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Striving for Sustainable Solutions: Optimizing Utility Properties of Recycled Paper with the Addition of Wet Strength Resin

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Abstract: Paper producers are increasingly challenged to meet customer demands for high-quality sanitary papers amidst rising price pressures and diminishing quality of recycled fibers. One promising avenue for enhancing paper quality involves augmenting wet strength. For this purpose, synthetic wet strength resins are used, among other things. This study explores the efficacy of utilizing a polyamide-epichlorohydrin resin-based agent for the internal sizing of white wastepaper. Such chemicals, when added to cellulosic fibers in proper amounts before the paper is made, can not only improve water resistance and air permeability of the finished product but also significantly affect both the dry and wet strength paper, which is a crucial aspect for sanitary papers. This study shows that the appropriate addition of resin allows the wetted recycled paper to retain even more than 30% of its dry strength, while in the dry state, the breaking strength of the paper is improved by approximately 46%. As the demand for more sustainable and resistant paper products continues to grow, the use of wet strength agents is expected to increase in the coming years, as well as the need for research in this field. This research therefore undoubtedly contributes to advancing sustainable practices within the paper industry, aligning with the principles of circular economy by optimizing the utility of recycled fibers while maintaining product quality.

Keywords: wastepaper; resin; wet strength; recycled fiber; waste management; sustainability

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1. Introduction

The recovery and recycling of wastepaper is becoming increasingly important due to high demand for paper products, especially as paper production in most countries has been lower than consumption for many years. Limitations in production are dictated by the capabilities of cellulose pulp manufacturing. In the coming years, many countries do not expect new cellulose pulp production lines to be established. Further development of paper production is therefore reliant on utilizing wastepaper, making the paper production process more economical. Efficient reuse of wastepaper is thus considered a key factor in the industry's efforts towards sustainable practices. A problematic issue lies in the fact that the utility properties of material from recycled pulp deteriorate with each recycling round due to the limited number of recycling cycles. It is, therefore, essential to develop appropriate processing methods and optimize the composition of secondary pulp to identify the best, most optimal processing techniques. These methods should guarantee that the resulting cellulose pulp from recycling meets the expectations of paper producers and ultimately consumers. This is particularly relevant for hygiene papers, which must not only be strong but also absorbent.

Paper is inherently a hydrophilic material with very poor barrier properties to water and vapor. This is due to the chemical structure of cellulose, which in its structure contains hydroxyl groups (-OH), which have a strong affinity for water. Due to the ability of water to form hydrogen bonds with the surface hydroxyl groups of the polysaccharide-rich material [1], cellulosic fiber materials are hygroscopic on the surface. The relatively high energy of interaction results in relatively low contact angles of water with cellulosic materials; the contact angle of water droplets of even completely smooth surfaces of pure cellulose is, depending on the degree of crystallinity, from 10 to 50°, which is significantly below the practical non-wettability threshold, which is usually assumed to be 90° [2]. Papers with a higher content of hemicelluloses and lignin are less waterproof, because these components are more hydrophilic than cellulose due to their amorphous nature [3,4] and numerous phenolic and acetal groups present in their structure [5,6].

The lack of a barrier to water and water vapor is also due to the capillary-porous structure of the fibrous materials. With pore sizes of 100–200 μm, there is a strong capillary effect, which is additionally increased by the low contact angle of their interior [7]. As a result, water is quickly absorbed into the interior of the paper, while water vapor, after penetrating into the pores, is retained on their inner walls, where it then diffuses into the interior of the fibers. Both factors cause the cellulosic materials to swell and then to weaken the inter-fiber bonds. Accordingly, the mechanical properties, in particular the tear and breaking strength, are impaired, eventually leading to a loss of structural integrity and the start of the defibering process [8]. In most cases, the lack of paper hydrophobicity properties is unfavorable. The porosity of the paper prevents it from fulfilling many functions and limits its use. In the hygiene paper sector, in humid conditions, excessively rapid wetting can cause a paper towel to come apart before its job of wiping and absorbing is complete. Excessive liquid absorption makes the paper structure weaker [9,10], but also leads to poor printing quality [11]. Therefore, one of the key properties that is highly valued in paper products is their wet strength [12]. In order to guarantee the desired mechanical strength of paper products when wet, it is necessary to strengthen the paper fibers beforehand. There are numerous methods for introducing hydrophobic properties to cellulose fiber-based materials. The majority of typical wet strength agents are introduced into the pulp prior to sheet formation at the "wet end" of the machine (wet end addition). Any additives that are not absorbed by the paper fibers need to be incorporated into the paper after the sheet has been formed. The introduction of waterproofing agents allows printing, writing, or painting on paper without fear that the color will show through to the other side. Thus, increasing the resistance of paper to liquids significantly expands the range of applications of paper.

