface area and reactivity.	Lower bonding efficiency and coating adhesion.
Crystallinity	Increase in crystalline regions due to drying and hornification.	Higher stiffness, lower water absorption.	Reduced flexibility and bonding potential.
Fines and ash accumulation	Retention of inorganic fillers and fines in recycled pulp.	Altered fiber chemistry and zeta potential.	Affects drainage, strength, and optical properties.

To mitigate these effects, researchers have explored controlled refining, enzymatic treatments, and chemical softening agents to restore flexibility and fibrillation in recycled fibers [65,68,73–76,79,84–87]. Gentle mechanical refining can reopen partially collapsed pores, increase external fibrillation, and improve fiber bonding, although over-refining accelerates fiber cutting. Enzymatic approaches, particularly the use of cellulases and hemicellulases, have shown promise in selectively removing surface impurities and enhancing fiber flexibility without excessive damage.

Consequently, the dimensional and morphological transformations induced by fiber recycling are central to understanding the limitations of recycled pulp performance. Fiber shortening, hornification, loss of fibrillation, lumen collapse, and accumulation of fines collectively define the degree of recyclability and the quality of the resulting paper. A thorough understanding of these phenomena is essential for developing strategies that maintain fiber integrity over multiple cycles and extend the sustainable use of recycled paper in the circular papermaking economy.

3.2. Chemical Composition and Functional Group Alterations

The recycling of cellulose fibers not only induces physical degradation but also triggers significant chemical transformations that alter their composition, molecular structure, and surface reactivity. These changes are primarily the result of mechanical stress, thermal exposure, oxidative conditions, and interactions with processing chemicals during pulping, de-inking, and drying. Over successive recycling cycles, the chemical composition of the fiber, comprising cellulose, hemicelluloses, lignin, extractives, and mineral residues gradually evolves, leading to reduced bonding capacity, altered hydrophilicity, and weakened fiber integrity [77,78,88,89]. Understanding these chemical and functional group alterations is therefore essential for assessing fiber recyclability and developing treatments to restore their papermaking potential.

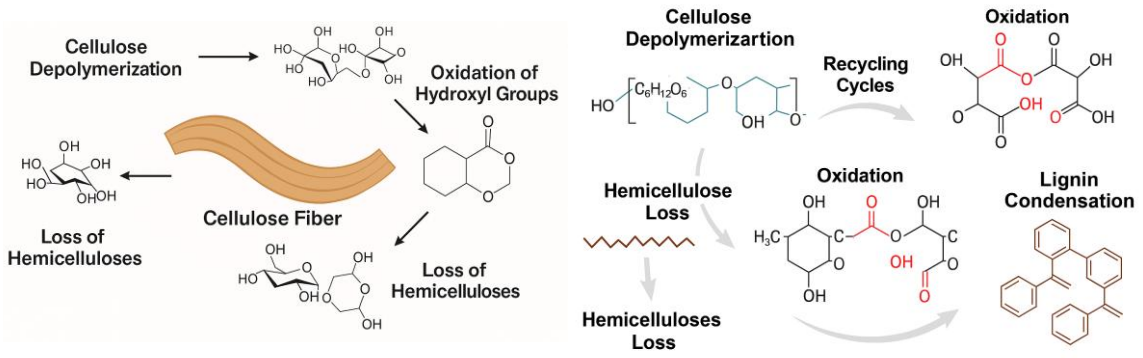
The main chemical transformations that occur during fiber recycling, including cellulose depolymerization, oxidation, hemicellulose depletion, and lignin modification are illustrated in Figure 5a, which summarizes the progressive chemical alterations affecting fiber reactivity and integrity.

At the molecular level, the cellulose backbone is subject to chain scission and depolymerization. Mechanical and chemical stresses during repulping and refining break β-(1→4)-glycosidic linkages within the cellulose polymer chain, decreasing the degree of polymerization (DP). As the DP decreases, the average molecular weight of cellulose declines, resulting in shorter macromolecules with fewer reactive hydroxyl sites available for hydrogen bonding [72,83]. These shortened cellulose chains exhibit reduced mechanical

strength and lower capacity to form inter-fiber bonds, which contributes to the overall deterioration of paper tensile and burst properties. In parallel, oxidative degradation, promoted by exposure to air, bleaching agents, and elevated temperatures, further fragments cellulose molecules, forming carbonyl and carboxyl groups at the cleavage sites. Coppola and Modelli (2020) demonstrated that oxidative degradation during paper recycling leads to significant chemical alterations in cellulose chains, particularly the formation of carbonyl and carboxyl functionalities due to the cleavage of glycosidic bonds and the oxidation of hydroxyl groups [79,90]. These modifications were confirmed through infrared and nuclear magnetic resonance spectroscopy, which revealed an increase in carbonyl absorption bands and a decrease in hydroxyl content. The oxidation process also promoted partial depolymerization and structural rearrangement of cellulose microfibrils, resulting in more compact and less flexible fiber surfaces. These chemical transformations contribute to reduced hydrogen-bonding ability and lower interfiber cohesion in subsequent recycling cycles. The mechanisms of cellulose chain scission and hemicellulose degradation that occur during repeated recycling cycles are schematically represented in Figure 5b, illustrating how depolymerization and carbohydrate loss reduce fiber reactivity and bonding potential.

Hemicelluloses, which play a key role in maintaining fiber flexibility and water retention, are particularly vulnerable during recycling. They are more hydrophilic and less crystalline than cellulose, making them susceptible to alkaline dissolution and hydrolysis under repulping conditions. As recycling progresses, hemicellulose loss leads to a reduction in fiber swelling and plasticity. The decrease in amorphous polysaccharides content results in reduced fiber porosity and water-holding capacity, aggravating hornification and impairing bonding [7]. The leaching of hemicelluloses also alters the surface charge balance of the fiber, reducing the number of available anionic carboxyl groups that contribute to electrostatic interactions in fiber flocculation and retention processes [80,91].

The lignin content of recycled fibers may also vary depending on the original pulp type and recycling intensity. In mechanical and semi-chemical pulps, lignin tends to become more condensed and less reactive during recycling due to oxidative cross-linking. This process enhances hydrophobicity and stiffness, further limiting the rewetting and bonding of fibers. In contrast, chemically pulped fibers, which contain minimal lignin, show fewer lignin-related effects but may still accumulate lignin-derived residues from recycled mixed paper or coatings. The oxidation of residual lignin during drying and reprocessing can lead to chromophore formation, contributing to fiber yellowing and brightness reversion, which are common problems in recycled paper production [17]. The oxidative transformation and condensation of lignin during recycling, and their contribution to fiber hydrophobicity and discoloration, are illustrated in Figure 5c, which highlights the structural modifications and chromophores formation occurring in lignin-rich fibers.



(**a**) (**b**)

Figure 5. *Cont.*

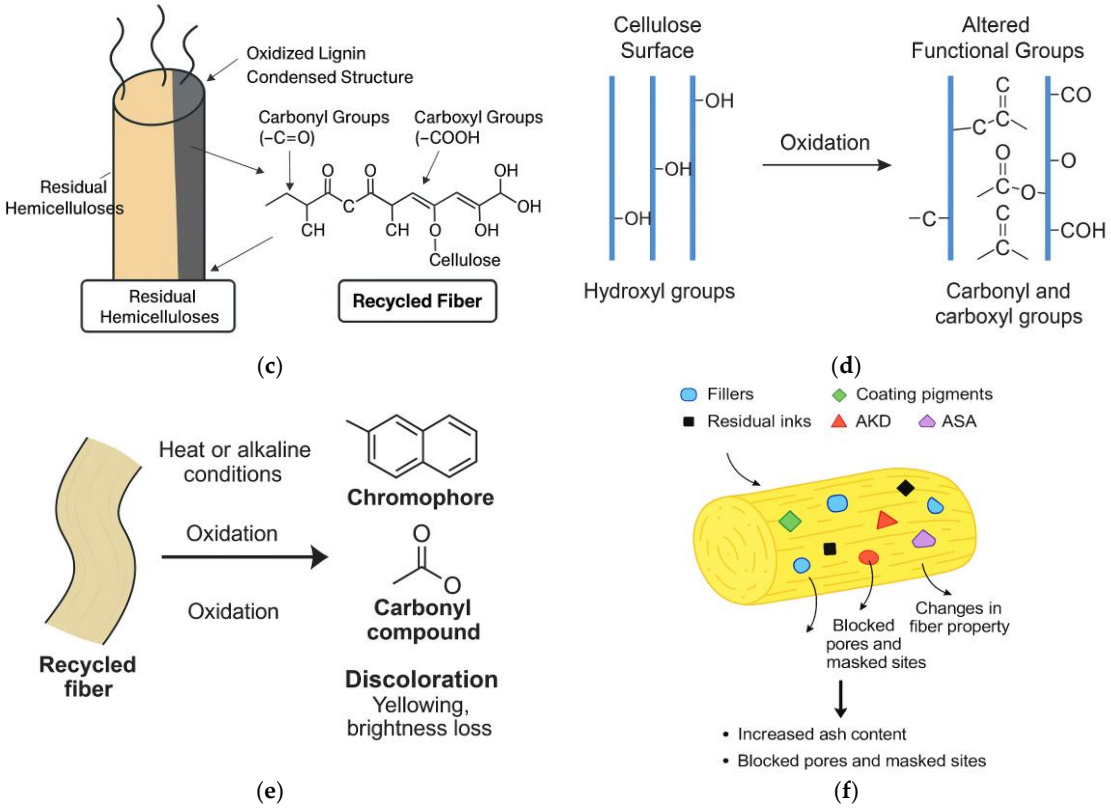


Figure 5. (**a**) Chemical composition and functional group changes: recycling induces cellulose depolymerization, hydroxyl oxidation to carbonyl/carboxyl groups, hemicellulose loss, and lignin condensation, progressively altering fiber chemistry; (**b**) Cellulose depolymerization and hemicellulose loss: successive recycling causes polymer chain scission, lower degree of polymerization, and hemicellulose dissolution, reducing flexibility and bonding strength; (**c**) Lignin behavior: oxidative condensation produces cross-linked, hydrophobic structures that stiffen fibers; chromophore formation within oxidized lignin causes yellowing and brightness decline; (**d**) Oxidation-induced surface changes: hydroxyl (–OH) groups convert into carbonyl (–C=O) and carboxyl (–COOH), increasing surface charge but reducing hydrogen bonding and fiber reactivity; (**e**) Chromophore and carbonyl formation: oxidation of cellulose and lignin under heat or alkaline conditions generates conjugated double bonds and carbonyls, producing visible yellowing and brightness loss; (**f**) Accumulation of non-fibrous additives: fillers ($CaCO_3$, kaolin, TiO_2), pigments, inks, and sizing agents (AKD, ASA) embed within the fiber matrix, blocking pores, masking reactive sites, increasing hydrophobicity, and weakening bonding (These representations support the analytical interpretation presented in later sections and clarifies terminology used throughout the review).

One of the most characteristic chemical consequences of recycling is the alteration of functional groups on the fibers surface. The hydroxyl (-OH) groups, which are responsible for hydrogen bonding between fibers, become less accessible due to hornification and increased crystallinity. Moreover, oxidation processes transform some hydroxyl groups into carbonyl (-C=O) and carboxyl (-COOH) groups, changing the surface chemistry and zeta potential of fibers. Aging/recycling chemistry tracked by FTIR/XPS shows growth of carbonyl/carboxyl bands in cellulose, consistent with oxidative scission and altered surface charge as key for additive adsorption and wet-end chemistry [81]. While carboxyl groups increase anionic charge and can improve wet-end chemical interactions, excessive oxidation weakens the cellulose backbone and reduces mechanical stability. FTIR and XPS analyses of recycled fibers consistently show an increase in carbonyl peak intensity, indicating progressive oxidation and formation of aldehydic and acidic moieties [70,81]. These transformations affect both the hydrophilic nature and the reactivity of the fibers toward retention aids and sizing agents. The oxidative conversion of cellulose surface

functional groups and its impact on fiber charge and bonding ability are depicted in Figure 5d, illustrating how hydroxyl groups are progressively transformed into carbonyl and carboxyl groups during recycling.

Recycling-induced degradation of cellulose fibers manifests primarily through changes in molecular integrity, swelling capacity, and drainage behavior. Although absolute numerical values vary among studies due to differences in pulp type, drying severity, and experimental conditions, consistent qualitative patterns have been reported across the literature. To consolidate these widely observed tendencies, Table 2 summarizes typical trends in degree of polymerization (DP), water retention value (WRV), and freeness (CSF) over successive recycling cycles, from virgin fibers to advanced recycled stages. The table also highlights how selected chemical or enzymatic interventions can partially reverse or mitigate these changes.

Table 2. Typical qualitative trends in degree of polymerization (DP), water retention value (WRV), and freeness (CSF) observed in cellulosic fibers during repeated recycling cycles, summarizing characteristic behavioral patterns from virgin fibers to those recycled multiple times, including changes induced by chemical, enzymatic, and swelling-based mitigating treatments.

Recycling Stage/ Condition	Degree of Polymerization (DP)	Water Retention Value (WRV)	Freeness (CSF)/Drainage	Representative References
Virgin/never-dried pulp	Highest DP; cellulose chains largely intact with minimal hydrolysis or oxidative damage.	High WRV, reflecting fully developed swelling capacity and accessible internal pore structure.	Baseline freeness determined by initial refining; used as reference for subsequent recycling behavior.	[82,92]
After first drying/first recycling cycle (no special treatment)	Pronounced initial decrease in DP compared with virgin pulp; largest relative drop often observed between cycle 0 and cycle 1.	Marked decrease in WRV due to hornification and partial collapse of the pore structure; reduced swelling and flexibility.	In many chemical pulps with fines retained, freeness tends to drop (slower drainage) mainly at the first cycle; in systems with fines loss, freeness can increase.	[93,94]
2–3 recycling cycles (no special treatment)	Further DP decrease, but the rate of decline is generally lower than in the first cycle; values begin to approach a plateau influenced by fiber origin and prior aging.	WRV continues to decline with each drying/recycling event, then tends toward a lower steady state; loss of hemicelluloses and increased crystallinity are commonly reported.	Reported trends depend on pulp type and system closure; some studies show continued freeness drop with fines accumulation, others report stabilization or slight increase when fines are lost.	[93,95]
≥4–5 recycling cycles (no special treatment)	Gradual, smaller DP decreases; molecular weight distribution increasingly influenced by oxidative history and prior thermal/chemical exposure rather than the number of cycles alone.	WRV typically remains at a relatively low level; hornification is largely developed and additional recycling induces only limited further changes in swelling.	Freeness behavior strongly process-dependent; in many laboratory studies further changes are modest, but in closed industrial systems fines management and additional refining can dominate drainage trends.	[92,93,96]
Recycled fibers with mitigating treatments (e.g., chemical swelling, refining, or enzymatic/chemical re-swelling)	DP can be maintained or only moderately reduced if oxidative severity is controlled; some treatments intentionally trade slight DP loss for improved bonding.	WRV can partially recover or even increase relative to untreated recycled pulp due to re-swelling, increased charge, or enhanced fibrillation.	Refining-based strategies typically reduce freeness (slower drainage) because of increased fibrillation and fines content; chemical/enzymatic swelling without intensive refining has a milder impact on drainage.	[48,94,97]

Another consequence of recycling-induced oxidation is the formation of chromophoric and carbonyl compounds, which contribute to fiber discoloration and brightness loss. The oxidation of polysaccharides and lignin generates conjugated double bonds and carbonyl structures that absorb visible light, leading to the characteristic yellowish hue of aged and recycled papers. This effect is particularly evident when recycled fibers are exposed to alkaline or thermal conditions, which accelerate oxidative degradation. De-inking

chemicals and peroxide bleaching, though essential for optical recovery, can exacerbate oxidation if not properly controlled, further degrading cellulose chains and reducing strength [72,83].

The processes leading to fiber discoloration and brightness loss during recycling are illustrated in Figure 5e, which depicts the oxidation of cellulose and lignin resulting in chromophore and carbonyl compound formation under thermal or alkaline conditions.

Changes in ash and extractive content are also noteworthy. With each recycling cycle, non-fibrous additives, including fillers (e.g., calcium carbonate, kaolin, titanium dioxide), coating pigments, and residual inks, accumulate within the fiber matrix. These inorganic and organic residues can physically block fiber pores and mask reactive sites on the surface, impeding hydrogen bonding. They also influence fibers zeta potential, drainage behavior, and interactions with wet-end additives. Kaolin particles are strongly negative (often <-25 mV at pH ≈ 7); coating them with cationic starch causes charge reversal and larger agglomerates, changing retention/adsorption behavior and competition for cationic strength aids [81,82,98,99]. The residual presence of sizing agents such as alkyl ketene dimer (AKD) or alkenyl succinic anhydride (ASA) can make recycled fibers more hydrophobic, reducing water absorption and swelling, which further compromises bonding performance [56,67]. The accumulation of fillers, pigments, and sizing agents within recycled fibers and their impact on surface chemistry and bonding are illustrated in Figure 5f, which shows how these inorganic and organic residues alter fiber hydrophilicity and reactivity during successive recycling cycles.

Overall, the combined effects of cellulose depolymerization, hemicellulose depletion, oxidative modification of functional groups, and accumulation of non-cellulosic materials lead to a progressive decline in fiber chemistry and reactivity. These chemical alterations are closely interlinked with morphological degradation phenomena, reinforcing each other over successive recycling loops. The resulting fibers are shorter, stiffer, less hydrophilic, and less capable of forming strong interfiber hydrogen bonds, which collectively deteriorate paper strength and durability.

To counteract these effects, several strategies are under investigation. The application of enzymatic and chemical treatments, such as cellulases, laccases, and mild oxidizing agents, can help remove oxidized residues, expose hidden hydroxyl groups, and improve fibers reactivity without excessive cellulose chain scission. Similarly, additive-assisted recycling using cationic polymers or surface-reactive agents can restore charge balance and improve bonding interactions. Such approaches are central to extending fiber life and enhancing the sustainability of recycling processes within the circular papermaking economy.

3.3. Chemical and Enzymatic Modification Strategies for Recycled Fibers

Recycled fibers undergo progressive structural and chemical deterioration, manifested in reduced DP, decreased WRV, hornification, and loss of bonding capacity, as discussed in previous subsections. In the last decade, and particularly in recent years, several chemical and enzymatic strategies have been proposed to mitigate these effects and to recover or enhance the performance of secondary fibers.

These approaches include the use of cellulose nanomaterials obtained from recycled pulp, "green" functionalization routes that modify fiber surfaces with more sustainable chemistries, and synergistic enzymatic treatments that reduce refining energy while improving fiber quality. The following subsections summarize representative advances and discuss their implications for circular papermaking.

3.3.1. Cellulose Nanomaterials from Recycled Pulp and Their Use in Recycled Paper

Recycled pulps are increasingly recognized as suitable feedstocks for the production of cellulose nanofibers (CNFs) and related nanomaterials. Early work showed that TEMPO-oxidized CNF can be successfully prepared from recycled deinked paper, with nanofibers exhibiting morphology and rheology comparable to those obtained from native cellulose resources. More recent studies and reviews on recycled-paper-based materials confirm that nanocellulose, including CNF produced from recycled sources, can significantly improve the mechanical performance of recycled paper when used as a wet-end additive or as part of fibre blends.

For instance, Filipova et al. (2023) showed that adding nanocellulose to furnishes containing waste paper fibers leads to marked increases in tensile and burst indices, while also reducing air permeability, thereby demonstrating the reinforcing potential of nanocellulose in recycled-based materials [50].

Signori-Iamin et al. (2024) investigated a dual system combining cationic CNF and enzymatically produced anionic micro/nanofibers, applied to both virgin and recycled paper [100]. They reported that this fully cellulose-based system not only enhanced the mechanical properties of recycled paper (breaking length increase of about 46.5%) but also outperformed conventional synthetic polyacrylamide as a retention and strength agent. These results support the view that nanocellulose, including materials produced from recycled or residual sources, is an effective reinforcing strategy in circular papermaking.