Over recent decades, the increasing demand for sanitary paper has spurred the research and development of highly cost-effective wet strength additives. As the demand for more sustainable and durable paper products increases, the use of wet strength agents is expected to continue its upward trend in the foreseeable future. Many wet strength agents are obtainable on the market, either synthetic or natural, each with its specific mechanism of action and benefits. Often used in the paper industry, wet strength agents are synthetic resins, such as melamine-formaldehyde (MF) and urea-formaldehyde (UF) [13,14], polyvinyl amines (PVAm) [15–17], and polyamidoamine epichlorohydrin (PAAE) [18,19]. The leading wet strength agent in the current world market, PAAE, has been in development since the 1960s and is currently in its fourth generation [20]. The additive accounts for more than 80% of the wet strength agents' market share [21]. All mentioned additives function by forming polymer networks through homo- and co-cross-linking with themselves and with the lignocellulosic fibers, resulting in gel-like structures.

Wet strength resins change the physical properties of paper, its dry strength, and its tendency to degenerate when wet, while improving the quality of the paper. For many types of paper, its high quality and wet strength are directly related. In addition to increasing the wet strength of the paper, these agents also play a vital role in improving the dimensional stability of paper products. By reinforcing the bonds between fibers, they increase the paper's resistance to changes in dimensions, not only in response to fluctuations in humidity or moisture but also under dry conditions. Consequently, the paper maintains its initial shape, size, and flatness, ensuring that it remains visually pleasing and functional. Dimensional stability is especially crucial for applications such as printing, converting, and packaging, where precise and consistent dimensions are essential. Resin chemicals also provide many other benefits, including improved stress distribution, improved retention and drainage, enhanced creeping control, and reduced chemical costs. Additionally, polymer wet strength reagents help to maintain the integrity of the paper when it is exposed to repeated wetting and drying cycles. This is especially important for applications such as paper towels, tissues, and wipes.

Wet strength resins therefore have a large impact on industrial costs, in terms of energy consumption and dewatering, they increase the efficiency of the production process [22,23]. In paper manufacturing, extensive drying is frequently necessary to eliminate moisture from the paper, leading to substantial energy consumption and heightened production expenses. Yet, the incorporation of wet strength agents can alleviate the requirement for excessive drying by enhancing the paper's resistance to moisture. This not only conserves energy but also enhances production efficiency by shortening drying durations and augmenting throughput. Moreover, by diminishing the likelihood of paper damage during wetting and drying phases, polymer wet strength agents help diminish waste and reject rates, thus generating cost savings for paper manufacturers. At the same time, these are agents that dissolve in the process of defibrating paper, enabling the recycling of used paper products [24].

The most essential areas of wet strength resin are in the production of hygienic papers, but products are also used in a variety of specialized papers that are required to retain a certain level of strength when moisturized, such as coffee filters, carrier boards, trays, paper plates, industrial filters, map papers, currency papers, etc.

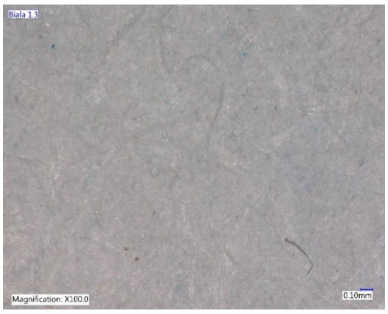
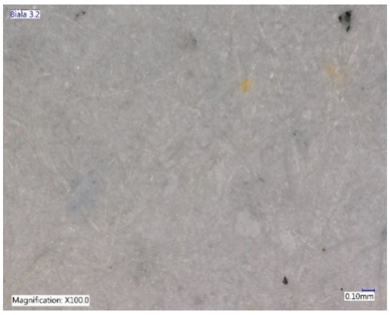
In theory, when fully saturated with water, a paper product will retain at least 15% of its dry strength due to the addition of resins to the stock [25]. However, the underestimation of this value is caused by many factors, such as too low pH that is not enough for efficient retention and cure of the resin, less refined pulp that is not able to absorb resin completely, excess of cationic starch, and degradation of wet strength resin by oxidizing agents. Wet strength additives can be modified or used in combination or added to polymers to produce desirable paper properties. When using these agents, a preliminary study is necessary to determine the proper dosage needed for assumed effects in specific paper products. Due to the above, in this study, the impact of the wet strength resin on the strength and surface properties of the recycled paper was assessed, and the optimal addition of the agent to the recycled pulp was established for the production of hygiene paper.