Complementary work on TEMPO-oxidized nanocellulose produced from waste newspapers confirms that recycled fibers can be used to obtain highly fibrillated, carboxyl-rich nanocellulose suitable for strengthening and functional applications [101]. Overall, the literature indicates that nanocellulose derived from recycled pulps represents a promising route to recover strength and stiffness in multi-cycle recycled papers, although trade-offs related to drainage and dewatering must be managed carefully.

3.3.2. Green Functionalization Routes: Cationic/Biobased Systems and Surface Modification

In parallel with nanocellulose, there is growing interest in "green" functionalization strategies that modify fiber surfaces using more sustainable chemistries. These approaches include cationization with bio-based or low-toxicity reagents and polymer systems, as well as bio-compatible cross-linking or grafting that improves bonding and dimensional stability.

Surface-characterization studies on pulps derived from mixed waste corrugated carton and office paper have shown that recycling and deinking alter surface chemistry and charge, thereby affecting compatibility with additives and coating systems. This provides a basis for targeted surface modification. In the textile sector, Azevedo et al. (2025) demonstrated that recycled cotton fibers can be reinforced by combinations of biodegradable polymers such as chitosan, carboxymethyl cellulose, starch, and silica-based additives, significantly improving tensile properties of recycled-fiber-based materials [102]. Although this work is focused on textiles, the underlying concepts, use of polysaccharide-based, biodegradable additives to restore strength and inter-fiber bonding are directly relevant to cellulosic packaging and papermaking [103].

Silane-based treatments have been extensively applied to cellulose fibers in composite materials to improve interfacial bonding, hydrophobicity, and mechanical performance. While most of these studies do not target papermaking directly, they illustrate that functionalized silanes can form stable siloxane bonds with cellulose, suggesting potential for carefully designed, low-toxicity coupling systems compatible with circular paper products [104]. Taken together, these results indicate that cationic and bio-based function-

alization routes, including polysaccharide-based systems and adapted silane chemistries, offer viable strategies to enhance bonding and durability of recycled fibers while remaining aligned with circular-economy and non-toxic-chemistry principles.

3.3.3. Synergistic Enzyme Systems and Integration with Biorefinery Concepts

Enzymatic treatments have emerged as an important tool for improving recycled fiber quality and reducing process energy demand. A systematic review by Rossi and Solé (2025) concluded that enzymatic refining of recycled fibers can reduce refining energy consumption by up to about 20% compared with purely mechanical refining, while simultaneously improving bonding and drainage, provided that enzyme formulations and process conditions are carefully optimized [105].

Experimental studies on enzymatic pretreatment of pulp show that cellulase or cellulase/xylanase mixtures can significantly modify fiber surfaces and water-holding capacity. For example, Shin et al. (2024) reported that cellulase-based treatments increase external fibrillation and WRV of hardwood kraft pulp, with mixed cellulase–xylanase systems selectively reducing xylan content and altering surface composition [106].

Nagl et al. (2023) characterized several commercial enzyme formulations for pulp refining and highlighted the importance of endoglucanase and xylanase activities in achieving energy savings and improved refining performance, underscoring the synergistic roles of different enzymes in the cocktails [107].

Synergistic enzyme systems have also been proposed in conjunction with nanocellulose-based additives and with retention aids, as illustrated by Barrios et al. (2024), who investigated enzyme-assisted strategies for dewatering and strength enhancement in papermaking [108]. In parallel, laccase-based oxidative systems, including laccase/mediator treatments, have demonstrated the ability to improve fiber-bonding capacity and mechanical properties of unbleached recycled pulps by modifying lignin at the fiber surface and increasing external fibrillation. These approaches can be integrated into broader biorefinery concepts, where enzymatic treatments not only upgrade fiber quality but also facilitate the valorizations of side streams such as hemicelluloses and lignin.

Overall, recent work indicates that enzyme-based strategies, alone or combined with mechanical refining and nanocellulose or polymer additives, offer a flexible toolbox to improve the performance of recycled fibers while advancing energy efficiency and sustainability in circular papermaking (Table 3).

Table 3. Representative advances (2018–2025) in the chemical and enzymatic modification of recycled fibers, summarizing key mechanisms, observed performance improvements, and recent literature contributions.

Strategy/System	Representative Mechanism	Observed Effects (Qualitative)	Representative References
CNF/nanocellulose from recycled or waste fibers	TEMPO-mediated or other oxidation followed by mechanical fibrillation of recycled or waste-paper pulps	CNF from recycled paper or waste fibers shows morphology and properties comparable to CNF from virgin fibers; used as wet-end additive or in fiber blends, it improves tensile strength and stiffness of recycled-paper-based materials	[50,65,109]
Dual CNF systems (anionic + cationic) in recycled paper	Cationization of CNF and combination with enzymatically produced anionic micro/nanofibers	Fully cellulose-based dual CNF system acts as both strength and retention aid; breaking length of recycled paper increased by ≈46.5%, outperforming synthetic polyacrylamide	[65]

Table 3. *Cont.*

Strategy/System	Representative Mechanism	Observed Effects (Qualitative)	Representative References
Bio-based polymer and polysaccharide functionalization of recycled fibers	Use of chitosan, CMC, starch and other biodegradable polymers as strengthening agents and cross-linkers	Significant improvement of tensile properties and dimensional stability in recycled-fiber-based materials (shown for cotton recycled fibers)	[102]
Surface modification of pulps from mixed waste papers	Deinking and surface treatments applied to mixed waste corrugated carton and office paper pulps	Changes in surface chemistry, charge and roughness documented; basis for targeted surface functionalization and improved compatibility with additives	[86]
Silane-based cellulose modification (composites context)	Formation of siloxane bonds between functionalized silanes and cellulose hydroxyl groups	Improved interfacial adhesion, hydrophobicity and mechanical properties in cellulose-based composites	[110]
Enzymatic refining of recycled fibers	Use of cellulases and hemicellulases as refining aids	Energy savings up to ≈20% and improved bonding and drainage when enzymatic refining complements mechanical refining	[105,107]
Cellulase/cellulase–xylanase pretreatment	Selective modification of fiber surface and hemicellulose content	Increased external fibrillation and WRV; altered surface composition; potential enhancement of flexibility and bonding	[111]
Laccase/laccase–mediator systems on recycled pulps	Oxidative modification and partial delignification of fiber surfaces	Improved fiber-bonding capacity, tensile and compressive strengths of unbleached recycled pulps	[86,112]

3.4. Hornification and Fiber Swelling Behavior

One of the most critical phenomena affecting the recyclability of cellulose fibers is hornification, a process that results in the irreversible loss of fiber swelling and flexibility upon drying and rewetting. Hornification represents a form of structural hardening and collapse of the cell wall microstructure, which occurs due to the formation of additional hydrogen bonds between adjacent cellulose microfibrils as the fiber dries [63,74]. These newly formed inter- and intramolecular bonds restrict the accessibility of hydroxyl groups and reduce the ability of fibers to reswell in subsequent papermaking cycles. The cumulative effect of hornification over successive recycling loops is a progressive decline in fiber conformability, bonding potential, and paper strength [83,113]. The structural evolution of cellulose fibers during drying and recycling, from a hydrated, swollen state to a compact, hornified configuration is illustrated in Figure 6a, highlighting the reduction in pore volume, water retention, and fiber flexibility associated with hornification.

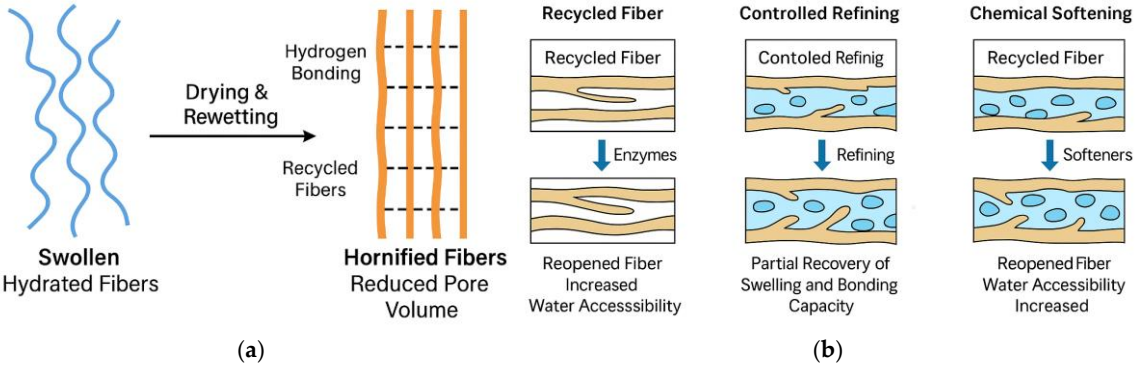


Figure 6. (**a**) Hornification and fiber swelling behavior: during recycling, cellulose fibers transform from hydrated, porous structures with high water retention into compact, hornified forms characterized by dense hydrogen bonding, reduced pore volume, lower flexibility, and diminished swelling capacity; (**b**) Mitigation strategies for hornification: enzymatic treatments, controlled refining, and chemical softening help reopen fiber pores, restore water accessibility, and partially recover swelling and bonding performance after multiple recycling cycles.

Hornification occurs primarily during the drying stage of papermaking, where the removal of water from the fiber wall leads to the approach and aggregation of cellulose microfibrils. During the initial stages of drying, capillary forces bring microfibrils into close contact, and hydrogen bonds form between hydroxyl groups that were previously separated by water molecules. Once established, these bonds are thermodynamically stable and difficult to break upon rewetting, resulting in a "locked" microstructure with diminished pore volume. Consequently, when hornified fibers are re-immersed in water during recycling, they exhibit reduced swelling capacity, lower water retention values (WRVs), and limited rehydration of the internal cell wall [17].

The extent of hornification depends on several interrelated factors, including fiber origin, pulping method, drying conditions, and recycling history. Chemical pulps derived from kraft or sulfite processes are more prone to hornification than mechanical pulps because of their higher cellulose purity and greater accessibility of hydroxyl groups. Fibers with high hemicellulose content tend to be less affected due to the amorphous, hydrophilic nature of hemicelluloses, which act as spacers between cellulose microfibrils and mitigate close packing during drying [72,83]. Conversely, fibers subjected to high drying temperatures, prolonged thermal exposure, or elevated pH undergo more severe hornification due to increased hydrogen bond formation and microfibril aggregation.

At the microscopic level, hornification manifests as a collapse of the cell wall structure and a reduction in the internal pore volume. According to Pinto et al. (2021), atomic force microscopy and X-ray diffraction analyses revealed that multiple recycling cycles cause substantial topographical and structural changes in kraft [84,114]. Recycled fibers exhibited flattened and compacted microfibrillar structures with reduced surface roughness compared to virgin fibers, indicating partial collapse of the cell wall and limited re-swelling capacity. These morphological changes were accompanied by an increase in cellulose crystallinity and loss of amorphous regions, reflecting hornification phenomena [73,84]. The study further showed that these structural modifications led to a progressive decline in tensile strength and flexibility, highlighting the direct relationship between microfibril aggregation, decreased hydrogen-bond formation, and reduced mechanical performance in recycled paper.

Measurements using mercury porosimetry and nuclear magnetic resonance (NMR) techniques have shown that the specific surface area and pore radius within hornified fibers can decrease by up to 50% after multiple drying and recycling cycles [69,80]. The smaller pore size limits water penetration and reduces the mobility of fiber components, restricting swelling and fibrillation. This structural densification also diminishes the accessibility of reactive hydroxyl groups on the fiber surface, lowering the potential for hydrogen bond formation during paper sheet consolidation.

Hornification significantly affects fiber swelling behavior, a key determinant of bonding ability and paper strength. In native or unhornified fibers, water absorption into the cell wall leads to swelling of amorphous cellulose and hemicellulose regions, promoting flexibility and conformability. This allows fibers to flatten and create extensive contact areas during pressing and drying, resulting in strong inter-fiber bonding. In contrast, hornified fibers absorb less water, remain stiff, and fail to conform adequately to adjacent fibers. The reduced swelling capacity can be quantified by lower WRVs or decreased fiber saturation points (FSPs). Typically, recycled kraft fibers exhibit a 20–30% decline in WRV after the first drying cycle and continue to lose swelling potential with each subsequent recycling loop [70,81].

The mechanisms underlying hornification are both physical and chemical in nature. Physically, the collapse of pores and the reorganization of microfibrils within the secondary wall lead to a denser fiber structure. Chemically, the formation of additional hydrogen

bonds between hydroxyl groups and possible covalent cross-linking between oxidized cellulose chains reinforce rigidity. The loss of accessible hydroxyl groups directly reduces the capacity for water adsorption and hydrogen bonding during repulping. Additionally, the increase in cellulose crystallinity associated with hornification limits molecular mobility within the cell wall, further reducing rehydration and reactivity [73,84].

Hornification also influences inter-fiber bonding and paper strength. As the fibers lose flexibility and swelling capacity, their ability to form intimate contacts with neighboring fibers during wet pressing and drying diminishes. This results in fewer and weaker hydrogen bonding and lower tensile and burst indices in recycled papers. The sheet becomes less dense, with increased porosity and reduced optical smoothness. The diminished bonding efficiency is especially problematic in high-grade printing and writing papers, where uniform surface properties are essential. Furthermore, hornification can intensify drainage and retention problems in the wet end of the papermaking process because of changes in fiber charge and surface energy [65,73,76,84].

A variety of analytical techniques have been used to characterize hornification and fiber swelling. Water retention value (WRV), fiber saturation point (FSP), and swelling ratio measurements are commonly used to quantify the extent of water uptake. Fourier transform infrared spectroscopy (FTIR) and solid-state NMR have been employed to track changes in hydrogen bonding and crystallinity, while atomic force microscopy (AFM) and scanning electron microscopy (SEM) provide visual evidence of lumen collapse and reduced surface fibrillation [63,73,74,83,84,113]. Together, these analyses confirm that hornification leads to both structural densification and chemical immobilization of the fiber wall components.

Efforts to mitigate hornification have focused on physical, chemical and enzymatic strategies aimed at restoring fiber flexibility and reactivity. One effective approach is the use of enzymatic treatments (e.g., endoglucanases, xylanases) that partially hydrolyze surface cellulose or hemicelluloses, opening up microfibrillar structures and enhancing water accessibility. Similarly, mechanical rehydration through controlled refining can reopen fiber pores and increase surface fibrillation, though excessive refining risks fiber cutting and fines generation [36,41,85,115]. The application of reactive polymers or softening agents that disrupt hydrogen bonding networks has also shown promise in reactivating hornified fibers. Furthermore, maintaining moderate drying conditions and minimizing high-temperature exposure during papermaking can help reduce the initial degree of hornification.

The main approaches developed to counteract hornification and recover fiber flexibility are summarized in Figure 6b, illustrating how enzymatic, mechanical, and chemical treatments can reopen fiber pores, enhance swelling, and improve inter-fiber bonding during recycling.

In the context of sustainable papermaking, understanding hornification is essential for optimizing fiber recycling and improving material efficiency. Since hornification directly affects both fiber chemistry and structure, it serves as a bridge between the morphological and chemical degradation phenomena described in earlier sections. The ability to limit hornification or reverse its effects is therefore key to extending fiber's life, enhancing recycled paper quality, and supporting the long-term viability of circular economy strategies in the pulp and paper sector.

3.5. Crystallinity and Cell Wall Structure

Recycling alters the ordering of cellulose chains and the architecture of the fiber cell wall, with direct consequences for swelling, bonding, and mechanical behavior. During drying in each cycle, water leaves the amorphous regions of the cell wall and adjacent microfibrils are drawn into closer contact. New hydrogen bonds form and parts of the previously disordered domains become more ordered. As a result, most studies report

an increase in the apparent crystallinity index (CI) of recycled fibers together with a reduction in amorphous content and accessible surface area [70,72,81,83]. This ordering is a key component of hornification and helps explain why hornified fibers show reduced re-swelling and lower bonding capacity [17].

3.5.1. From Hydrated Networks to Compact Walls

In never-dried pulp, amorphous cellulose and hemicelluloses hold significant amounts of bound water, maintaining a porous, hydrated network that allows the wall to expand and conform to neighboring fibers. Drying collapses part of this network. Microfibrils in the S2 layer approach each other and form stable hydrogen bonds, the internal pore volume shrinks, and diffusion pathways for water and chemicals become longer and more tortuous. Upon rewetting, only a fraction of the initial pore volume is recovered; the remaining closure is largely irreversible. This densification of the secondary wall reduces flexibility and limits inter-fiber contact during sheet consolidation [17,69,80].

The progressive transition from an open, hydrated fiber wall to a compact, hornified structure during drying and recycling is illustrated in Figure 7a, highlighting the collapse of pores, microfibril aggregation, and loss of swelling capacity within the cell wall.

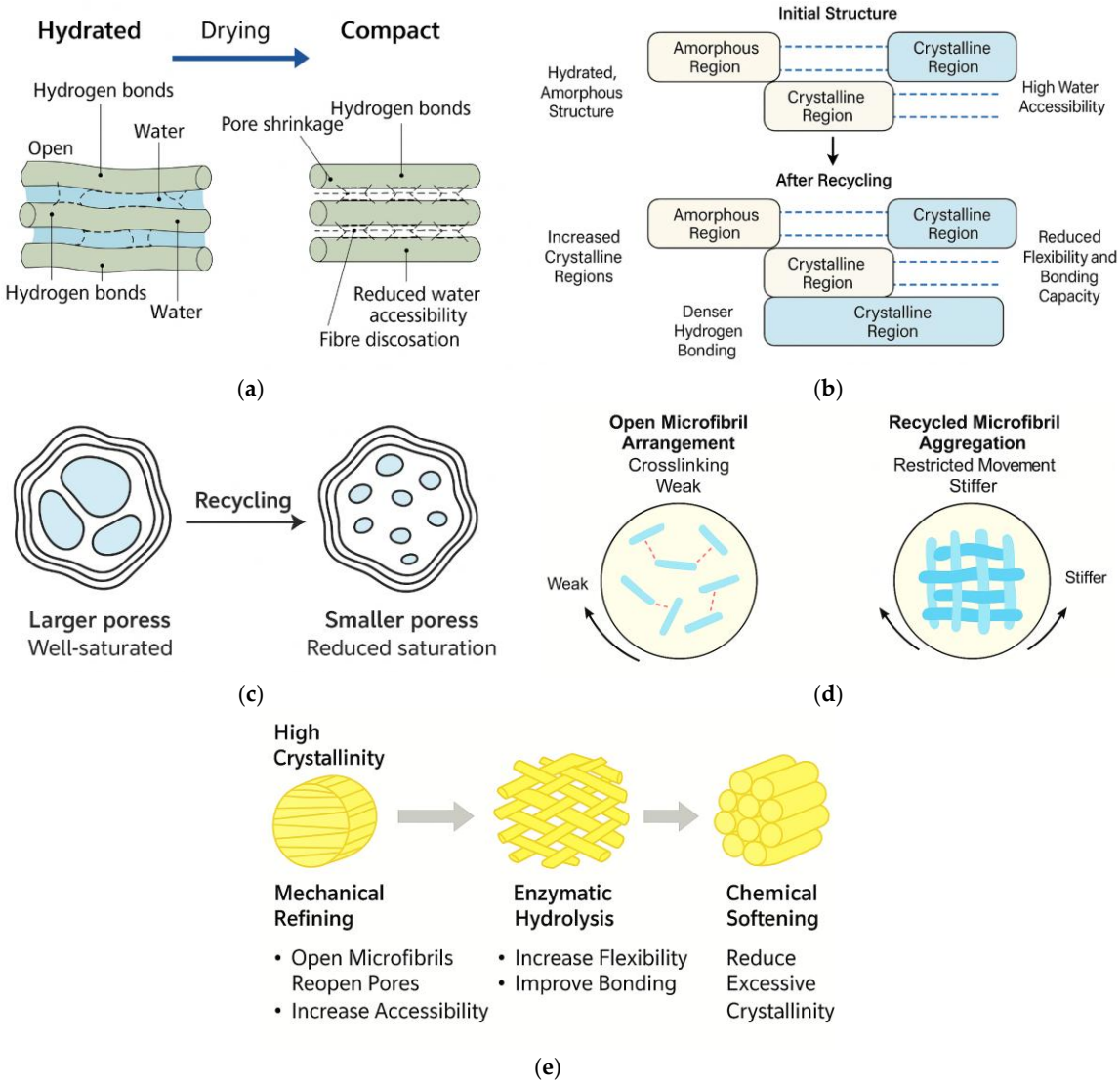


Figure 7. (**a**) Transformation of cellulose fiber walls: during drying and recycling, hydrated open pores collapse as microfibrils form dense hydrogen bonds, reducing pore volume, re-swelling, and water accessibility;

(**b**) Crystallinity changes: fibers evolve from hydrated, amorphous structures with high accessibility to denser, more ordered ones with increased crystalline regions, stronger hydrogen bonding, and reduced flexibility; (**c**) Pore size distribution: recycling decreases pore diameter and water saturation—hydrated fibers show large, accessible pores, while recycled ones exhibit compact walls and limited permeability; (**d**) Microfibril arrangement and mechanics: unprocessed fibers display open, flexible networks, whereas recycled fibers form aggregated, stiff structures with reduced deformability; (**e**) Interaction of refining, enzymatic hydrolysis, and chemical softening: these treatments reopen pores, lower excessive crystallinity, enhance flexibility, and improve bonding capacity in recycled cellulose fibers.

3.5.2. Crystallinity Changes and What They Mean

The increase in apparent CI during recycling is usually interpreted as loss of amorphous domains and enhanced packing of chains within or between microfibrils. Practically, this means fewer accessible hydroxyl groups for water sorption and for forming new hydrogen bonds with other fibers or with cationic additives. At the same time, higher CI correlates with greater stiffness of the wall, which helps preserve sheet bulk in some grades but generally reduces tensile and burst strength because fibers cannot conform and bond effectively [72,83,86,116].

The structural transition of cellulose fibers toward higher crystallinity during recycling is illustrated in Figure 7b, showing how amorphous regions with high water accessibility become progressively ordered and densely hydrogen-bonded, resulting in stiffer, less flexible fibers.

Two clarifications are important. First, routine papermaking and recycling do not convert cellulose I to cellulose II (a mercerization/alkali-swelling process would be required). The main change is a shift in the amorphous–crystalline balance and in the lateral aggregation of existing cellulose I microfibrils. Second, "increase in CI" is method-dependent: X-ray diffraction (XRD) peak-height methods, peak deconvolution, solid-state 13C NMR, FTIR ratios (e.g., 1427/895 cm^{-1}), and Raman metrics can yield different absolute numbers. Still, across methods the trend of higher apparent order with repeated drying is consistent [7,72,83].

3.5.3. Pore Size Distribution and Accessibility

Alongside higher order, recycling shifts the pore size distribution toward smaller radii and lowers total pore volume. Mercury intrusion porosimetry, water retention value (WRV), fiber saturation point (FSP), and NMR relaxometry show declines that track with the closure of meso- and macropores and with immobilization of bound water [69,80]. Lower accessibility limits (i) fiber swelling, (ii) penetration of de-inking and bleaching chemicals, and (iii) adsorption of wet-end polymers. Together with increased CI, this mass-transfer limitation explains slower re-hydration and the need for stronger refining or chemical assistance in later recycling loops [72,83].

The progressive reduction in pore size and fiber wall accessibility during recycling is illustrated in Figure 7c, which compares the open, hydrated structure of fresh cellulose fibers with the compact, less permeable structure of recycled fibers exhibiting reduced diffusion and water retention.

3.5.4. Microfibril Arrangement and Mechanics

Recycling affects not only order but also microfibril arrangement. Repeated drying and mechanical handling increase microfibril aggregation and reduce internal fibrillation. Stiffer S2 walls and reduced lamellar slippage lower fiber conformability. At the sheet scale, this manifests as lower tensile index, lower bonding contribution to strength, and sometimes higher modulus but lower elongation. In packaging grades, partial stiffening

can help maintain bulk, yet the typical outcome in printing/writing or tissue grades is loss of strength and softness [17,66,77].

The structural and mechanical evolution of cellulose microfibrils during recycling is illustrated in Figure 7d, showing how microfibril aggregation and compaction reduce flexibility and fibrillation, and leading to stiffer fibers with diminished bonding potential.

3.5.5. How Refining and Treatments Interact with Crystallinity

Refining after each cycle can partially offset densification by increasing external fibrillation and reopening parts of the pore network. However, over-refining shortens fibers and produces fines, which worsens drainage and may not recover bonding. Enzymatic or mild chemical treatments (e.g., xylanase, endoglucanase, or softening agents) can expose hidden hydroxyls and improve accessibility without excessive chain scission, effectively counteracting the functional consequences of higher CI [17,87,105].

The effects of different treatments on cellulose fiber crystallinity and structure are summarized in Figure 7e, illustrating how mechanical refining, enzymatic hydrolysis, and chemical softening modify microfibril organization, enhance accessibility, and partially reverse crystallinity-related rigidity in recycled fibers.

3.5.6. Tools to Measure and Monitor

A combination of structural and sorption measurements is recommended to track these changes:

- XRD/WAXS for CI, crystallite size, and peak broadening;
- Solid-state 13C NMR for crystalline vs. amorphous fractions and paracrystalline disorder;
- FTIR/Raman band ratios linked to order and hydrogen-bonding environment;
- WRV/FSP and NMR relaxometry for bound water and accessible porosity;
- AFM/SEM for surface fibrillation and wall densification.
- Used together, these techniques link micro- and macro-scale behavior, enabling targeted interventions in refining and chemical conditioning [69,70,72,80,81,83].

3.5.7. Implications for Circular Use

The crystallinity-related stiffening and pore collapse explain why recycled fibers need periodic supplementation with virgin pulp and why performance declines after multiple loops. Managing CI-linked accessibility, through gentle refining, selective enzymatic action, and careful drying profiles, is central to extending fiber lifetimes while keeping energy and chemical inputs reasonable [17,72,83]. In short, crystallinity and wall architecture are the molecular levers behind hornification; controlling them is essential for maintaining fiber bonding, strength, and processability across recycling cycles.

3.6. Surface Chemistry and Fiber Reactivity

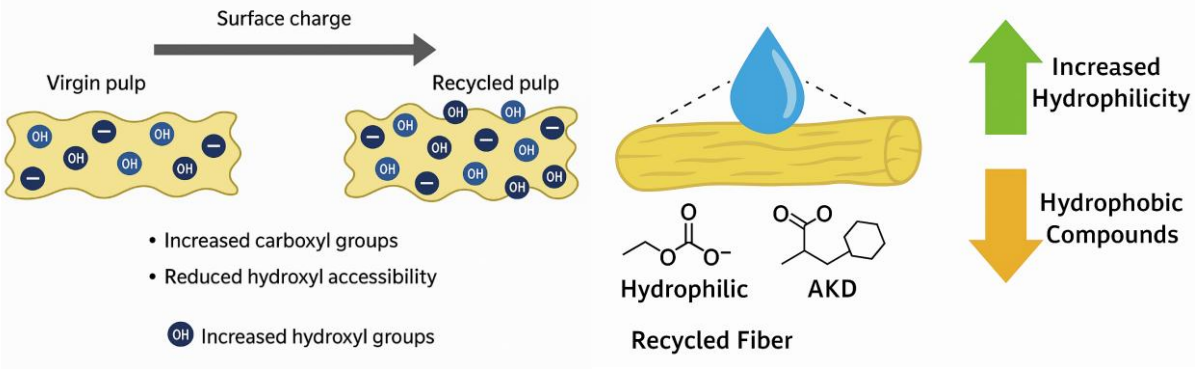
Recycling alters not only the internal structure of cellulose fibers but also the chemical state of their surfaces, where most interactions relevant to papermaking occur. The availability and accessibility of surface functional groups (primarily hydroxyl and carboxyl), the distribution of charges, and the presence of sorbed contaminants together determine wettability, zeta potential, adsorption of additives, ink detachment, flocculation–retention behavior, and ultimately the bonding capacity of fibers in the sheet. Because the papermaking wet end is governed by colloid and interface phenomena, even modest changes in surface chemistry, caused by drying/rewetting, oxidation, residual sizing, fillers, and "anionic trash" can produce large process effects [36,41,88,117].

From a charge perspective, recycled pulps typically display a complex anionic character arising from carboxyl groups on oxidized cellulose/hemicelluloses, anionic dispersants

from inks and coatings, and dissolved/colloidal substances released during repulping. At the same time, hornification reduces the fraction of accessible hydroxyl sites, masking portions of the surface and lowering "effective" charge despite equal or higher total carboxyl content [89,118]. The net result is often an increased cationic demand at the wet end to achieve equivalent retention, drainage, and strength relative to never-dried fibers. This behavior is routinely quantified by polyelectrolyte titration (e.g., with poly-DADMAC to measure anionic demand) and by zeta potential or streaming potential measurements that reflect the electrokinetic environment of the fiber–filler suspension. Because charge titration and surface potential measurements are not yet standardized across laboratories, differences in methodology often lead to divergent quantitative values [90,119].

The electrochemical evolution of recycled cellulose fibers and its implications for charge balance in papermaking systems are illustrated in Figure 8a, showing the increase in anionic carboxyl groups, the reduction in accessible hydroxyl sites, and the resulting rise in cationic demand for charge neutralization. Electrolyte composition further modulates surface interactions: Ca^{2+} and Al species (from PAC/alum) compress the diffuse layer, promote bridging/charge neutralization, and can reverse adverse effects of high anionic trash by improving fines and filler retention, though overdosing may cause deposits or loss of formation quality [72,83].

Wettability and surface energy evolve during recycling. Oxidation and loss of extractives tend to increase hydrophilicity (raising the density of $–COO^-$ at neutral–alkaline pH), favoring adsorption of cationic dry-strength agents (e.g., cationic starch, PAE) via electrostatic attraction and hydrogen bonding. Conversely, residual hydrophobes from prior cycles, chiefly alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), printing oils, and stickies can impart local hydrophobic patches that reduce water uptake, swelling, and bonding, and interfere with the uniform distribution of wet-end polymers [91,120]. The tension between these tendencies explains the often-reported need to "recondition" recycled surfaces before high-quality bonding and sizing can be re-established. Contact angle tests (Cobb, dynamic contact angle) and XPS/FTIR analyses typically show greater carbonyl/carboxyl signatures after recycling together with evidence of hydrophobe carryover, consistent with mixed hydrophilic–hydrophobic surface [70,81,92,121]. The coexistence of hydrophilic and hydrophobic domains on recycled cellulose fiber surfaces is illustrated in Figure 8b, highlighting how oxidation increases water affinity while residual hydrophobes such as AKD, ASA, and stickies create localized water-repellent patches that reduce bonding and polymer adsorption.



(a) (b)

Figure 8. *Cont.*

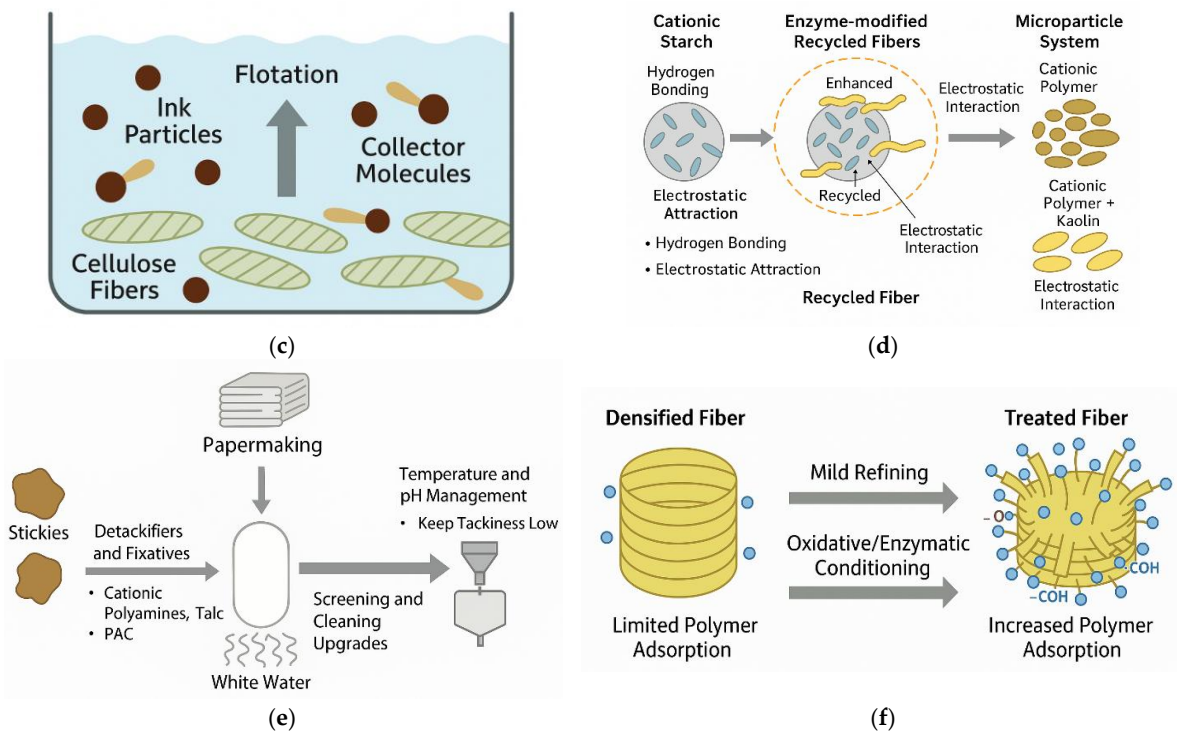


Figure 8. (**a**) Changes in surface charge and electrokinetic properties of recycled fibers: oxidation increases carboxyl content and anionic charge, while hornification limits hydroxyl accessibility, raising cationic demand and altering zeta potential; (**b**) Evolution of wettability and surface energy: hydrophilic regions rich in $–COO^-$/–OH attract water and cationic polymers, while hydrophobic patches from AKD, ASA, and stickies repel water, reducing swelling and bonding; (**c**) De-inking process: hydrophobic ink particles attach to air bubbles and float, while hydrophilic fibers remain suspended. Surfactants, hydrophobicity, pH, and ionic strength govern ink removal and selectivity; (**d**) Adsorption of strength and retention aids: negatively charged sites bind cationic polymers (starch, PAE) via electrostatic and hydrogen bonds; hornification limits uptake. Enzymatic or chemical treatments and microparticle systems enhance retention in filler-rich systems; (**e**) Stickies and latex residues: hydrophobic contaminants agglomerate under heat/shear, weakening bonding and fouling equipment. Controlled by detackifiers, fixatives, temperature/pH management, and screening before micro-stickies form; (**f**) Crystallinity and wall densification: increased crystallinity and compaction reduce amorphous hydration and polymer adsorption; mild refining or enzymatic conditioning restores fibrillation, reactive sites, and bonding capacity.

Surface chemistry also governs de-inking efficiency. Successful flotation depends on creating a difference in hydrophobicity between ink particles (preferably hydrophobic) and fiber surfaces (preferably hydrophilic). Aging and recycling increase fiber anionicity and can improve ink detachment with appropriate surfactants; however, oxidative over-treatment or alkaline darkening can produce small, strongly attached particles that are harder to float, while hydrophobes on the fiber compete for collector molecules, reducing selectivity. Thus, surfactant choice, ionic strength, and pH must be tuned to the altered surface state of recycled fibers [93,94,122,123]. The mechanism of de-inking and the contrasting roles of fiber hydrophilicity and ink hydrophobicity are illustrated in Figure 8c, showing how surfactants and air bubbles facilitate ink particle removal while fiber surface chemistry, pH, and ionic strength influence flotation efficiency.

The adsorption of strength and retention aids is highly sensitive to charge and accessibility. Cationic starch and PAE wet-strength resins rely on electrostatic attraction to negatively charged sites and on hydrogen bonding to hydroxyls; hornification diminishes both by masking sorption sites and reducing surface hydration. Selective enzymatic pretreatments (e.g., low-dose endoglucanase/xylanase) or carboxymethylation can expose

additional hydroxyls/carboxyls and increase anionic charge, thereby enhancing polymer uptake without excessive chain [95,124]. Microparticle systems (cationic polymer + bentonite/colloidal silica) remain effective with recycled pulps but often require higher cationic demand compensation to manage dissolved/colloidal anionics. In filler-rich systems, calcium carbonate and kaolin contribute surface charge and compete for cationic polymers; appropriate sequencing (e.g., fixatives → strength aid → microparticle) can restore retention and drainage under elevated anionic loads [96,125]. The mechanisms governing the adsorption of strength and retention aids on recycled cellulose fibers are illustrated in Figure 8d, showing how surface charge, accessibility, and treatment strategies influence the binding of cationic polymers, the role of microparticle systems, and the competitive effects of fillers on adsorption efficiency.

A particularly problematic facet of recycled furnish is stickies and latex residues, which alter surface chemistry by adsorbing onto fibers, contaminating white water, and agglomerating under heat/shear. These hydrophobic, often pressure-sensitive materials disrupt hydrogen bonding and weaken interfiber contact, while fouling wires and felts. Control strategies rely on (i) detackifiers and fixatives (e.g., cationic polyamines, talc, PAC) to immobilize colloidal hydrophobes on fines/fillers, (ii) temperature and pH management to keep tackiness low, and (iii) screening/cleaning upgrades to remove macro-stickies before they fragment into micro-stickies that are more difficult to control [51,97,98,126]. Systematic analyses have identified polyvinyl alcohol, polyacrylates, and styrene-butadiene rubber from pressure-sensitive adhesive labels and hot-melt glues as the main sources of deposits that contaminate paper machine wires and felts and reduce bonding between fibers; their control requires the use of detackifying agents, fixatives, and careful charge management [97]. Mill data show web breaks correlate with stickies exposure at sheet/machine–clothes interfaces, explaining why equal ppm levels can behave very differently depending on dispersion/state [50,61].

The occurrence and mitigation strategies of stickies and latex residues in recycled fiber processing are illustrated in Figure 8e, showing how these hydrophobic contaminants adhere to fibers and affect bonding and equipment performance, and how detackifiers, process control, and screening systems help minimize their impact.

At the fiber scale, surface reactivity is further impacted by increases in apparent crystallinity and by wall densification. Both phenomena reduce the fraction of hydrated amorphous regions where sorption and polymer interdiffusion are favored. Thus, even when titrations indicate adequate charge, the kinetics of adsorption slow and the areal coverage of polymers decreases. Targeted countermeasures include mild refining to renew external fibrillation (increasing accessible surface area) and low-severity oxidative or enzymatic conditioning to generate/activate surface carboxyls without severe chain scission, measures that have been shown to recover polymer uptake and bonding in recycled kraft pulps [8,17]. The influence of crystallinity and wall densification on fiber surface reactivity, along with the beneficial effects of refining and enzymatic treatments in restoring polymer adsorption and bonding, is illustrated in Figure 8f.

Therefore, the surface of recycled fibers is a contested interface: hornification and increased order reduce hydration and available hydroxyls; oxidation increases anionicity but may weaken chains; contaminants add hydrophobe patches and consume cationic demand; fillers contribute additional surfaces and charge competition. Managing this interface by balancing charge, sequencing wet-end additions, conditioning the surface to enhance wettability and accessible functionality, and suppressing hydrophobic contaminants is central to restoring reactivity and bonding and thereby to sustaining paper quality across recycling loops.