2. Materials

2.1. Fibrous Material

White wastepaper was selected from the paper mill for research, including products made from bleached pulps—scraps of wood-free paper, with little print, no glue, no waterproof paper, and no colored paper (ranked as 3.04 according to the EN643 "List of European standard types of wastepaper" [26]). For comparative purposes, two types of white wastepaper were selected for the research, marked as 1.3 and 3.2. In previous research analyses conducted on these wastepapers [27], it was possible to remove a minimum of 80% of the fine mineral fraction, obtaining an average wastepaper mass efficiency of 76.5%, as well as the best strength properties. These are also wastepaper with very similar chemical composition and impurity content indicator (Table 1).

Table 1. Non-fibrized substances, chemical composition, and surface microscopic images of wastepaper pulps [27].

Wastepaper	Non-Fibrized Substances	Ash	Extractives	Dissolved Substances	Holocellulose	Kappa Number	Polymerization Degree
	[%]	[%]	[%]	[%]	[%]	[-]	[-]
White 1.3 	0.00	16.71	0.22	3.28	78.33	5.34	840
White 3.2 	0.35	16.90	0.41	0.65	79.59	13.60	643

Wastepaper delivered from the paper mill was separated into homogeneous fractions, shredded manually, and mixed to ensure that the sample was mixed homogeneously. The wastepaper prepared in this way was placed in the described PP foil bags, which were subsequently stored in barrels with tight covers to protect the samples from moisture and contamination. After mechanical shredding, the wastepaper samples were packed in tight containers and stored at a constant temperature of approximately 15 °C.

2.2. Wet Strength Agent—Polyamide-Epichlorohydrin Resin

As a wet strength additive in the research, a polyamide-epichlorohydrin resin was used, applied mainly in a neutral environment (optimally at pH 6–8). Polyamide-epichlorohydrin wet strength resin has good retention properties, which means that it remains in the paper fibers and does not become washed away during the papermaking process. This is important for maintaining the high strength of the paper products (like tissue, towels, and paperboard) when the material is wetted.

The action of the resin is based on the opposite of its ionic charge to the fiber. This agent has a high cationic charge, and so connects with fibers with an anionic charge, thus creating cross-linking—bonds that strengthen the paper in the wet state. Moisture resistance can be obtained through two mechanisms: (1) resin/fiber co-crosslinking, which involves direct covalent bonding between cellulose fibers through a resin molecule, and (2) resin–resin homo-crosslinking, which involves crosslinking of the resin with itself without creating covalent bonds with cellulose.

In laboratory tests, various amounts of resin (0.05 ÷ 2.50%) were added to determine the optimal addition of the product to the secondary fibrous pulp.

3. Methods

3.1. Preparation of Pulps for Research

The procedure of preparing the pulps for further research consisted of cleaning, screening and washing processes, optimized as part of previous research work on the wastepaper. These processes made it possible to remove the fine mineral fraction as well as impurities that could adversely affect the washing process of the wastepaper pulp and cause accelerated wear of the screen or its damage. It should be noted that the pulps used for the tests were devoid of heavy impurities (sand, paper clips, etc.), which were separated during the sorting of the wastepaper samples.

The first step was to defiber the pulp in a laboratory vortex pulper. The rewetted pulp samples (22.5 g d.w. samples were soaked in water for 24 h) were subjected to disintegration with the use of a laboratory JAC SHPD28D propeller pulp disintegrator (Danex, Katowice, Poland) at 23,000 revolutions, in accordance with ISO 5263-1 (2004) [28]. After defibration, the pulps were subjected to a purification process in a laboratory hydrocyclone with a diameter of 60 mm, with a pressure difference of 1.5 bar. Then, the acceptance of the pulp after the cleaning process was subjected to the screening process with the use of a membrane screener PS-114 (Danex, Katowice, Poland) at an amplitude of 25 mm and a frequency of 2 Hz. The installation was equipped with gap screen with 0.15 mm gap widths. The process consisted in the flow of the proper fibrous fraction (determined after the process as the sorted pulp) through the sorting plate under the influence of the hydrostatic pressure of the water column and the movement of the vibrating membrane under the screen plate. After screening, the fibrous fraction was discharged through an overflow spigot to a container below, where it was drained on a sieve. The rejects remained on the sorting plate, from where they were removed after each screening.

3.2. Washing of Wastepaper

The washing process consists of multi-stage dewatering, during which impurities smaller than the screen openings are removed (fine fraction, fillers, shorter fibers, or other small elements). The process was carried out on a screener, on a sieve with the number 180 (mesh 90 µm), washing the pulps with a specific volume of water, while gently mixing to avoid the formation of a filter layer on the screen plate.

3.3. Preparation of Paper Sheets

Laboratory paper sheets were prepared from the screened and washed wastepaper pulps. Sheets of paper were formed in a Rapid-Koethen apparatus (Danex, Katowice, Poland) in accordance with PN-EN ISO 5269-2 (2007) [29]. Each paper sheet had a base weight of 80 g/m^2 (according to ISO 536:2019 [30]). Only sheets with base weights between 79 and 81 g/m^2 were used for further investigation.

The paper samples were conditioned at 23 °C and 50% relative humidity according to ISO 187:2022 [31] for a minimum of 24 h before the examination was conducted.

3.4. Analysis of the Paper Properties

Roughness of the paper surface was also determined in accordance with ISO 8791-2:2013—TMI 58-27 Bendtsen Roughness Tester (Kontech, Lodz, Poland) [32]. Air permeability was determined according to ISO 5636-3:2013—TMI 58-27 Bendtsen Roughness Tester (Kontech, Lodz, Poland) [33].

Optical parameters were determined using the X-rite Exact spectro-densitometer in accordance with ISO 2470-1:2016 [34]. Measurements for selected samples were obtained immediately after preparing paper sheets and after 14 days of storage. Three measurements were recorded for each sample, and the means were calculated. All color measurements were presented according to the L*, a*, and b* values, then color differences (ΔE) were calculated. The CIELab system provides values for L*a*b*, where L* represents lightness, a* the red–green axis, and b* the yellow–blue axis.

The priority strength properties of papers were conducted using Zwick 005 ProLine testing machine (ZwickRoell, Ulm, Germany), in accordance with PN-EN ISO 1924-2:2010 [35], coupled with testXpert III software. The tensile paper properties were examined for dry and wet samples as follows:

- I_B: breaking length [m];
- F_B: tensile force at break [N];
- $\sigma_T{}^b$: width-related force at break [$N \cdot m^{-1}$];
- $\sigma_T{}^W$: force at break index [$Nm \cdot g^{-1}$];
- ε_T: strain at break [%];
- $W_T{}^b$: energy absorption [$J \cdot m^{-2}$];
- $W_T{}^W$: energy absorption index [$J \cdot g^{-1}$];
- E^b: tensile stiffness [$N \cdot m^{-1}$];
- E^w: tensile stiffness index [$Nm \cdot g^{-1}$];
- E*: Young's modulus [MPa].

A detailed statistical analysis was performed for the individual research series, determining the basic indicators—arithmetic mean, extended deviation, and percentage relative error.

4. Results and Discussion

A very important property which greatly contributes to the functional properties of paper, as well as being an important indicator for the production process control of sanitary papers, is air permeability. Porosity quantifies the volume of air capable of passing through a sheet in a given time; thus, higher values indicate a "tighter", less permeable sheet where airflow takes longer to traverse the material. It indicates the porosity of the product and thus its absorbency and also tensile properties, which is crucial, especially for sanitary papers.

Most of the studied papers produced from wastepaper pulps were characterized by high air permeability values exceeding the measuring range of the Bendtsen device. Only the addition of resin exceeding 1.25% caused a decrease in air permeability, noticeable already very significantly with the highest addition of the agent used, i.e., 2.5% (Table 2). It can therefore be concluded that the addition of resin to some extent does not affect air permeability; only higher amounts of agent added to the recycled pulp reduce the porosity of the paper.