3.7. Fines Formation and Its Role in Recycled Fiber Systems

Fines as the smallest solid constituents of pulp suspensions are central to the behavior of recycled furnishes. Operationally, fines are usually defined as particles that pass a 200-mesh screen or are smaller than ~200 μm; they comprise cell-wall fragments (primary fines), fibrillar debris produced by refining (secondary fines), ray cells, parenchyma, and, in recycled pulps, substantial fractions of ash-bearing particles originating from fillers ($CaCO_3$, kaolin, TiO_2), coating pigments, ink fragments, and micro-stickies [85,99,115,127]. Their abundance rises with each recycling cycle because repulping, dispersion, and refining cut fibers and delaminate walls, while white-water closure recirculates mineral fines and dissolved/colloidal substances (DCSs). As a result, recycled furnishes often contain higher fines contents (commonly 10–25% of dry solids, grade-dependent) than comparable virgin pulps [100,128].

The principal categories of fines typically encountered in recycled paper systems are illustrated in Figure 9, emphasizing their diverse origins and effects on pulp behavior and sheet formation.

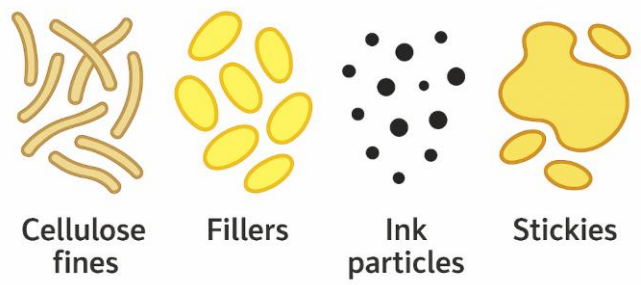


Figure 9. Main types of fines in recycled paper systems, showing cellulose fines (fiber fragments), mineral fillers, ink particles, and stickies as the dominant micro-components influencing fiber bonding, drainage, and surface chemistry.

3.7.1. Origins and Types of Fines in Recycling

During re-pulping and subsequent refining, shear and compression generate secondary fines by peeling external fibrils and breaking off S2/S1 wall fragments. Concurrently, primary fines (native debris from the original pulp) remain present and may be enriched through fractionation in the process loop. Recycled paper introduces non-fibrous fines: detached coating pigments, filler fragments, sub-micron ink particles from de-inking, and micro-stickies derived from adhesives and latexes that pass through coarse screening [50,85]. The composite nature of fines in recycled systems explains their heterogeneous chemistry and charge as cellulosic pieces are typically anionic and hydrophilic, whereas pigment-laden and sticky fines can be more hydrophobic and carry different surface charges. The main origins and categories of fines generated during paper recycling are depicted in Figure 10a, illustrating their diverse sources and compositional heterogeneity within recycled pulp systems.

3.7.2. Effects of Fines on Suspension Behavior, Drainage, and Retention

Fines strongly shape wet-end rheology and drainage. Because they have high specific surface area and carry charge, fines adsorb polymers and electrolytes, increasing cationic demand and complicating charge balance. They also clog the fiber mat during sheet formation, slowing drainage and raising vacuum/pressing loads [72,83]. In closed white-water circuits, fines recirculate and build up, elevating turbidity and solids in the headbox feed. Microparticle retention programs (e.g., cationic polymer + bentonite/colloidal silica) are widely used to aggregate fines and restore drainage; the dosage required is often higher in recycled furnishes due to the combined presence of DCSs, pigment fines, and micro-

stickies [51,62,85,115]. In closed white-water systems, calcium carbonate dissolution raises Ca^{2+}, triggering multi-issue deposits/foaming and perturbing charge balance, evidence of inorganic carryover affecting chemistry and runnability [101,129]. The influence of fines on suspension behavior and the mechanisms by which retention programs mitigate their effects are illustrated in Figure 10b, highlighting how fines interact with fibers, clog drainage channels, and respond to polymer–microparticle treatment systems.

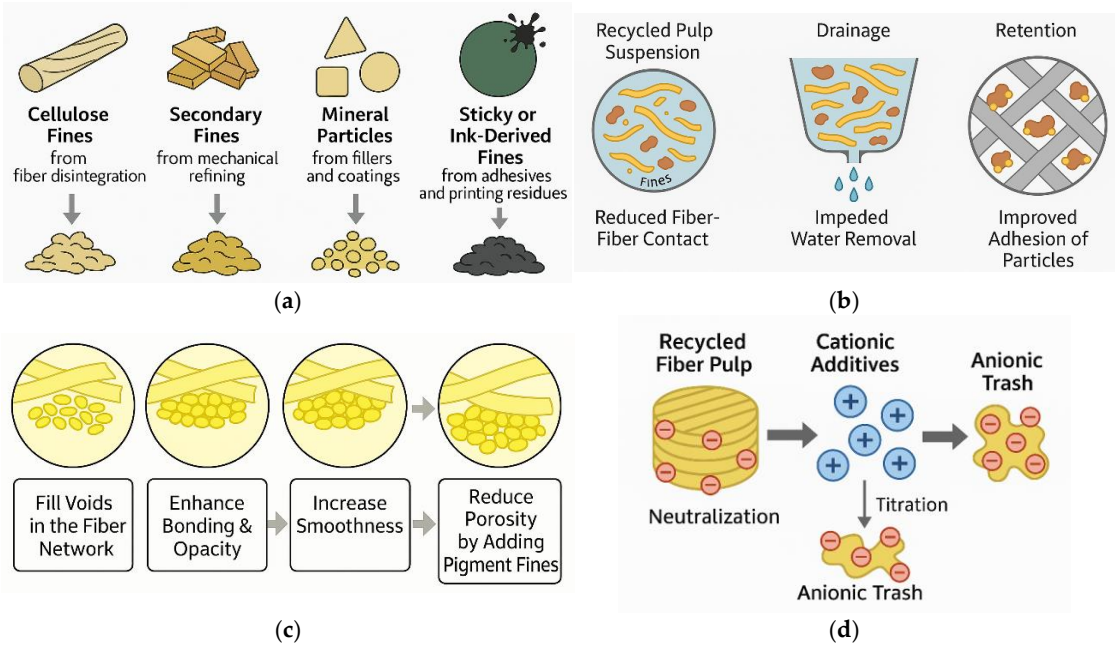


Figure 10. (**a**) Origins and types of fines: recycled paper systems contain cellulose fines from fiber disintegration, secondary fines from refining, mineral particles from fillers and coatings, and sticky or ink-derived fines from adhesives and printing residues; (**b**) Effects of fines on suspension behavior: fines accumulate in the fiber network, clog pores, and slow drainage while increasing cationic demand by adsorbing polymers. Microparticle systems (cationic polymer + bentonite/silica) help flocculate fines and restore drainage efficiency under high colloidal loads; (**c**) Role of fines in sheet structure: cellulosic fines fill fiber voids, enhancing smoothness, formation, and density; however, excess fines reduce bulk, air permeability, and tear strength. Mineral and pigment fines add brightness and opacity but weaken bonding when overrepresented; (**d**) Chemical interactions and anionic trash: dissolved and colloidal substances (DCSs)—including dispersants, latex residues, and AKD/ASA—adsorb onto fines and fibers, increasing anionic charge and competing with cationic additives. Fixatives like polyamines or PAC neutralize charge and improve additive retention.

3.7.3. Contributions of Fines to Sheet Structure and Properties

The influence of fines on dry-sheet properties is two-edged. Cellulosic fines fill voids between fibers, increasing sheet density, smoothness, and formation, beneficial for printability and surface quality. At the same time, excessive fines reduce bulk and air permeability, and can depress tear strength by interrupting fiber networks [102,130]. In packaging grades, moderate fines levels can help develop basis-weight efficiency and surface strength; however, too many fines impair press dewatering and raise steam consumption in drying.

The dual influence of fines on the structural and mechanical properties of recycled paper sheets is illustrated in Figure 10c, showing how appropriate fines levels enhance smoothness and formation, while excessive accumulation compromises bulk, strength, and dewatering efficiency. For tissue and towel grades, fines tend to reduce softness and absorbency because they collapse pores and hinder water uptake. Mineral-rich fines increase ash content, altering opacity and brightness, but they also dilute fiber–fiber bonding when they occupy bonding sites.

3.7.4. Chemical Interactions and "Anionic Trash"

By virtue of their surface chemistry, fines act as carriers and sinks for dissolved/colloidal matter. Ink dispersants, sizing residues (AKD/ASA), latexes, and extractives can adsorb onto fines, increasing hydrophobic patches and interfering with polymer adsorption on fibers. This pool of anionic trash competes for cationic strength agents (e.g., cationic starch, PAE) and fixatives, thereby lowering additive efficiency and necessitating higher dosages [17,96,125]. Where fines are pigment-rich, they can also buffer pH and contribute calcium or aluminum ions, modifying electrokinetic conditions and the performance of retention programs. The interactions between anionic fines, dissolved and colloidal substances, and cationic additives in recycled pulp systems are summarized in Figure 10d, highlighting how charge competition and fixation chemistry influence retention and wet-end stability.

3.7.5. Interplay with Hornification and Crystallinity

As recycling progresses, hornification and apparent crystallinity increase (Sections 3.4 and 3.5), reducing macroscopic fiber swelling. In this context, fines, especially fibrillar secondary fines can partially compensate for lost bonding area by providing additional contact sites and by acting as "bridges" between stiffened fibers. Yet this compensation is limited when fines are dominated by mineral or hydrophobic components, which do not contribute to hydrogen bonding and may even shield potential bonding sites [17,70,81].

3.7.6. Process Control and Management Strategies

Effective management of fines in recycled systems balances product quality, machine runnability, and energy use:

- Fractionation and white-water management. Hydrocycloning and fine-screening can remove grit and macro-contaminants while allowing retention of beneficial fibrillar fines. White-water clarification (DAF, save-all filters) prevents uncontrolled fines accumulation and closes the mass balance without overloading the headbox [72,83].
- Optimized refining. Light, targeted refining increases external fibrillation (beneficial fines) without excessive fiber cutting that would flood the system with detrimental fines. Refining intensity and specific edge load should be tuned to grade: packaging vs. print/tissue require different fines spectra [103,131].
- Retention/fixation programs. Sequential addition of fixatives (e.g., polyamines, PAC) to immobilize anionic trash on fines, followed by strength aids and a microparticle system, improves fines capture and drainage. Proper ionic strength and pH enhance floc architecture and release in the forming zone [53,64,104,132].
- De-inking and stickies control. Flotation conditions that produce larger, hydrophobic ink agglomerates minimize sub-micron ink fines. Detackifiers and talc can transfer micro-stickies onto fines in a controlled, retainable form, reducing deposition risk [75,86,93,122].
- Ash management. Where pigment fines dominate, partial purge or controlled ash targets help sustain bonding and reduce steam load. Coupling with filler make-up maintains optical properties without excessive fines recirculation [105,133].

3.7.7. Implications for Circular Performance

Because fines accumulate with reuse, their management is essential to extending fiber lifetimes within a circular model. Well-controlled fines improve formation and can enhance basis-weight efficiency, whereas unmanaged fines penalize drainage, energy consumption, and strength. The optimal strategy is grade-specific: high-smoothness

printing grades benefit from a higher fraction of fibrillar fines with good retention chemistry; packaging grades require a balance that preserves bulk and stiffness; and tissue grades need minimized fines to protect softness and absorbency [99,106,127,134]. Across grades, linking fractionation, retention programs, and white-water closure delivers the highest material efficiency while mitigating the well-known drawbacks of fines build-up in recycled loops.

3.8. Influence of Additives, Fillers, and Contaminants on Fiber Chemistry

The chemical and physical environment of recycled fiber systems is strongly influenced by the wide range of additives, fillers, and contaminants accumulated from previous papermaking and recycling cycles. These components, while initially introduced to enhance paper properties or processing performance, undergo complex transformations during pulping, de-inking, and drying, which alter their reactivity, distribution, and interactions with cellulose [107,135]. Their cumulative presence affects fiber surface chemistry, charge balance, bonding potential, and overall paper quality. The principal types of additives, fillers, and contaminants typically present in recycled fiber systems are illustrated in Figure 11.

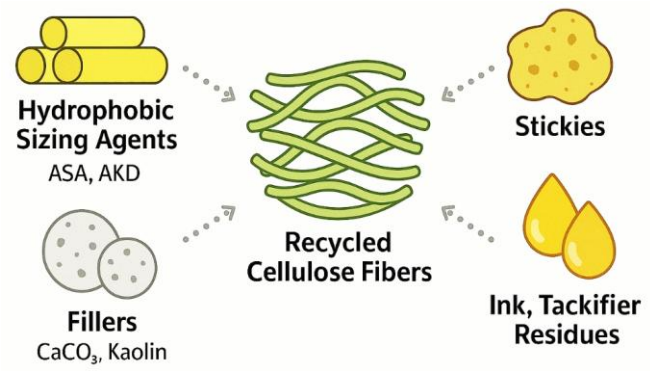


Figure 11. Overview of the main additives, fillers, and contaminants present in recycled fiber systems, showing their typical origins and distribution across papermaking and recycling processes.

A clearer understanding of how additives, fillers, and contaminants influence recycled fiber systems can be achieved by examining their specific chemical roles and interactions. These components not only modify fiber surface charge, bonding, and hydrophilicity but also determine the overall behavior of recycled pulps during papermaking. Depending on their nature and concentration, they may enhance or hinder fiber–fiber and fiber–polymer interactions, affecting strength, drainage, and retention.

A closer inspection of recent experimental studies illustrates how additives and fillers modulate recycled fiber properties via chemical and colloidal interactions. For example, Małachowska (2025) investigated cationic polyelectrolytes (acrylamide-based and cationic acrylic derivatives) in recycled furnishes and found that at a low dosage of 0.2% (*w*/*w*), the breaking length dropped by ~31% relative to the blank (from ~3750 m to ~2600 m), while the tensile index decreased from ~36.2 Nm/g to ~24.9 Nm/g, before partially recovering at higher dosages (up to 1.0%) to ~29.6 Nm/g [51,62]. This non-linear response reflects that the cationic additive, by modifying fiber and fines charge distributions, can improve retention and drainage, but at the cost of weakening fiber–fiber bonds when overdosed. Meanwhile, Filipova et al. (2023) blended recycled waste fibers with small fractions of oxidized nanocellulose and hemp or kraft fibers; they reported that the addition of just 10% mixed fibers (KF + HF), i.e., modifying the chemical and surface environment, improved mechanical strength more than a 50% addition of virgin kraft alone, illustrating the potent effect of surface chemistry and interfiber interactions even at modest additive levels [45,50]. Together, these studies quantitatively confirm that chemical interactions

(charge neutralization, hydrogen bonding, ionic shielding) mediated by additives or filler constituents can strongly influence fiber–fiber and fiber–polymer interactions in recycled systems, thereby affecting strength, drainage, and retention behavior.

Additives used in papermaking, such as sizing agents, retention aids, strength resins, dyes, and wet-end polymers, play dual roles during recycling. On one hand, residual additives can improve processing efficiency by providing surface charge stabilization or hydrophobicity control; on the other, their partial degradation or uncontrolled accumulation generates new challenges. For example, residual alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) sizing agents persist through several recycling loops. These hydrophobes react with hydroxyl groups on cellulose, creating ester linkages that resist hydrolysis and reduce surface wettability [108,136]. Table 4 summarizes the major categories of such materials, highlighting their chemical composition, effects on fiber chemistry and paper properties, and the principal management or mitigation strategies applied in recycling operations [36,41,50–52,54,56,61–63,65,85,105,109–112,115,133,137–140].

Table 4. Chemical influence of major additives, fillers, and contaminants in recycled fiber systems, summarizing their composition, effects on fiber chemistry and paper properties, and typical management or mitigation strategies.

Category	Typical Components	Chemical Effects on Fibers	Management and Control Strategies
Sizing agents	Alkyl ketene dimer (AKD), Alkenyl succinic anhydride (ASA), Rosin size	React with cellulose hydroxyl groups forming hydrophobic ester bonds; uneven distribution causes hydrophobic patches; reduces fiber wettability and bonding potential.	Optimize pH and temperature during recycling; use mild oxidative or enzymatic treatments to remove residual hydrophobes; employ retention aids for uniform dispersion.
Fillers and coating pigments	Calcium carbonate ($CaCO_3$), Kaolin ($Al_2Si_2O_5(OH)_4$), Titanium dioxide (TiO_2)	Block hydrogen-bonding sites, reduce swelling, and increase anionic demand; enhance opacity and brightness but weaken tensile strength if excessive.	Balance filler content by grade; control pH to prevent $CaCO_3$ dissolution; apply optimized retention and drainage aids; partial purge of mineral fines when necessary.
Retention and strength aids	Cationic starch, PAE resin, Polyacrylamides (PAMs), Bentonite, Colloidal silica	Improve flocculation and inter-fiber bonding; adsorption limited by hornification and DCS interference; high charge demand in recycled systems.	Use sequential addition (fixative → strength aid → microparticle); monitor cationic demand; adjust polymer dosage and mixing intensity.
Dissolved and colloidal substances (DCSs)	Degraded hemicelluloses, dispersants, surfactants, extractives, latex residues	Increase anionic charge, compete with cationic polymers, destabilize flocs; adsorb on fines and fibers, leading to stickies and deposit formation.	Employ fixatives (polyamines, PAC, alum); use DAF and washing to reduce DCSs; maintain balanced white-water chemistry.
Inks and pigments	Carbon black, Organic dyes, Metal oxide pigments, Binder polymers	Alter fiber surface energy and zeta potential; create hydrophobic regions that interfere with sizing and bonding; may cause brightness reduction.	Use optimized flotation and surfactant chemistry; peroxide bleaching for optical recovery; minimize ink fragmentation during pulping.
Stickies and adhesives	Latex, Polyvinyl acetate (PVA), Styrene–butadiene rubber (SBR), Hot-melt adhesives	Hydrophobic and pressure-sensitive materials deposit on fibers and equipment; disrupt hydrogen bonding and cause sheet defects.	Apply detackifiers (talc, bentonite, PAC); control temperature and pH to minimize tackiness; install fine screening to remove macro-stickies.
Coating binders and latex residues	SBR, PVA, Acrylic copolymers	Modify zeta potential and drainage; contribute to hydrophobic surface areas and non-uniform sizing response; generate oligomers during degradation.	Use enzymatic pre-treatment to hydrolyze residues; adjust retention programs to manage increased hydrophobicity; enhance washing stages.

Over time, however, oxidative cleavage and migration of these compounds may lead to uneven hydrophobic patches, producing non-uniform water absorption, lower bonding, and difficulties in repulping and re-saturation. The carryover of sizing agents from previously coated or printed papers is a major source of variation in surface energy and inter-fiber adhesion in recycled pulps. The dual influence of papermaking additives

on fiber recycling processes is illustrated in Figure 12a, highlighting how residual agents may either support or hinder fiber reactivity and bonding performance.

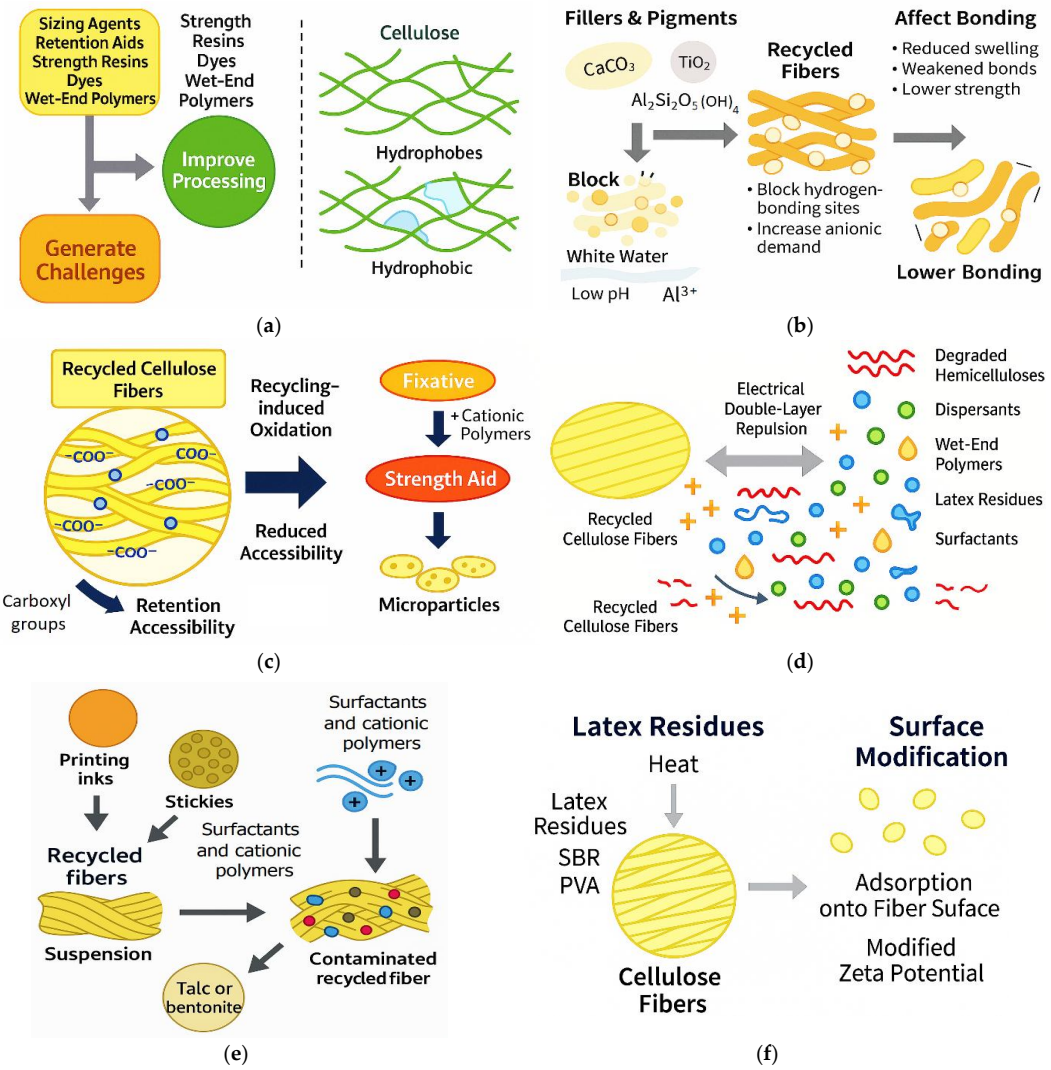


Figure 12. (**a**) The dual role papermaking additives play during recycling, as sizing and retention agents stabilize charge and hydrophobicity while degraded residues (AKD, ASA) create uneven hydrophobic patches that reduce wettability and inter-fiber bonding; (**b**) The detachment and redeposition of fillers and pigments ($CaCO_3$, kaolin, TiO_2) within fibers; (**c**) The interaction of retention and strength aids (cationic starch, PAE, PAM, bentonite, colloidal silica) with anionic fiber surfaces, where oxidation enhances adsorption but hornification limits polymer diffusion and bonding; (**d**) The impact of dissolved and colloidal substances (DCSs) from degraded hemicelluloses, latexes, dispersants, and surfactants, which compete for cationic additives and destabilize wet-end chemistry; controlled through polyamine or alum neutralization, washing, and circuit management; (**e**) The fragmentation of printing inks, adhesives, and stickies into micro-stickies that adsorb surfactants and cationic polymers, lowering efficiency and causing redeposition, mitigated by talc, bentonite, or enzymatic/oxidative treatments; (**f**) The partial degradation of coating binders and latex residues (SBR, PVA) into oligomers that adsorb on fibers, modify zeta potential, increase hydrophobicity, and lead to uneven drainage in recycled papers.

Fillers and coating pigments, primarily calcium carbonate ($CaCO_3$), kaolin ($Al_2Si_2O_5(OH)_4$), and titanium dioxide (TiO_2), constitute another key component influencing recycled fiber chemistry. During repeated cycles, a portion of these inorganic particles becomes detached from the fiber network and re-deposited within pores or lumen cavities. Their fine particulate nature allows them to block hydrogen-bonding sites and hinder

fiber swelling. Excessive filler loading increases the anionic demand of the system, raising the need for cationic polymers to achieve retention and drainage control [52,63,113,141]. Furthermore, the dissolution of calcium carbonate under acidic or CO_2-rich conditions alters the ionic balance of white water, affecting pH buffering and the efficiency of alum or PAC-based fixation systems. The presence of titanium dioxide and kaolin contributes to light scattering and brightness but may weaken inter-fiber bonding, reducing tensile and tear indices if not properly distributed.

The mechanisms through which inorganic fillers and pigments influence recycled fiber chemistry are illustrated in Figure 12b, highlighting their detachment, re-deposition, and impact on surface interactions and papermaking chemistry. Retention and strength aids, including cationic starch, polyamide–amine–epichlorohydrin (PAE), polyacrylamides (PAMs), and microparticle systems (e.g., bentonite, colloidal silica), interact closely with the charged surfaces of recycled fibers.

Their effectiveness depends on surface accessibility, charge density, and the presence of dissolved or colloidal anionics. Recycling-induced oxidation increases surface carboxyl content, which favors adsorption of cationic polymers, but hornification and pore closure restrict polymer diffusion and interpenetration. Consequently, higher dosages or tailored sequences of polymer addition (e.g., fixative → strength aid → microparticle) are often required to maintain optimal retention and drainage performance [72,83].

The mechanisms through which retention and strength aids interact with recycled fibers are illustrated in Figure 12c, emphasizing the role of surface charge, functional groups, and polymer addition sequence in maintaining retention and drainage performance.

A persistent challenge in recycled fiber systems is the accumulation of contaminants and dissolved colloidal substances (DCSs), collectively referred to as "anionic trash." These materials include degraded hemicelluloses, dispersants, wet-end polymers, latex residues, and surfactants derived from coatings, inks, and adhesives. They compete with fibers for cationic additives, forming unstable complexes that reduce polymer efficiency, induce pitch deposition, and destabilize wet-end chemistry [51,56,67,97]. Over time, this accumulation increases the electrical double-layer repulsion between fibers, hindering flocculation and inter-fiber bonding. Control measures include charge-neutralization through polyamine or alum addition, enhanced washing or flotation to remove DCSs, and closed-loop water management systems that prevent excessive build-up of dissolved organics. The accumulation and impact of dissolved and colloidal substances (DCSs) in recycled fiber systems are illustrated in Figure 12d, showing their interactions with fibers, competition for additives, and the main approaches used to mitigate their adverse effects.

Printing inks, adhesives, and stickies represent another category of recalcitrant contaminants with a pronounced chemical impact. During recycling, heat and mechanical shear can fragment these hydrophobic materials into micro-stickies that remain dispersed in the fiber suspension. Their surfaces readily adsorb surfactants and cationic polymers, reducing their effectiveness in wet-end control and potentially redepositing on fibers, wires, and felts. Ink pigments and binders also influence the surface charge of recycled fibers, introducing hydrophobic domains that interfere with sizing uniformity and polymer retention [45,70]. Detackifiers such as talc or bentonite are commonly employed to immobilize stickies, while enzymatic or oxidative pre-treatments can break down residual latex and pressure-sensitive adhesive polymers into more manageable fragments. The generation and behavior of printing inks, adhesives, and stickies during recycling are illustrated in Figure 12e, showing how these hydrophobic contaminants form micro-stickies, interact with additives, and are managed through detackification and enzymatic treatments.

Coating binders and latex residues, such as styrene–butadiene rubber (SBR) and polyvinyl acetate (PVA), further contribute to surface modification during recycling. Their

partial thermal degradation generates oligomers that can adsorb onto fiber surfaces, modifying zeta potential and affecting drainage behavior. The presence of such hydrophobic residues also explains the increased variation in contact angle and sizing response observed in recycled papers with multiple prior coating layers [51,97]. The influence of coating binders and latex residues on fiber surface chemistry is illustrated in Figure 12f, highlighting how partially degraded SBR and PVA compounds modify surface charge, hydrophobicity, and sizing response during recycling.

Consequently, the combined presence of additives, fillers, and contaminants in recycled fiber systems profoundly influences surface charge distribution, fiber wettability, and bonding capacity. The delicate balance between beneficial and detrimental effects depends on process control, water chemistry, and the sequence of treatments applied. Effective management of these chemical interactions, through optimized retention systems, targeted fixation, and enhanced contaminant control is essential to maintain stable paper quality and recycling efficiency in closed-loop operations.

3.9. Relationship Between Chemical and Morphological Degradation of Recycled Fibers

Recycling exposes cellulose fibers to repeated mechanical, thermal, and chemical stresses that act together rather than in isolation. The resulting loss of papermaking performance is therefore a *coupled phenomenon*: chemical changes (oxidation, hemicellulose loss, depolymerization, contaminant carryover) drive and reinforce morphological changes (hornification, pore collapse, loss of fibrillation, fiber cutting and fines formation) and vice versa. Understanding these feedbacks is essential to explain why performance declines non-linearly with successive cycles and why single-measure remedies (e.g., more refining alone) often yield diminishing returns [17,72,83].

3.9.1. Drying-Induced Coupling: From Chemistry to Structure

During drying, removal of bound water promotes additional hydrogen bonding among adjacent microfibrils, increasing apparent crystallinity and causing hornification, as the irreversible reduction in swelling and flexibility (Sections 3.3 and 3.4). Concurrently, prior oxidation of cellulose and hemicelluloses introduces carbonyl and carboxyl groups and lowers the degree of polymerization (DP). These chemical changes stiffen the wall (fewer hydrated amorphous domains) and facilitate closer chain packing, which in turn accelerates hornification. Drying-induced hornification reduces accessible pore volume and bonding sites; Luo and Zhu (2011) quantified these effects across substrates, explaining performance losses over recycling loops [59,70]. The resulting pore shrinkage and lumen collapse reduce rehydration upon recycling and limit the number of accessible hydroxyls available for bonding [69,70,80,81].

The coupling between chemical oxidation and structural hornification during drying is illustrated in Figure 13a, which highlights how hemicellulose loss and increased hydrogen bonding lead to densification and reduced fiber swelling.

3.9.2. Accessibility Feedbacks: From Structure Back to Chemistry

As the wall densifies, diffusion pathways for water, surfactants, and reactive species lengthen and the accessible surface area falls. This has two consequences. First, enzymes and wet-end polymers adsorb more slowly and less uniformly, so higher dosages are needed to achieve equivalent effects. Second, residual chemicals (sizing agents, inks, latex oligomers) are more likely to remain trapped within the wall or in lumen cavities, where they shield hydroxyl groups and create hydrophobic patches that further depress swelling and bonding. In short, morphological densification reduces access, which locks in adverse surface chemistry and magnifies the functional impact of even modest chemical changes [63,73,74,84].

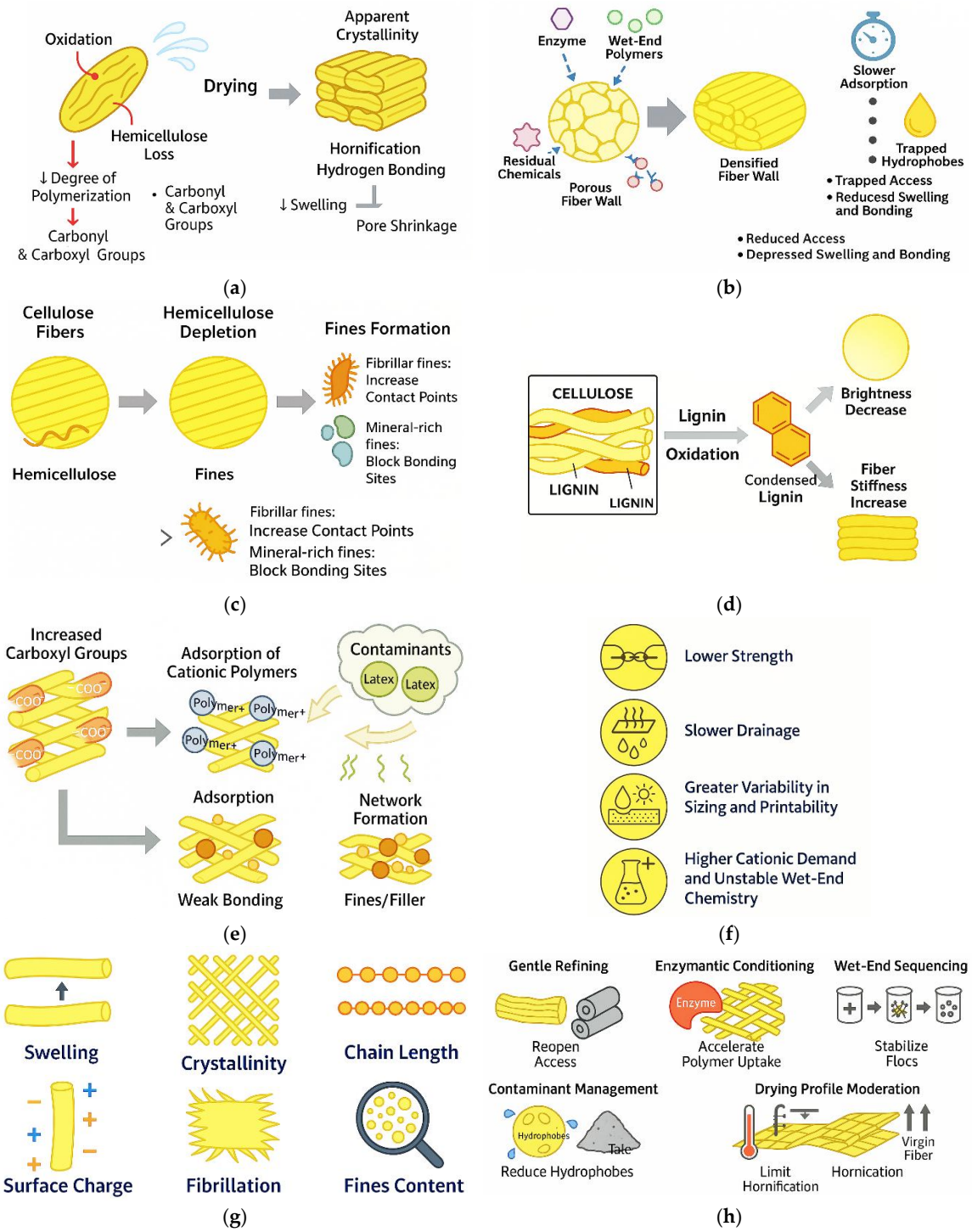


Figure 13. Schematic overview of the coupled mechanisms affecting recycled cellulose fibers: (**a**) Chemical aging and structural densification as oxidation and hemicellulose loss lower DP, increase carbonyl/carboxyl groups, and promote hornification; (**b**) Reduced wall accessibility limiting enzyme and polymer diffusion, trapping hydrophobes, and reducing swelling; (**c**) Hemicellulose depletion and fines generation during alkaline repulping and refining, producing bonding-active and mineral-rich fines that raise cationic demand; (**d**) Lignin oxidation trade-offs, where chromophore formation causes yellowing while peroxide bleaching restores brightness but weakens fibers; (**e**) Surface charge and contaminant effects, as added $–COO^-$ groups enhance polymer affinity while DCSs, surfactants, and stickies hinder adsorption; (**f**) Macroscopic impacts including strength loss, slower drainage, higher steam demand, and surface heterogeneity; (**g**) Integrated diagnostics combining WRV/FSP, XRD/FTIR/NMR, DP, and zeta potential with AFM/SEM and fines/ash analysis; (**h**) Application of these diagnostics to link chemical and structural indicators with furnish performance and guide refining, enzymatic, and wet-end optimization.

The concept of accessibility feedbacks is depicted in Figure 13b, showing how structural densification limits chemical interactions and locks in residual hydrophobic compounds that hinder fiber reactivity and bonding.

3.9.3. Hemicellulose Depletion and Fines Formation: Chemical–Mechanical Interactions Governing Bonding in Recycled Fibers

Loss of hemicelluloses, readily leached or hydrolyzed in alkaline repulping removes the flexible, hydrophilic matrix that spaces microfibrils, thereby promoting hornification and raising crystallinity on re-drying. Meanwhile, mechanical handling and refining generate secondary fines and increase the proportion of ash-bearing fines (fillers, pigments, ink fragments). Fibrillar fines can partially compensate for lost bonding by filling voids and increasing contact points; mineral-rich fines, however, block bonding sites and raise cationic demand, undermining strength and drainage. Thus, the *type* of fines produced by morphological damage determines whether the net effect on bonding is mitigating or aggravating [65,76,114,142]. The mechanisms linking hemicellulose depletion and fines generation are illustrated in Figure 13c, which shows how the chemical loss of hemicelluloses and mechanical fragmentation collectively influence fiber bonding and strength during recycling.

3.9.4. Lignin Oxidation Pathways and the Optical–Mechanical Tradeoffs in Recycled Fiber Systems

In lignin-containing furnishes (mechanical or packaging grades), recycling promotes lignin oxidation and condensation, creating chromophores that drive brightness loss and yellowing. These chemical pathways correlate with increased stiffness and reduced swelling, compounding the structural tendency toward hornification. Attempts to restore brightness (e.g., with peroxide) can, if poorly controlled, increase cellulose oxidation, reduce DP, and weaken fibers, an illustration of how optical recovery can trade off against mechanical integrity [115,116,143,144]. The coupled chemical and structural processes underlying the optical–mechanical tradeoffs in lignin-containing recycled fibers are illustrated in Figure 13d.

3.9.5. Surface Charge Dynamics, Contaminant Interactions, and Their Impact on Fiber Network Mechanics

Rising carboxyl content increases anionic charge and can, in principle, improve adsorption of cationic strength aids. But hornification masks sites and slows adsorption kinetics; simultaneously, anionic trash (DCSs: dispersants, surfactants, latex residues) and stickies compete for cationic polymers, consuming charge and reducing polymer efficiency. The network that forms during sheet consolidation thus has fewer true fiber–fiber hydrogen bonds and more fiber–fines/filler contacts, lowering tensile and burst indices even when basis weight and apparent formation look acceptable [117,118,145,146]. The interplay between surface charge modification, contaminant competition, and their combined impact on fiber network mechanics is depicted in Figure 13e.

3.9.6. Macroscopic Manifestations of Coupled Chemical and Morphological Degradation in Recycled Cellulose Fibers

The intertwined chemical–morphological degradation manifests as [51,62,73,84,87,105,109,137]:

— Lower tensile, burst, and often tear strength, attributable to shorter, stiffer fibers with reduced bonding area and to chemically weakened chains (lower DP).
— Slower drainage and higher steam demand, caused by fines build-up and altered surface charge; densified walls also release water less readily in pressing.

— Greater variability in sizing and printability, due to mosaic hydrophilicity/hydrophobicity from residual sizes and latexes on less-wettable surfaces.
— Higher cationic demand and unstable wet-end chemistry, reflecting the combined effects of increased carboxyls, DCSs, and mineral fines.

The macroscopic consequences of the intertwined chemical and structural degradation processes are summarized in Figure 13f, which illustrates the main physical, hydraulic, and chemical manifestations observed in recycled fiber systems.

3.9.7. Integrated Diagnostics for Correlating Chemical, Structural, and Performance Metrics Across Scales

Because no single test captures the coupled degradation, a multi-metric panel is advisable [70,81,90,117,119,145].