Table 2. Structural properties of papers.

Resin Addition [%]	Air Permeability [mL/min]		Roughness [mL/min]	
	1.3	3.2	1.3	3.2
Ref.	5000	5000	406	553
0.05	5000	5000	556	741
0.10	5000	5000	551	758
0.1875	5000	5000	593	739
0.25	5000	5000	676	794
0.50	4220	5000	490	771
0.75	5000	5000	549	717
1.25	5000	4122	576	617
1.875	2824	3231	396	554
2.50	1358	1746	359	504

A similar relationship was observed for the roughness parameter. Roughness measurements examine the surface of the paper, and lower roughness values indicate a smoother sheet. Only the addition of resin above 1.875% caused a decrease in this parameter (Table 2). This is quite an important observation because roughness of the material's surface not only conditions many properties of the material, but also affects a variety of other characteristics, such as appearance, aesthetics of the product, as well as functional values, which is important, especially in the case of the sanitary papers.

The roughness can be controlled not only by the amount of bonding between fibers, but also by materials filling in the holes between fibers. If the holes are filled up, these papers can be more effective as gas barriers, which confirms the relationships observed in the results for the porosity and roughness of the tested samples.

Considering that the polyamide-epichlorohydrin resin dosage correlates with the strength of the sheet, physical testing, such as wet tear index, dry tear index, wet tensile index, and dry tensile index, is carried out to determine the optimum dosage. The tensile properties of paper sheets after soaking with water, but also in a dry state, are fundamental, especially for sanitary papers. Therefore, the effects of resin addition on the wet and dry strength papers were analyzed, and the full tensile analysis is summarized in Table 3 (1.3 white wastepaper) and Table 4 (3.2 white wastepaper).

Table 3. Tensile properties of paper from 1.3 white wastepaper.

Conditions	**Resin Addition**	$\mathbf{I_B}$	$\mathbf{F_B}$	$\boldsymbol{\sigma_T}^{\mathbf{b}}$	$\boldsymbol{\sigma_T}^{\mathbf{W}}$	$\boldsymbol{\varepsilon_T}$	$\mathbf{W_T}^{\mathbf{b}}$	$\mathbf{W_T}^{\mathbf{W}}$	$\mathbf{E^b}$	$\mathbf{E^w}$	$\mathbf{E^*}$
	[%]	**[m]**	**[N]**	**[N/m]**	**[Nm/g]**	**[%]**	**[J/m^2]**	**[J/g]**	**[N/m]**	**[Nm/g]**	**[MPa]**
Dry	Ref.	2700	30.9	2095	26.4	1.60	22.1	0.278	320,667	4033	2915
	0.05	2450	28.1	1933	23.9	1.53	23.3	0.288	277,267	3424	2488
	0.1	2800	31.9	2200	27.2	1.58	21.2	0.262	266,350	3289	2390
	0.1875	2650	29.9	2058	25.4	1.45	23.2	0.286	269,467	3328	2417
	0.25	2450	27.9	2048	23.9	1.37	21.3	0.254	279,645	3518	2544
	0.5	2600	30.9	2067	25.7	1.38	18.5	0.230	297,167	3702	2703
	0.75	3100	35.1	2416	29.8	1.60	24.0	0.297	287,367	3549	2578
	1.25	2300	27.2	1845	22.4	1.25	14.4	0.176	282,167	3422	2568
	1.875	3550	40.2	2769	34.2	1.68	30.4	0.376	328,833	4061	2950
	2.5	3950	46.2	3120	38.7	1.82	36.2	0.449	349,333	4328	3172
Wet	Ref.	–	–	–	–	–	–	–	–	–	–
	0.05	250	3.0	206	2.5	0.42	0.6	0.007	103,400	1277	928
	0.1	500	5.9	405	5.0	0.47	1.0	0.013	111,267	1374	998
	0.1875	400	4.8	327	4.0	0.52	0.8	0.009	113,217	1398	1016
	0.25	400	3.5	290	3.7	0.55	0.8	0.010	117,250	1488	1069
	0.5	700	7.0	569	7.1	0.73	2.2	0.028	157,333	1958	1432
	0.75	900	10.4	716	8.8	0.82	4.3	0.053	161,500	1994	1449
	1.25	750	7.9	597	7.2	0.68	2.1	0.026	162,333	1970	1473
	1.875	1100	12.7	876	10.8	0.98	5.0	0.062	169,667	2095	1522
	2.5	1400	15.1	1102	13.7	1.01	6.7	0.083	172,333	2138	1568

Table 4. Tensile properties of paper from 3.2 white wastepaper.

Conditions	**Resin Addition**	$\mathbf{I_B}$	$\mathbf{F_B}$	$\boldsymbol{\sigma_T}^{\mathbf{b}}$	$\boldsymbol{\sigma_T}^{\mathbf{W}}$	$\boldsymbol{\varepsilon_T}$	$\mathbf{W_T}^{\mathbf{b}}$	$\mathbf{W_T}^{\mathbf{W}}$	$\mathbf{E^b}$	$\mathbf{E^w}$	$\mathbf{E^*}$
	[%]	**[m]**	**[N]**	**[N/m]**	**[Nm/g]**	**[%]**	**[J/m^2]**	**[J/g]**	**[N/m]**	**[Nm/g]**	**[MPa]**
Dry	Ref.	3750	42.6	2932	36.2	2.53	54.2	0.669	408,133	5040	3662
	0.05	3650	41.2	2840	35.1	2.30	51.9	0.641	400,117	4941	3590
	0.1	3750	42.5	2925	36.1	2.42	55.4	0.684	384,183	4744	3447
	0.1875	3650	41.6	2862	35.3	2.48	56.1	0.693	400,167	4942	3590
	0.25	3600	40.8	2811	34.7	2.53	49.4	0.610	400,267	4943	3591
	0.5	3700	42.2	2904	35.9	2.43	55.8	0.689	418,017	5162	3750
	0.75	4300	48.9	3366	41.6	2.57	59.4	0.733	402,717	4973	3613
	1.25	4450	50.7	3492	43.1	2.60	62.7	0.775	415,617	5132	3729
	1.875	4950	56.1	3863	47.7	2.65	73.7	0.911	420,917	5198	3776
	2.5	5500	62.4	4296	53.1	2.85	87.7	1.083	445,117	5497	3993

Table 4. *Cont.*

Conditions	Resin Addition	I_B	F_B	$\sigma_T{}^b$	$\sigma_T{}^W$	ε_T	$W_T{}^b$	$W_T{}^W$	E^b	E^w	E^*
	[%]	[m]	[N]	[N/m]	[Nm/g]	[%]	[J/m^2]	[J/g]	[N/m]	[Nm/g]	[MPa]
Wet	Ref.	–	–	–	–	–	–	–	–	–	–
	0.05	350	4.2	292	3.6	0.62	1.3	0.017	133,400	1647	1197
	0.1	500	5.6	389	4.8	0.72	1.7	0.022	142,300	1757	1277
	0.1875	600	6.6	455	5.6	0.78	2.0	0.024	144,467	1784	1296
	0.25	550	6.2	424	5.2	0.85	1.8	0.023	149,567	1847	1342
	0.5	1000	11.6	800	9.9	1.13	5.3	0.065	198,767	2455	1783
	0.75	1250	14.0	960	11.9	1.25	9.1	0.113	201,750	2491	1810
	1.25	1350	15.4	1058	13.1	1.50	11.0	0.135	202,433	2500	1816
	1.875	1600	18.1	1245	15.4	1.40	14.0	0.172	213,850	2641	1919
	2.5	2000	22.5	1552	19.2	1.73	16.6	0.205	219,200	2707	1967

Particularly important for the evaluation of the usefulness of sanitary papers is their high breaking resistance and elasticity, rendering these papers the most attractive for use. Depending on the addition of resin, the breaking length of the paper after soaking in water decreased by 64–90%, while the extensibility decreased by 39–73% (Tables 3 and 4). With the addition of resin in the range of 1.25–2.5%, the papers retained over 30% of their dry strength. The addition of resin also improved the dry strength of the paper. Studies have shown that a 2.5% addition of resin increases the dry breaking strength of the paper by approx. 46% compared to the reference sample. Other researchers report that the addition of PAAE to the papermaking process can increase the wet-to-dry strength ratio up to 35% [36–41].