- WRV/FSP (swelling) and XRD/FTIR/NMR (apparent crystallinity and hydrogen-bonding environment) to track hornification.
- DP (viscometry or SEC) for cellulose chain length; zeta potential and cationic demand for surface charge state.
- AFM/SEM for fibrillation and surface topography; fines/ash fractionation to characterize the fines spectrum.

Correlating these with tensile/burst indices, drainage curves, and energy use reveals the degree to which chemical vs. morphological pathways dominate in a given furnish [69]. To capture the interdependence between chemical and morphological degradation processes, Figure 13g presents an integrated diagnostic framework linking fiber-scale properties with macroscopic performance indicators.

3.9.8. Coupled Mitigation Strategies Integrating Chemical, Morphological, and Process Controls in Recycled Fiber Systems

Mitigation is most effective when it targets the coupling [51,62,63,74,112,119,140,147]:

- Gentle, targeted refining to restore external fibrillation and reopen access without excessive cutting (controls morphology, improves chemistry access).
- Selective enzymatic conditioning (low-dose endoglucanase/xylanase) or mild surface carboxymethylation to expose/reactivate sites and accelerate polymer uptake, while avoiding deep chain scission (improves chemistry, aided by morphological reopening).
- Wet-end sequencing (fixative → strength aid → microparticle) with ionic-strength/pH control to out-compete DCSs and stabilize floc architecture (chemistry control supporting structure).
- Contaminant management (detackifiers, talc, enhanced screening/DAF) to reduce hydrophobe carryover that would otherwise lock in poor wettability on densified walls.
- Drying profile moderation (temperature and residence time) and periodic virgin fiber supplementation to limit step-changes in hornification and restore long-fiber bonding scaffolds.

To illustrate the holistic approach needed to counteract recycling-induced degradation, Figure 13h presents the main coupled mitigation strategies that simultaneously target chemical reactivity, surface structure, and process stability.

So, chemical degradation (oxidation, hemicellulose loss, contaminant accumulation) and morphological degradation (hornification, pore closure, fibril loss, fines generation) are mutually reinforcing. Accessibility is the nexus: chemical changes reduce hydration and reactivity; structural changes reduce access and lock in chemistry. Effective recycling strategies therefore treat both simultaneously, using gentle mechanical activation to reopen

structure while tuning surface chemistry and wet-end conditions to re-establish strong, numerous fiber–fiber bonds across cycles.

3.10. Mitigation Strategies and Chemical Approaches to Preserve Fiber Integrity

Preserving the integrity of cellulose fibers through multiple recycling loops requires an integrated approach that addresses both chemical degradation and morphological deterioration. Each recycling cycle introduces cumulative changes: hornification, oxidation, fiber cutting, fines generation, and additive accumulation that progressively compromise fiber bonding potential, strength, and reactivity [63,65,74,76]. Therefore, mitigation strategies must act on several fronts simultaneously: (i) limiting structural collapse and hornification; (ii) restoring surface chemistry and accessibility; (iii) maintaining process balance and contaminant control; and (iv) optimizing chemical treatments and fiber reconditioning.

3.10.1. Physical and Process-Based Mitigation

At the mechanical level, refining is a key tool for restoring fibrillation and surface area in recycled fibers. However, excessive refining accelerates fiber shortening and internal fibrillation loss, leading to reduced bonding potential. Gentle, targeted refining, especially with conical or double-disk refiners at low energy input can reopen collapsed pores, increase external fibrillation, and improve flexibility without excessive damage. Combining refining with careful drying profile control is equally essential: slow or moderate drying rates and lower peak temperatures (below 120 °C) reduce irreversible hornification and maintain fiber swelling capacity. In paper machines, adjusting pressing pressure and dwell time can further moderate the extent of wall densification during consolidation. Reported outcomes in the literature differ significantly because refining trials vary widely in plate pattern, specific edge load, fiber origin, and energy input, which explains the inconsistent results found across studies [63,74,103,120,131,148]. The key physical and operational strategies employed to limit structural deterioration and restore fiber functionality during recycling are summarized in Figure 14a.

On the process side, periodic supplementation with virgin fibers introduces longer, more flexible fibers that help reestablish the mechanical network lost through repeated recycling. The addition of high-yield pulps (e.g., CTMP or BCTMP) in limited proportions can improve sheet bulk and porosity while maintaining acceptable bonding strength. Similarly, optimized wet-end operation, including the sequence of polymer and filler addition, is essential to preserve retention and drainage behavior while minimizing chemical overuse.

3.10.2. Enzymatic and Biochemical Treatments

Enzymatic treatments represent one of the most effective and sustainable strategies for mitigating recycling-induced degradation. Low-dose endoglucanase or xylanase treatments selectively cleave disordered or hemicellulosic regions of cellulose fibers, reopening microvoids and enhancing water retention without significant chain scission. These treatments increase fiber flexibility, surface hydroxyl accessibility, and bonding strength. Enzyme-assisted deinking and decontamination also improve surface cleanliness, reduce hydrophobe accumulation, and lower the demand for harsh chemical treatments such as hydrogen peroxide or sodium hydroxide [119,120,147,148]. Figure 14b summarizes key enzymatic and biochemical strategies that restore cellulose fiber reactivity and bonding capacity by selectively modifying surface chemistry and internal structure. Combined mechanical–enzymatic fibrillation strategies frequently show synergistic effects, where partial enzymatic loosening of the fiber wall improves fibrillation efficiency and reduces refining energy demand in recycled pulps.

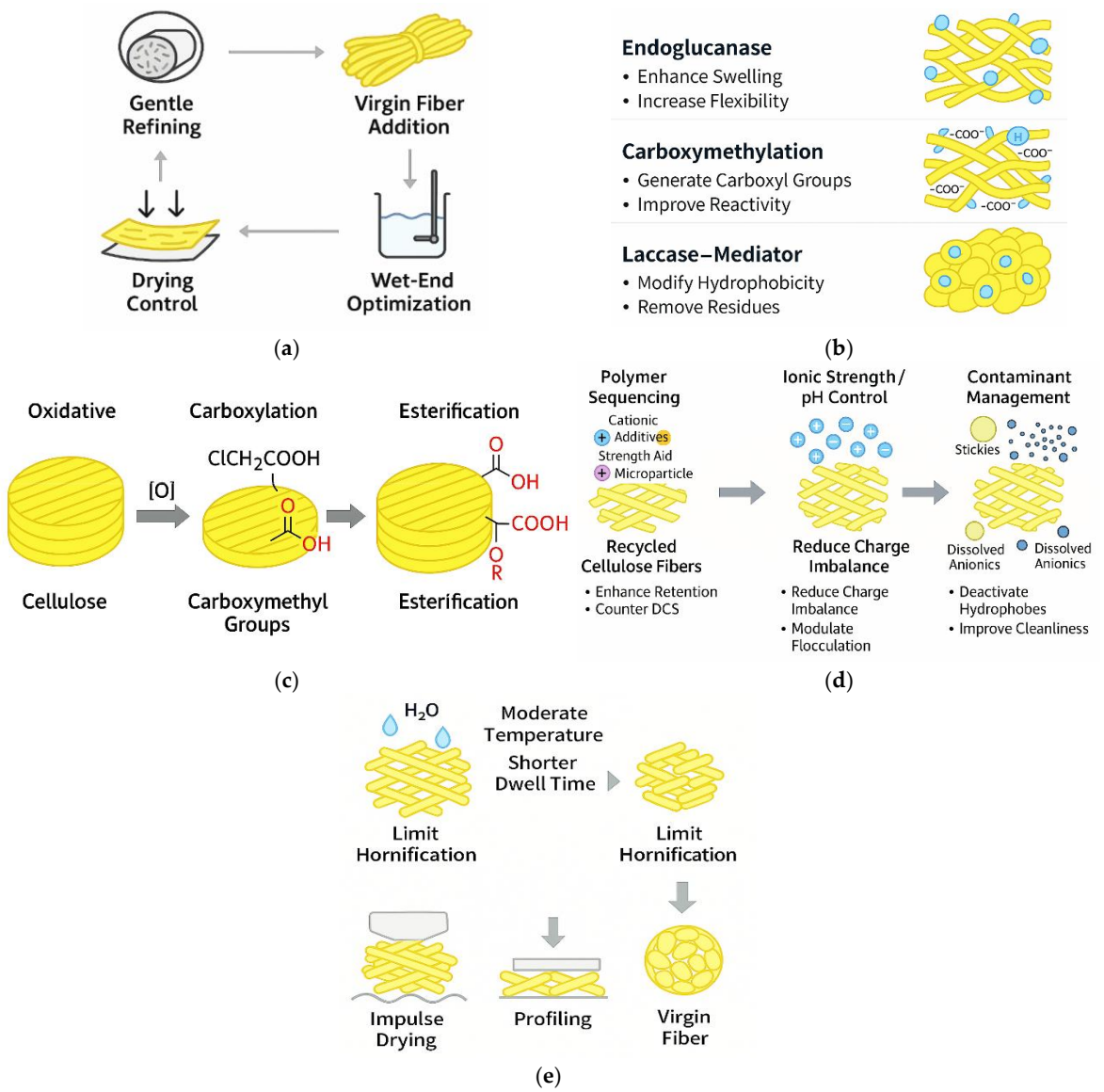


Figure 14. (**a**) Physical and process-based strategies for preserving fiber integrity, including gentle refining to reopen collapsed walls, controlled drying to limit hornification, optimized pressing for flexibility, and selective virgin fiber addition to strengthen bonding; (**b**) Enzymatic and biochemical treatments such as endoglucanase for swelling, carboxymethylation for restoring carboxyl sites, and laccase–mediator systems for residue removal and hydrophobicity control; (**c**) Chemical surface modification of recycled cellulose via carboxymethylation, TEMPO oxidation, and cationization, introducing –COOH, –CHO, and quaternary ammonium groups that enhance charge, hydrophilicity, and polymer adhesion; (**d**) Wet-end optimization through additive sequencing, ionic balance control, and removal of stickies and dissolved anionics to improve retention, drainage, and bonding; (**e**) Thermal and drying control using moderate temperatures, short dwell times, and impulse drying, with moisture profiling and limited virgin fiber addition to reduce hornification and maintain bonding.

In recent developments, laccase–mediator systems and oxidoreductase enzymes have been explored to selectively modify lignin-containing recycled fibers. These systems remove chromophoric groups while maintaining cellulose integrity, providing both brightness improvement and strength retention. Variability in results among enzymatic studies is largely due to differences in enzyme specificity, dosage optimization, substrate accessibility, and interactions with fines, which makes cross-study comparison difficult [49,60,75,86]. When combined with mild refining, enzymatic activation can restore surface charge balance and reduce anionic trash interference. Laccase-mediated systems, particularly when com-

bined with phenolic mediators, enable selective surface functionalization and can enhance fiber–fiber adhesion without significantly degrading pulp viscosity.

3.10.3. Chemical Surface Modification

Chemical treatments can compensate for lost functionality by introducing reactive or hydrophilic groups on fiber surfaces. Carboxymethylation and TEMPO-mediated oxidation, when applied at controlled severity, enhance anionic charge density and reintroduce carboxyl sites that facilitate polymer adsorption and hydrogen bonding. These reactions increase swelling and improve fiber–fiber adhesion while minimizing oxidative degradation of the cellulose backbone. However, TEMPO-mediated oxidation has been shown to reduce the degree of polymerization while increasing surface carboxyl content, thereby enhancing fiber swelling and fines–fiber interactions in recycled pulp system [31,36,121,149–151]. Periodate–chlorite oxidation and dialdehyde cellulose pathways typically decrease crystallinity and facilitate fibrillation, leading to improvements in nanofibril yield and inter-fiber bonding potential [152].

Cationization (using quaternary ammonium reagents) offers an alternative pathway for improving compatibility with anionic additives, increasing floc strength, and enhancing fines retention. The main chemical modification routes applied to refunctionalize recycled fibers and improve their bonding capacity are illustrated in Figure 14c.

Antioxidants and stabilizing agents, such as magnesium salts, ethanolamines, or radical scavengers, can suppress cellulose oxidation during alkaline recycling and bleaching. Similarly, the inclusion of crosslinking inhibitors prevents uncontrolled hornification by blocking the formation of irreversible hydrogen bond networks between cellulose chains. Carboxymethyl cellulose and cationic starch grafting techniques improve fiber surface reactivity by altering charge density and zeta potential, which promotes better retention and bonding in closed water-loop conditions. These measures collectively help sustain fiber plasticity and bonding activity through multiple recycling loops. Across these modification techniques, the functional outcomes for recycled fibers are primarily reflected in changes in DP, crystallinity index, nanofibril release, surface charge evolution, and wet-end chemistry—parameters that directly shape strength development and processability in circular papermaking systems.

3.10.4. Wet-End Chemistry Optimization

Because surface chemistry changes markedly during recycling, controlling wet-end chemistry becomes a key mitigation strategy. Recycled furnishes generally exhibit increased anionic demand and contain dissolved and colloidal substances (DCSs), fillers, and stickies that hinder polymer efficiency. Sequential chemical addition, starting with fixatives (e.g., polyamines, alum, or polyDADMAC), followed by strength aids (e.g., cationic starch or PAE resin), and concluding with microparticles (e.g., bentonite or colloidal silica) can stabilize charge balance and enhance retention [51,97,119,147]. This ordered approach minimizes competitive adsorption and optimizes floc structure formation. Figure 14d illustrates the key components and sequential interactions involved in optimizing wet-end chemistry for recycled fiber systems, highlighting the balance between additive sequencing, ionic control, and contaminant management.

The ionic strength and pH of white water must also be regulated, as fluctuations can destabilize polymer interactions and promote deposition. Closed water systems, though environmentally advantageous, exacerbate DCS accumulation; hence, partial water replacement or dissolved air flotation (DAF) systems are often integrated to control contaminant buildup. Incorporating talc or precipitated calcium carbonate (PCC) as detackifiers further mitigates stickies and latex aggregation [90,119,122,123,153,154].

3.10.5. Thermal and Drying Control

Thermal management plays a critical role in preventing chemical–mechanical coupling during recycling. Excessive drying temperatures accelerate hornification and cellulose oxidation, while uneven moisture distribution induces stress localization and microcracking in fiber walls. Figure 14e illustrates the main process-based strategies applied in thermal and drying control to reduce hornification, preserve flexibility, and maintain the mechanical integrity of recycled fibers during repeated cycles.

Optimized drying curves with stepwise temperature increases and controlled humidity, help preserve water-accessible amorphous regions and prevent excessive crystallization. The use of infrared moisture profiling and online dryer control systems enables mills to minimize thermal damage and ensure consistent sheet formation [46,58,64,75].

3.10.6. Integrated Approach and Future Outlook

A holistic mitigation strategy requires coupling mechanical, chemical, and enzymatic interventions within a feedback-controlled process. Physical reopening of fiber structures facilitates chemical and enzymatic reactivity, while optimized chemistry stabilizes those morphological gains. Integrated recycling lines equipped with real-time monitoring (for charge demand, WRV, and fines content) allow dynamic adjustment of refining intensity and chemical dosing to maintain optimal performance.

To provide a consolidated overview of the performance differences among major fiber-refunctionalization strategies, Table 5 summarizes representative strength-improvement trends reported in the literature for chemical oxidation treatments, enzymatic activation, laccase-mediated systems, nanocellulose reinforcement, and combined enzymatic–mechanical fibrillation. Because quantitative results vary significantly between studies due to differences in pulp origin, recycling history, treatment severity, and testing protocols, the table presents qualitative trends together with key mechanistic notes and representative references. This comparative synthesis complements the more detailed mechanistic discussions that follow in Section 4.3.

Table 5. Representative strength-improvement trends reported for chemical, enzymatic, laccase-based, nanocellulose, and combined enzymatic–mechanical treatments applied to recycled fibers (typical mechanisms, qualitative strength effects, and key operational conditions, together with representative literature references).

Treatment Type	Representative Mechanism	Typical Strength Improvement Trend	Key Notes/ Conditions	Representative References
Chemical modification (e.g., TEMPO, CMC grafting)	Increased surface carboxylation, enhanced swelling and charge balance, improved polymer adsorption	Moderate–high tensile and bonding gains when oxidation is controlled; improved internal bonding and sometimes tear strength	Performance depends on pulp type, oxidation severity, and degree of polymerization (DP) loss; over-oxidation can reduce strength or increase brittleness	[151,155–157]
Enzymatic treatment (e.g., cellulases, xylanases)	Selective hydrolysis of amorphous/hemicellulosic regions; fiber-wall loosening and external fibrillation	Low–moderate tensile gains; improved bonding, sometimes at reduced refining energy	Dosage-sensitive; best results when mild treatment is integrated with refining strategy; excessive hydrolysis may shorten fibers or weaken the sheet	[105,106,108]
Laccase-mediator or laccase-only systems	Selective lignin activation and phenolic crosslinking; increased surface charge and functional groups	Moderate strength improvements (tensile, burst, sometimes wet strength), particularly in lignin-containing or OCC furnishes	Effect strongly influenced by mediator type and pulp lignin content; brightness and kappa number may also change	[93,136,156]

Table 5. *Cont.*

Treatment Type	Representative Mechanism	Typical Strength Improvement Trend	Key Notes/ Conditions	Representative References
Nanocellulose reinforcement (CNF/CNF from virgin or recycled pulp)	High-surface-area fibrils fill interfiber voids and create a nanoscale bonding network	High tensile-strength gains and improved stiffness at relatively low addition levels; often strongest reinforcement among the listed strategies	Drainage and dewatering become limiting at higher dosages; effect depends on nanocellulose type (CNF vs. CNC), fibril morphology and dispersion quality	[158–161]
Combined enzymatic–mechanical fibrillation	Enzyme-assisted loosening of the fiber wall that facilitates subsequent mechanical fibrillation	Moderate–high strength gains with reduced specific refining energy compared with purely mechanical routes	Synergistic effects when mild enzymatic pretreatment is followed by optimized mechanical refining; effectiveness depends on enzyme type and treatment time	[105,108,162]

Looking forward, green chemistry approaches, such as bio-based sizing agents, biodegradable polymers, and enzymatically generated carboxylation, promise to extend recyclability while reducing environmental burdens. Combined with AI-driven process optimization and machine learning-based prediction of fiber degradation, these innovations will enable circular, resource-efficient recycling systems capable of sustaining both paper quality and environmental performance across multiple reuse cycles.

4. Influence of Recycled and Reused Fibers on Papermaking Performance

4.1. Impact of Recycled and Reused Secondary Cellulose Fibers on Paper Strength and Quality

The macroscopic performance of papers containing recycled and reused secondary cellulose fibers emerges from coupled chemical and morphological changes that occur with each loop of use–repulping–dewatering–drying [36,43]. Oxidation, hemicellulose loss and degree-of-polymerization (DP) decline reduce the intrinsic strength and bonding functionality of the fibers, while hornification, pore closure, external fibril loss and fiber shortening restrict inter-fiber contact and load sharing in the sheet. In parallel, fines and ash fractions rise, surface energy becomes heterogeneous because of hydrophobe carryover (AKD/ASA, latex, printing oils), and wet-end chemistry grows more anionically demanding [63,74,121,149]. Chen et al. (2016) reported that repeated recycling of wheat-straw and hardwood pulps caused a drop in the degree of polymerization of cellulose chains and a loss of hemicelluloses, accompanied by lower WRV and increased brittleness of fibers [47,58]. These chemical degradations directly led to morphological stiffening and poor interfiber bonding.

Together, these shifts lower tensile, burst and tear indices, alter compression performance, slow drainage and increase property variability unless counterbalanced by targeted fiber reconditioning and wet-end control [17,70,72,81,83]. To visualize how successive recycling cycles influence fiber structure, chemistry, and macroscopic performance, Figure 15 integrates the main mechanisms that govern the deterioration and partial recovery of paper strength and quality.