Apart from samples with the lowest addition of resin, almost all papers met the theoretical requirement of maintaining a minimum of 15% of its dry strength. Only after 30 s of water wetting did the water resistance of the tested papers drop below 15%. The water resistance of the tested wastepapers is depicted in Figure 1.

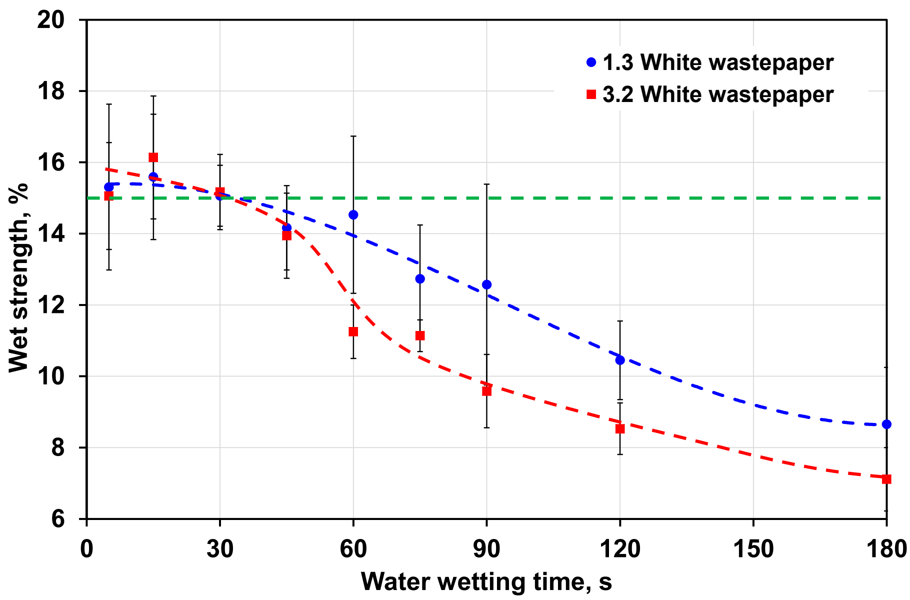


Figure 1. Water resistance of tested wastepaper as a function of wetting time.

Also, for other mechanical properties, the overall trend is that the strength grew with the increase in resin addition, irrespective of the wastepaper type (Tables 3 and 4). However, higher strength values were observed for 3.2 wastepaper, which indicates heterogeneity of the raw material.

The optical characteristics are presented in Figures 2 and 3 and Table 5. Similar ranges of L*a*b* values for both type of tested recycled pulps were observed. However, the 3.2 wastepaper showed a lower lightness than the 1.3 type (Figures 1 and 2), confirming the previous observation about the heterogeneity of the recycled material.