4.2. Mechanical, Structural, and Surface Property Evolution in High-Recycled-Content Papers

Tensile and burst strength decline primarily because the bonded area per unit mass shrinks and the quality of each bond deteriorates. Hornified walls re-swell less, accessible –OH sites are fewer, and fibril interdiffusion across fiber–fiber contacts is limited. Oxidative chain scission reduces DP and intrinsic fiber strength, so even when refining restores some surface area, the network cannot transfer stresses as efficiently. When fines and mineral pigments accumulate at fiber interfaces, they reduce cellulose–cellulose contact and weaken z-direction bond integrity (Scott bond), increasing the likelihood of surface picking under high-tack inks. Strength aids (e.g., cationic starch, PAE) and mild enzymatic activation

can recover part of the loss, but their efficiency depends on charge balance and access into partially closed wall structures [70,81,124,163].

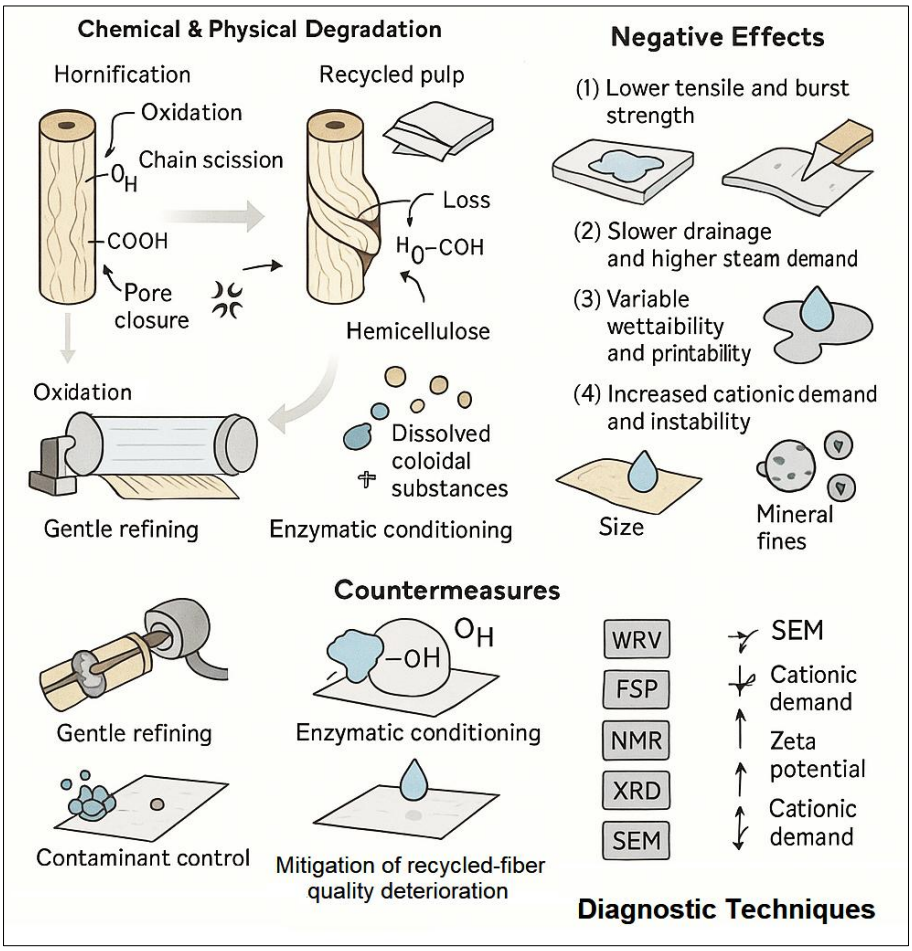


Figure 15. Schematic overview of the effects of recycling and reuse on cellulose fiber structure, surface chemistry, and paper properties. The illustration links microscopic changes, such as hornification, oxidation, fiber shortening, and hemicellulose loss, to macroscopic outcomes including decreased tensile, burst, tear, and compression strength, altered wettability, and increased fines accumulation. It also highlights mitigation strategies such as gentle refining, enzymatic activation, and optimized wet-end chemistry that restore bonding capacity and improve recycled paper quality.

Tear resistance and fracture toughness are particularly sensitive to fiber length distribution and flexibility. Reuse cycles shorten fibers and increase stiffness; the reduced pull-out work at crack tips leads to earlier tear initiation and faster propagation. Packaging grades that rely on long-fiber bridging across spans show this penalty sooner than fine-paper grades in which bond strength dominates. Carefully limited, low-intensity refining can improve bonding without excessive cutting, but over-refining accelerates length loss and compromises tear [52,63,125,164].

Compression metrics in containerboard, such as short-span compression (SCT), ring crush (RCT) and edge crush (ECT), depend on junction quality and network rigidity. Recycling often increases sheet density but shifts contact points from fiber–fiber to fiber–filler/fines, so junctions carry less effective load. Moisture sensitivity rises as walls re-swell less and drying profiles become more critical to final corrugated performance. As a result, compression can plateau or decline at constant basis weight unless junction quality is rebuilt by selective refining, charge control and, where needed, virgin reinforcement [72,83,126,165].

Formation, bulk and porosity evolve with fines content. Cellulosic fines improve formation and surface smoothness, yet excessive fines and ash reduce bulk and air permeability, increase steam demand, and complicate moisture profiles, which feed back into strength scatter. In tissue and towel, hornification and fines accumulation are doubly detrimental: pores collapse, capillary uptake drops, and softness (handfeel) declines. Gentle external fibrillation, enzymatic flexibility enhancement and through-air or moderated drying profiles can partly restore absorbency and bulk in these grades [51,62,127,166].

Surface energy, sizing agents and barrier behavior become heterogeneous in recycled systems. Oxidation and extractives loss raise anionic charge and hydrophilicity, favoring cationic polymer adsorption, but residual AKD/ASA and latex create hydrophobic patches that resist wetting, reduce swelling and cause uneven size response. The result is variable Cobb and dynamic contact angle, nonuniform ink hold-out, and localized picking in printing and writing grades. Reconditioning surfaces by light refining or low-severity enzymatic/chemical activation and sequencing fixative → strength aid → microparticle before size addition improves uniformity [121,128,149,167].

Optics and cleanliness also shift. In lignin-containing furnishes (mechanical pulps, recycled packaging), oxidation and condensation generate chromophores that lower brightness and induce yellowing; peroxide brightening can recover optics but risks added cellulose oxidation and DP loss if severity is unchecked. Incomplete de-inking leaves hydrophobe-coated ink particles that alter surface chemistry and interfere with bonding; pigments such as TiO_2 and kaolin enhance opacity but, when concentrated at interfaces, weaken junctions [21,26,129,168].

Drainage and runnability degrade as fines and dissolved/colloidal substances (DCSs) accumulate and zeta potential drifts. Higher cationic demand and unstable charge balance slow water release, raise vacuum and press loads, and increase steam consumption. Microparticle programs (cationic polymer + bentonite/colloidal silica) remain effective, but dosages typically rise in recycled furnishes and must be paired with DCS control (DAF, selective purges) to stabilize retention and formation [51,97,104,132].

Grade-specific implications help frame realistic performance targets at increased recycled content. Printing/writing papers can regain smoothness and acceptable tensile with careful fines management and uniform sizing, but high brightness and pick resistance require efficient de-inking and charge control. Containerboard benefits from low-severity refining to enhance junction quality while preserving length, plus moisture-profile discipline for compression. Tissue demands strategies that protect bulk and absorbency (gentle fibrillation, enzymatic conditioning, moderated drying) and minimize hydrophobe carryover. Across grades, strategic blends with virgin long fibers provide scaffolding that recycled fibers alone cannot fully supply after multiple cycles [130,131,169,170].

Diagnostic links to properties are essential for targeted improvement. Water retention value (WRV) or fiber saturation point (FSP) track swelling loss; XRD/FTIR/NMR indicate crystallinity and hydrogen-bonding environments; DP reflects chain scission; zeta potential and cationic demand quantify wet-end charge state; AFM/SEM visualize fibrillation; and fines/ash fractionation clarifies particle spectra. Correlating these with tensile/burst/SCT, drainage curves and energy use distinguishes chemistry-limited from morphology-limited regimes and guides the most efficient intervention [69,70,80,81,131,170].

Practical levers to protect strength and quality in high-recycled-content papers therefore combine: gentle, targeted refining to renew external fibrillation without shortening; selective enzymatic conditioning (endoglucanase/xylanase) to reopen access and accelerate polymer uptake; wet-end sequencing under controlled pH/ionic strength to out-compete DCSs; vigilant contaminant control (detackifiers, improved screening/DAF) to limit hydrophobe carryover; moderated drying profiles to limit step-changes in hornification; and

grade-specific virgin reinforcement where network scaffolding is otherwise insufficient. In this integrated approach, physical reopening of structure and chemical refunctionalization act synergistically to recover bonded area and junction quality, stabilizing paper strength and end-use performance as recycled content rises [87,105].

4.3. Effect of Recycled and Reused Fibers on Dewatering and Drying Behavior

The dewatering and drying performance of recycled and reused fibers is governed by their evolving morphology and surface chemistry during repeated processing cycles. As these fibers are subjected to successive wetting, drying, and mechanical treatment, their capacity to interact with water, both within the fiber wall and across the sheet changes markedly. The efficiency of water removal through pressing or drying becomes increasingly dependent on the extent of structural densification, surface charge alterations, and accumulation of fines and dissolved or colloidal substances (DCSs).

With continued recycling, secondary cellulose fibers experience progressive hornification, marked by the closure of internal pores and the formation of additional hydrogen bonds within the cell wall. This reduces their swelling potential and water retention value (WRV), leading to slower drainage and higher residual moisture compared with virgin fibers. The reduced porosity of the fiber network lowers permeability and contributes to uneven dewatering behavior across the web [46,57,73,84].

Mechanical treatment of secondary fibers generates increasing amounts of fines as small fiber fragments and colloidal particles that accumulate between fibers and obstruct water pathways. These fines raise the anionic charge of the suspension, increase cationic demand, and interfere with polymer adsorption and flocculation, thereby diminishing retention and drainage uniformity. The dense, fine-rich mat that forms during sheet consolidation further slows water release and promotes moisture variability [85,115].

Chemically, the recycled fibers develop a more anionic and heterogeneous surface due to oxidation, extractive loss, and deposition of hydrophobic contaminants such as AKD, ASA, latex, and stickies. This heterogeneous surface energy results in localized wetting differences, creating areas of reduced moisture removal and inconsistent drying [128,167].

During the drying stage, the recycled fibers with compacted walls and accumulated fines retain water more tightly, increasing steam consumption and extending drying times. Their limited reswelling capacity makes moisture control more difficult and contributes to greater energy demand during sheet consolidation [43,48].

To mitigate these limitations, secondary fibers benefit from moderate pressing, temperature-controlled drying, and selective refining or enzymatic conditioning, which can reopen partially collapsed pores and enhance water release. The use of optimized retention aids and microparticle systems stabilizes drainage by regulating fines distribution and floc structure, while efficient contaminant control minimizes the negative influence of hydrophobic residues [10].

Consequently, the dewatering and drying behavior of secondary fibers reflects the combined influence of hornification, charge imbalance, fines accumulation, and contaminant interference. Managing these interrelated factors through targeted physical and chemical strategies is essential for maintaining efficient water removal, energy savings, and consistent paper quality in recycling-based papermaking systems. The combined influence of hornification, fines accumulation, and altered surface chemistry on the dewatering and drying performance of recycled fibers is summarized in Figure 16. This schematic highlights how structural densification, increased anionic charge, and hydrophobic contaminants collectively hinder water removal during pressing and drying, leading to slower drainage, higher residual moisture, and greater energy consumption compared with virgin fibers.

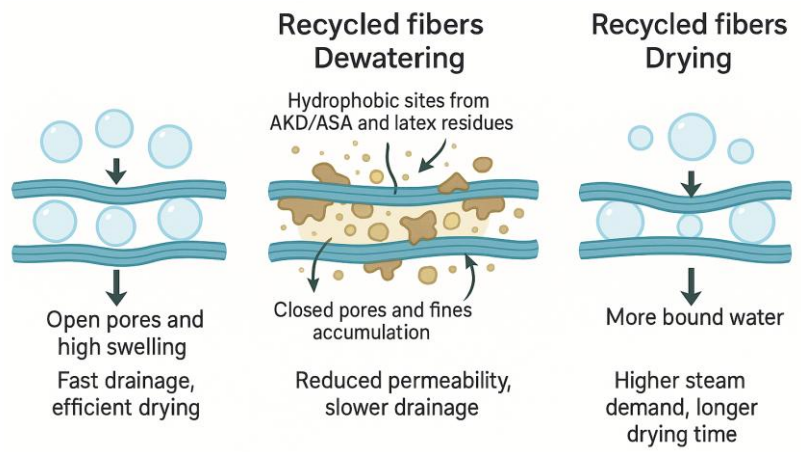


Figure 16. Schematic representation of the effects of recycling on dewatering and drying behavior of cellulose fibers. Compared with virgin fibers, recycled fibers exhibit hornification and pore closure, fines accumulation, and increased anionic charge, which together slow drainage and reduce permeability. During drying, bound water retention and hydrophobic surface patches (AKD, ASA, latex residues) cause uneven wetting, higher steam demand, and longer drying times.

4.4. Influence of Recycling Cycles of Fibers on Paper Quality: Evolution of Mechanical and Optical Parameters with Successive Reuse

Successive reuse of secondary cellulose fibers produces a characteristic trajectory in paper properties because the fiber wall, surface chemistry, and network topology evolve together with each cycle of repulping–sheeting–drying. Chemically, oxidation and hemicellulose loss reduce the degree of polymerization (DP) and alter functional groups; structurally, hornification closes micropores, increases apparent crystallinity, and stiffens the wall; mechanically, refining and handling shorten fibers and generate fines and ash-rich particulates that migrate to interfaces. These coupled mechanisms explain the non-linear decline in strength indices and the gradual drift of optical attributes that mills observe as recycled content increases or as the same fiber cohort is reused multiple times.

4.4.1. Mechanical Properties: Typical Trajectories Across Cycles

The mechanical integrity of paper composed of secondary cellulose recycled and reused fibers evolves predictably with each reuse cycle, reflecting the cumulative impact of structural densification, chemical modification, and fiber shortening. As recycling progresses, both intra- and inter-fiber bonding capacities deteriorate, leading to measurable declines in key strength parameters such as tensile, tear, compression, and z-direction bonding. The following subsections describe the typical trajectories of these mechanical properties across recycling cycles, emphasizing how physical degradation and surface heterogeneity collectively shape the strength performance of recycled fiber-based papers.

Tensile strength and burst strength exhibit a consistent monotonic decline with increasing recycling cycles (Figure 17). Reduced swelling and fewer accessible –OH sites shrink the true bonded area; higher crystallinity and wall densification limit fibril interdiffusion; and oxidative chain scission lowers intrinsic fiber strength. Even when light refining restores external fibrillation, the chemical accessibility deficit prevents full recovery, so tensile and burst often show a "step-down then plateau" pattern after the first few cycles. Where fillers and pigment fines concentrate at interfaces, z-bond quality (Scott bond) declines faster than in filler-lean webs [132,171,172].

Tear and fracture toughness are highly dependent on fiber length and flexibility, both of which degrade progressively with repeated recycling (Figure 17). Progressive shortening and stiffening reduce pull-out work at crack tips, so tear commonly drops more steeply than tensile after several cycles. Grades that rely on long-fiber bridging (e.g., containerboard

liners) are most sensitive; fine papers, in which bond-controlled strength dominates, exhibit a slower tear decline provided refining is restrained [133].

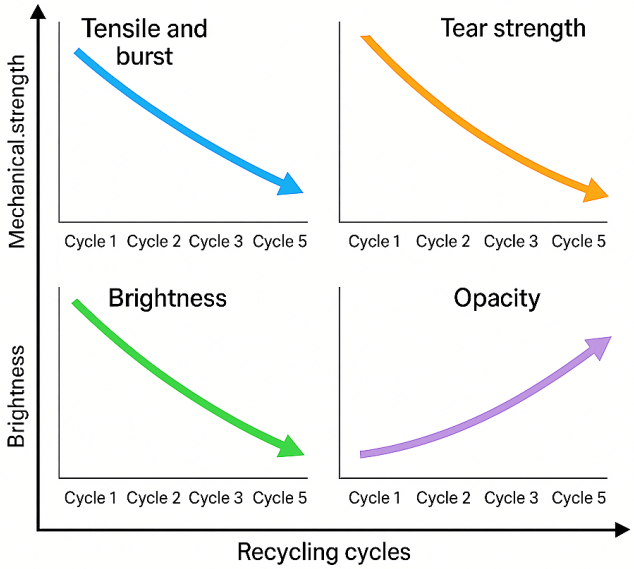


Figure 17. Schematic representation of the evolution of mechanical and optical properties of cellulose fibers with successive recycling cycles. The figure illustrates the progressive decline in tensile, tear, and compression strength due to hornification, oxidation, and fiber shortening, accompanied by brightness loss and moderate opacity increase. Structural changes such as pore closure, fines accumulation, and surface contamination collectively shape the non-linear property trajectories observed in recycled fiber systems.

Compression strength evaluated through short-span compression (SCT), ring crush (RCT), and edge crush (ECT) tests depends on the combined effects of network rigidity and junction integrity within the paper structure. Recycling can increase apparent sheet density yet lower the effective load-bearing junctions as contact shifts from fiber–fiber to fiber–fines/filler. Moisture sensitivity increases as hornified fiber walls exhibit reduced re-swelling, causing compression indices to plateau or decline at constant basis weight unless connection quality is restored through targeted refining and wet-end control [73,134].

Z-direction bond and surface strength deteriorate progressively as recycling alters both the physical connectivity and chemical uniformity of secondary cellulose fiber networks. Internal bond declines as fibril interdiffusion across interfaces wanes and as hydrophobe carryover (AKD/ASA, latex oligomers) creates mosaic wetting that interrupts stress transfer. Surface picking becomes more likely under high-tack inks unless charge balance and polymer adsorption kinetics are restored via mild refining/enzymatic conditioning and appropriate sequencing of fixative → strength aid → microparticle [17,173].

4.4.2. Optical Properties: Brightness, Shade, Opacity, and Print Uniformity

The optical behavior of secondary cellulose fibers changes markedly with repeated processing. Chemical oxidation, fines buildup, and residual hydrophobes alter light reflection and absorption, affecting brightness, opacity, and print uniformity. The following section outlines how these transformations develop across recycling cycles, linking chemical and structural changes to the visual quality of recycled-containing papers.

Brightness lowering and yellowing are major optical changes during the recycling of lignin-containing furnishes such as mechanical pulps and recycled packaging grades (Figure 17). With each cycle, lignin and carbohydrates undergo oxidation and condensation, forming chromophores that lower brightness and shift the color parameter (b*) toward yellow. Peroxide bleaching can partially restore optics, but excessive severity accelerates

cellulose oxidation and reduces the degree of polymerization (DP), compromising fiber integrity and offsetting the optical gains [44,49].

Rising fines and ash often increase *opacity and scattering*, which can be desirable in printing grades (Figure 17). However, the same particulates tend to weaken bonding if concentrated at interfaces. Thus, opacity gains may coincide with tensile/burst losses, especially beyond the second–third reuse [70,72,81,83].

Cleanliness and print mottle are critical aspects of visual quality in papers produced from recycled fibers. Incomplete de-inking and the presence of micro-stickies lead to visible specks and mottled areas that disrupt surface uniformity. Hydrophobic residues persisting through successive recycling cycles interfere with ink hold-out and affect drying and setting behavior, resulting in uneven print coverage. Maintaining print uniformity therefore requires careful adjustment of surfactant chemistry and flotation conditions to account for the altered surface characteristics of recycled furnishes [51,97].

Thus, successive recycling cycles drive predictable drifts in mechanical and optical parameters through coupled chemical–structural aging. The steepest early losses arise from hornification, accessibility decline, and fiber shortening; optical penalties concentrate in lignin-containing streams via chromophore formation. The cycle-to-cycle slope can be materially reduced, though not eliminated by gentle refining, selective enzymatic/chemical refunctionalization, robust wet-end charge management, and moderated drying, supplemented by strategic virgin reinforcement when network scaffolding becomes limiting.

5. Environmental and Economic Impact of Fibers Recycle and Reuse

A wide range of life cycle assessment (LCA) and cost–benefit studies have evaluated the environmental performance of recycled versus virgin fiber systems. Although methodologies differ in system boundaries, allocation rules, and regional energy mixes, these analyses consistently highlight the contribution of recycling to lower greenhouse-gas emissions, reduced energy demand, and overall resource efficiency. At the same time, differences in water use, effluent characteristics, and deinking energy emphasize the need for contextual interpretation. Table 6 summarizes representative LCA studies, outlining their scope and the principal insights relevant to the environmental assessment discussed in this section.

Table 6. Representative life cycle assessment (LCA) and cost–benefit studies comparing virgin and recycled fiber systems. The table highlights system boundaries, functional units, and main conclusions relevant to circularity performance, resource efficiency, and environmental trade-offs in papermaking.

Study (Year)	System Boundaries	Functional Unit	Key Findings/Conclusions
[174]	Cradle-to-gate; EU kraft pulp mill and recycled pulp line	1 ton paper	Recycling generally lowers energy use and GHG emissions; results sensitive to electricity mix and recycling rate.
[175]	Cradle-to-grave; packaging paper loop	1 ton packaging paper	Recycled fibers reduce carbon footprint but may increase water impacts depending on deinking configuration.
[176]	Cradle-to-gate; Asian mixed-furnish mill	1 ton newsprint	Deinking step dominates energy demand; recycled furnish beneficial unless low-quality waste increases rejects.
[177]	Consequential LCA; EU circular-economy scenario	1 ton recovered fiber	Increasing recycling rate shifts burdens upstream; marginal benefits decrease after ~75% recovery.
[18,19]	EU industry-level LCA synthesis	Sector-wide	Recycling outperforms virgin production in GHGs; trade-offs exist in water use and effluent loads depending on water-loop closure.

5.1. Comparison of Energy, Water, and CO2 Footprints: Primary vs. Secondary Fibers

From a life-cycle perspective, manufacturing paper from secondary (recycled) fibers generally outperforms primary (virgin) fibers on energy, water, and greenhouse-gas (GHG) indicators, though the magnitude varies by grade (newsprint vs. packaging vs. printing papers), technology (with or without de-inking), and mill integration (cogeneration, water closure). The gap between controlled laboratory studies and the complexity of mill environments means that some reported laboratory improvements are not easily replicated under industrial operating conditions.

- Recycled pulping avoids wood preparation and most chemical pulping stages, so total process energy per tonne is typically lower. Literature and industry LCAs report 20–60% lower process energy for many recycled grades compared with virgin equivalents, with the upper end for de-inking-free streams (e.g., Old Corrugated Containers (OCC) for packaging) and the lower end where de-inking and high consistency dispersion are required. Mills equipped with CHP/cogeneration further reduce the cradle-to-gate footprint by displacing grid electricity and improving steam efficiency [26,31].

— Recycled mills often operate with tighter water circuits; despite wash steps in de-inking, specific make-up water can be similar or lower than virgin mills when white-water closure and DAF are implemented. Reported savings range from 15 to 50% relative to virgin kraft baselines, but local water management (e.g., loop closure vs. purge for DCS control) drives outcomes [135,178].

— Several mechanisms reduce net GHGs: (i) avoided landfill prevents methane from anaerobic decomposition of paper, (ii) lower process energy (especially with CHP/renewables) cuts Scope 1–2 emissions, and (iii) biogenic carbon retention in recycled products extends storage time. Practical, cited rules-of-thumb indicate that recycling one tonne of paper avoids both energy use and GHG emissions, while meta-analyses show 20–70% lower cradle-to-gate GHG intensity depending on furnish and mill configuration [24,29]. When de-inking is intensive and electricity is carbon-intensive, the advantage narrows; conversely, clean OCC streams in efficient mills deliver the largest benefit.

Key cautions: Results are system-boundary-sensitive (collection, sorting, and transport must be included), and trade-offs exist: de-inking improves brightness but adds energy/chemicals; high water closure saves water but may raise DCS loads unless managed. Conflicting trends in brightness and mechanical strength reported in the literature arise from variations in ink content, lignin levels, and pulping conditions, which influence the degree of fiber damage during recycling. Still, across grades, secondary fiber systems typically show a smaller environmental footprint than primary fiber systems when best-available operations are used [14,17,26,31,136,179].

5.2. Economic Efficiency: Cost Savings, Employment, and Waste Reduction

The **economic efficiency** of recycling-based papermaking lies in reducing costs, creating jobs, and minimizing waste. Using recovered fibers instead of virgin pulp lowers raw material and processing expenses while supporting local employment and improving resource resilience. The following section outlines the main economic aspects: cost savings, employment, waste reduction, and risk management associated with high-recycled-content paper production.

Recovered fiber (e.g., OCC, mixed office paper) is generally less expensive than virgin pulp on a delivered-to-mill basis, although its price fluctuates cyclically. Savings compound through lower wood handling, reduced chemical pulping energy, and (for packaging grades) elimination of bleaching. Offsetting costs include collection/sorting, de-inking chemicals and energy (for printing/writing grades), disposal of rejects/ash, and capex for screen-

ing/cleaning/DAF upgrades. On balance, for many mills and regions, high-OCC packaging lines remain cost-competitive or lower-cost than virgin alternatives at comparable product specifications [67,78,137,138,180,181].

Recycling supports distributed jobs in the collection, sorting, brokerage, and reprocessing segments, often net-positive relative to landfilling or waste-to-energy. Upstream jobs (forestry, sawmilling) remain vital for virgin streams; circular systems diversify employment across urban supply chains [139,140,182,183]. Every ton recycled is a ton diverted from landfill or incineration, reducing tipping fees and long-term liabilities. Mills that stabilize recovered fiber procurement and improve yield (e.g., better stickies control → fewer breaks → higher overall equipment effectiveness) also see lower unit costs through reduced downtime, fewer quality downgrades, and energy savings in drying [141,184]. Sourcing flexibility (mixing virgin and multiple recovered grades) hedges price shocks. Quality volatility in recovered streams can be mitigated by supplier specs (EN 643 grades), pre-acceptance testing, and on-machine control (zeta potential, cationic demand, fines sensors), improving economic predictability [140,142,183,185].

5.3. Contribution to the Circular Economy and Resource Conservation

5.3.1. Pathways Toward Circularity and Sustainable Resource Utilization

Fiber recycling supports sustainability and circular economy goals across the paper value chain, encompassing material recovery, ecosystem protection, process efficiency, design optimization, and systemic value restoration, as follows [3,143,186]:

— Material circularity:

Paper is one of the most successfully recycled materials globally; corrugated recovery rates above 90% have been reported in mature systems, and overall paper recovery commonly sits near two-thirds or higher. According to CEPI Key Statistics 2023, the European paper recycling rate reached approximately 79.3%, confirming the EU's position as a global leader in fiber recovery. Similarly, the EPRC Monitoring Report 2023 reports a recycling rate close to 80% for paper and board, reflecting stable circularity performance in the EU [18,19].

Because cellulose fibers can be reused multiple times (practically ~5–7 loops before quality loss dictates virgin make-up), the sector exemplifies closed-loop material cycling [38,43,87,144].

— Forest and biodiversity pressure:

Each recycled tonne substitutes virgin fiber, tempering pressure on forests and allowing more selective, longer-rotation forestry, with co-benefits for biodiversity and carbon stocks (within the constraints of regional wood markets and certification systems) [23,28,145,146,187–189].

— Water and chemical stewardship:

Circular mills implement white-water closure systems, dissolved air flotation (DAF), and targeted purges to effectively control dissolved and colloidal substances (DCSs) while minimizing effluent discharge. Additionally, the use of microparticle retention systems combined with optimized chemical sequencing reduces excessive polymer consumption. Together, these process-integrated practices lower eutrophication and toxicity potentials, enhance water and chemical efficiency, and maintain stable paper machine runnability [147,148,190,191].

— Design for recyclability

Upstream choices (ink systems, adhesives, barrier coatings, de-inkability, fiber-friendly packaging design) determine downstream circularity. Standards such as EN

643 (CEPI—Brussels) for recovered paper grades and de-inkability guidelines align supply with mill capability, reducing contamination and improving yield [104,132,149,192].

— System value restoration

Circular operations retain material value, reduce waste externalities, and anchor regional industrial ecosystems by linking municipalities, MRFs, converters, and mills. Life-cycle modeling consistently shows that shifting tonnes from landfill/incineration to high-yield recycling delivers net environmental gains and economic value when supported by quality-focused collection, modern mill technology, and stable policy signals (e.g., EPR, recycled-content targets) [143,150,186,193].

5.3.2. Practical Implications for Mills and Policymakers

Practical implementation of fiber recycling requires coordinated action between mills and policymakers to ensure both environmental and economic effectiveness. Key measures focus on improving collection quality, optimizing process efficiency, monitoring operational parameters, and promoting design choices that enhance recyclability and resource circularity across the paper value chain, as follows [15,16,151,194]:

- Pair collection quality (source-separated streams, EN 643 adherence) with mill-side contaminant control (detackifiers, improved screening, DAF) to maximize both environmental gains and economic yield.
- Invest in energy efficiency and CHP to compound the GHG advantage of recycled operations; monitor steam per tonne and drying profiles to capture easy wins.
- Use real-time wet-end metrics (zeta potential, cationic demand, ines/ash) to stabilize retention and drainage, cutting energy and chemical overuse.
- Encourage design-for-recycling across the value chain (inks, adhesives, barrier choices) to improve de-inkability and fiber recovery, sustaining the sector's circular performance.

The main environmental, economic, and circular benefits of fiber recycling and reuse, integrating the findings discussed above, are synthesized in Figure 18.

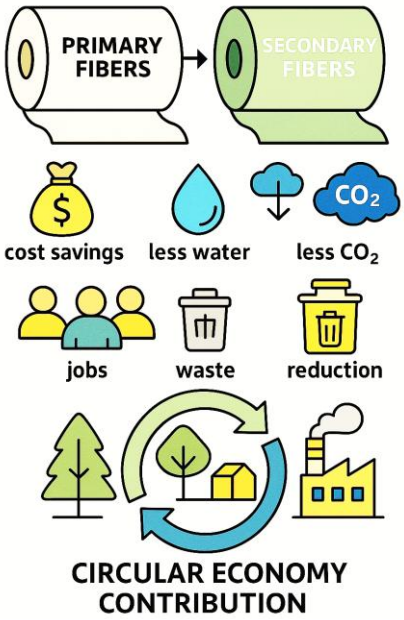


Figure 18. Comparative overview of the environmental, economic, and circular benefits of paper fiber recycling and reuse, highlighting reduced energy, water, and CO_2 footprints relative to virgin production, cost and employment advantages from resource recovery, and systemic contributions to circular economy through material reuse, forest conservation, and design-for-recyclability.

6. Research Gaps and Future Perspectives

Despite significant progress in understanding the behavior and upgrading of recycled fibers, important scientific and technological gaps remain. These gaps limit the systematic optimization of recycled-fiber-based papermaking under increasingly stringent circularity, sustainability, and resource-efficiency requirements. Based on the critical analysis presented in this review, several areas emerge where targeted research is needed to advance both fundamental knowledge and industrial applicability.

A first major challenge concerns the lack of harmonization in laboratory recycling protocols. Studies differ considerably in the number of recycling cycles applied, drying intensity, disintegration conditions, refining severity, chemical environment, and sheet-forming procedures. These variations complicate direct comparison across the literature and hinder the development of universally applicable structure–property relationships. There is a pressing need to standardize or, at minimum, clearly benchmark recycling methodologies to ensure that results are comparable and reproducible.

A second gap relates to the limited mechanistic understanding of how specific chemical and enzymatic modifications influence fiber structure and bonding throughout repeated recycling. While many studies report improvements in tensile properties, opacity, or interfiber bonding, few explicitly quantify changes in molecular-level parameters such as DP evolution, crystalline/amorphous ratio, pore structure, or swelling capacity in relation to these treatments. Multiscale characterization, from molecular spectroscopy to 3D fiber network modeling, would be essential to elucidate how modification pathways interact with hornification and fiber fatigue processes.

Third, the rapid growth of research on nanocellulose derived from recycled fibers highlights promising reinforcement paths, yet the performance of these materials across multiple recycling loops remains insufficiently studied. Questions persist regarding fibril stability, retention efficiency in closed-loop water systems, interactions with fines, and the long-term recyclability of CNF- and T-CNF-modified sheets. Systematic studies comparing nanocellulose from virgin and recycled sources, normalized to fibrillation degree and charge density, are still lacking.

Another important gap concerns scale-up and integration under mill-relevant conditions. Many promising chemical, enzymatic, or surface-modification strategies are validated at laboratory scale but have yet to be thoroughly assessed in industrial environments characterized by high process-water closure, variable raw material quality, and complex additive interactions. Pilot-scale trials are needed to determine whether laboratory-reported strength gains, drainage behavior, or energy reductions are robust when confronted with process variability and industrial constraints.

A further area requiring attention involves techno-economic and environmental assessments of modification strategies. Although several individual studies report benefits such as reduced refining energy or improved bonding, very few include rigorous LCA or cost–benefit analyses that evaluate chemical and enzymatic strategies relative to alternative solutions. Future research must integrate environmental and economic dimensions to determine which treatments can be realistically implemented in industrial circular-economy frameworks.

In line with these gaps, we propose several testable research hypotheses to guide future investigations:

1. Selective enzymatic surface modification prior to secondary refining increases external fibrillation without significant DP reduction, resulting in measurable improvements in bonding after three or more recycling cycles.

2. Dual nanocellulose systems combining cationic and anionic fibrils yield superior strength enhancement compared with single-component CNF additives when applied to hornified fibers from advanced recycling loops.
3. Bio-based polymer grafting (e.g., chitosan–CMC hybrids) can establish more resilient hydrogen-bond networks that retain bonding efficiency during subsequent drying–rewetting events and over multiple recycling cycles.
4. TEMPO-oxidized nanocellulose produced from recycled pulps exhibits reinforcement efficiencies comparable to CNF from virgin sources when normalized to carboxyl content and fibril aspect ratio.
5. Enzymatic pre-loosening of fiber walls reduces refining energy demand in closed-loop water circuits while maintaining strength improvements when scaled from laboratory to pilot-plant environments.

Addressing these gaps and validating these hypotheses will be essential to establish robust, scalable, and environmentally responsible modification strategies capable of supporting the long-term viability of circular papermaking systems based on recycled fibers.

7. Conclusions

This comprehensive study provides an integrated analysis of the interrelated physical, chemical, and operational phenomena that govern fiber suspension behavior, additive efficiency, and product quality in papermaking and paper recycling systems. Across the examined processes—refining, fines generation and management, retention and fixation programs, de-inking and stickies control, and ash optimization—the findings collectively demonstrate that process efficiency and environmental performance depend on a delicate balance between colloidal chemistry, hydrodynamics, and process control.

At the microscopic level, the study highlights the fundamental role of fines and dissolved/colloidal substances as dynamic carriers and sinks of organic and inorganic matter. Their surface chemistry governs the adsorption of dispersants, extractives, and sizing agents, influencing hydrophobicity, polymer accessibility, and charge balance in the wet end. These mechanisms underpin the observed variations in strength additive efficiency, drainage, and retention behavior. It becomes evident that the fine fraction, often regarded as waste or nuisance, can be harnessed constructively when its generation and surface chemistry are properly controlled.

Optimized refining emerges as a cornerstone of sustainable process control. Light, targeted refining that enhances external fibrillation without inducing excessive fiber cutting produces beneficial fines capable of improving bonding and sheet formation. The research underscores that refining intensity, specific edge load, and energy input must be adapted to furnish type and end-product requirements—whether for packaging, printing, or tissue applications—to yield a fines spectrum that supports strength development while maintaining drainage and operational stability.

The examination of retention and fixation programs reveals that the sequential use of fixatives, cationic strength agents, and microparticle systems provides superior control over fines and colloidal materials. Polyamines, polyaluminum compounds, and low-molecular-weight cationic polymers act as first-line fixatives, immobilizing anionic trash and enabling the subsequent polymers to function effectively. The optimized combination of charge neutralization, bridging, and microparticle-induced reflocculation under controlled ionic strength and pH ensures high fines capture, stable drainage, and uniform sheet formation. These systems exemplify how fine-tuned chemical sequencing can reconcile process stability with resource efficiency.

De-inking and stickies control are identified as pivotal steps for maintaining quality and operability in recycling loops. The study emphasizes that flotation efficiency depends

not only on collector chemistry but also on hydrodynamic conditions that promote the formation of larger, hydrophobic ink agglomerates and minimize submicron ink fines. The synergistic action of detackifiers and talc or other mineral surfaces transfers micro-stickies onto retainable fines, transforming them into controlled, removable forms rather than problematic deposits. Such strategies support continuous operation, reduced downtime, and extended felt life in high-recycle systems.

Ash and filler management is equally crucial for maintaining the balance between product performance and process sustainability. In systems dominated by pigment-rich fines, controlling the overall ash content through partial purge or defined ash targets helps sustain fiber bonding strength and reduce energy demands in drying. The coordinated replenishment of fillers ensures the maintenance of key optical properties (such as brightness and opacity), together with essential surface properties, including smoothness, while preventing excessive fines recirculation. This coupling of ash control with filler make-up represents a pragmatic route toward both resource efficiency and product consistency.

From an industrial and environmental perspective, the study reinforces that modern papermaking can no longer rely on isolated process optimization. Instead, a holistic approach—linking chemical, mechanical, and operational strategies—is necessary to manage fines behavior, retention, drainage, and filler dynamics within increasingly closed water circuits. The integration of real-time monitoring tools, zeta potential control, and charge demand analysis offers new possibilities for predictive and adaptive process management.

Based on the findings, several operational recommendations emerge.

- Wet-end chemistry should be continuously monitored and adjusted through online charge and turbidity sensors to stabilize electrokinetic conditions.
- Refining intensity and chemical dosing should be tailored to furnish composition, aiming to maximize bonding fines while limiting detrimental fiber shortening.
- Sequential dosing of fixatives, cationic starch or PAE, and microparticles should be optimized by timing and mixing energy to enhance fines fixation and minimize additive waste.
- Periodic ash purging, combined with filler make-up strategies, should be implemented to maintain optical uniformity and thermal efficiency in drying.
- Detackifier and mineral surface treatments must be integrated into de-inking circuits to minimize stickies deposition and ensure cleaner white water systems.

These measures not only improve operational stability but also contribute to lower chemical and energy consumption, supporting the transition toward environmentally responsible papermaking.

Looking ahead, the convergence of process chemistry, materials science, and digital technologies offers promising pathways for further advancement. Future research should focus on:

- Developing bio-based and biodegradable polymers as multifunctional fixatives and retention agents compatible with closed water loops;
- Implementing machine-learning-based models to predict fines generation, floc structure evolution, and retention performance under varying conditions;
- Exploring the synergistic use of nanocellulose, biopolymers, and smart fillers to improve strength and optical properties at reduced fiber input;
- Investigating water and energy integration strategies that couple wet-end optimization with wastewater treatment and heat recovery systems.

By combining such innovations with rigorous process control and sustainability-oriented design, the pulp and paper industry can move toward a new operational paradigm, one where fiber efficiency, additive performance, and environmental integrity are co-

optimized. The insights presented in this work thus serve as both a comprehensive synthesis of current understanding and a strategic foundation for next-generation papermaking systems that align performance, profitability, and planetary responsibility.

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