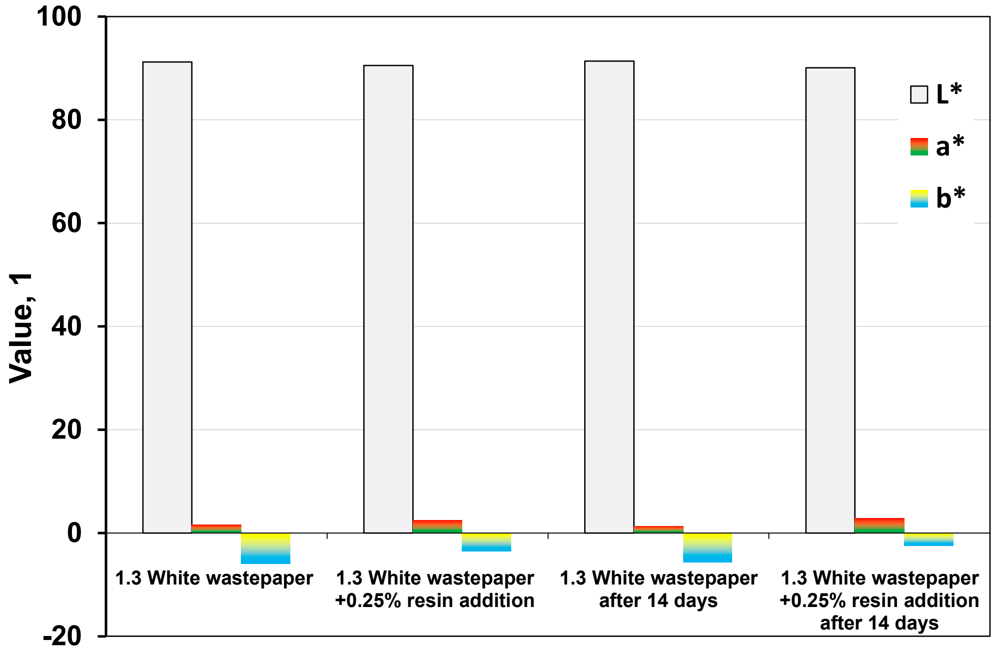


Figure 2. Values of the CIELab color space components of 1.3 white wastepaper (where L* represents lightness, a* the red–green axis, and b* the yellow–blue axis).

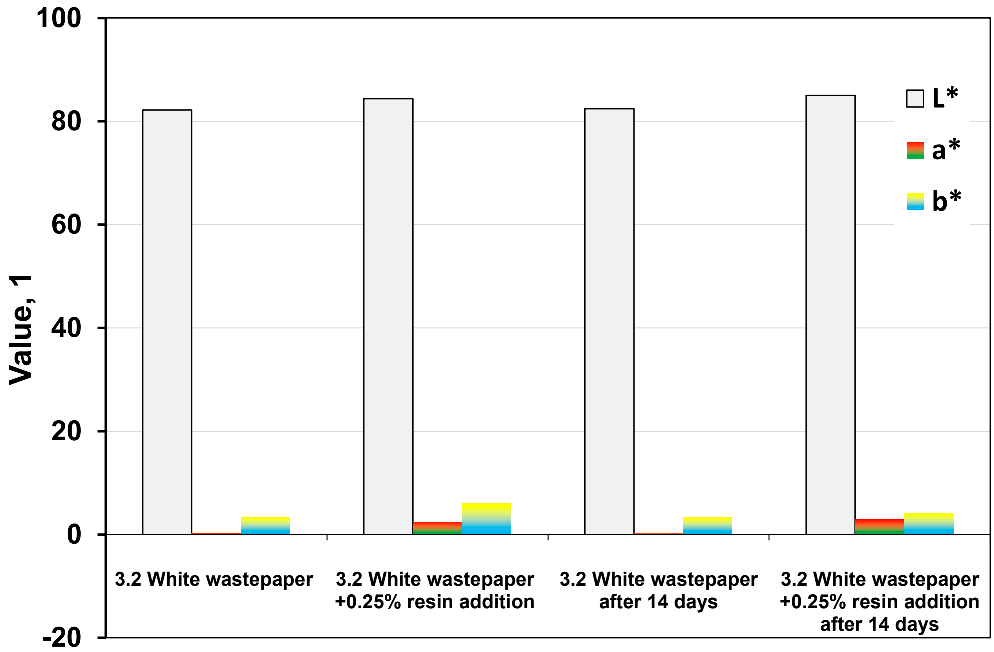


Figure 3. Values of the CIELab color space components of 3.2 white wastepaper (where L* represents lightness, a* the red–green axis, and b* the yellow–blue axis).

Table 5. Evaluation of the wastepaper color difference delta E.

ΔE in CIELab Color Space		
1.3 White wastepaper +0.25% resin addition	1.3 White wastepaper after 14 days	1.3 White wastepaper +0.25% resin addition after 14 days
2.67	0.47	3.87
3.2 White wastepaper +0.25% resin addition	3.2 White wastepaper after 14 days	3.2 White wastepaper +0.25% resin addition after 14 days
4.03	0.27	3.96

Table 5 shows the mean of the ΔE color difference parameters for initial samples immediately after preparation and after 14 days of storage, with and without the addition of wet strength agent. Significant differences between the papers with and without resin addition were observed. The color difference in the samples without the addition of resin after 14 days was imperceptible (within the measurement error) and, depending on the type of wastepaper, it was 0.27–0.47. The addition of resin to the pulp causes clearly noticeable color differences (ΔE of about 3 ÷ 4) of the final product, which is already visible on the reference samples (Table 5). This is due to the color of the resin itself and its properties; resin has the potential for yellowing of the paper product over time, as it is sensitive to light and heat, leading to discoloration of the paper. Even if it is an acceptable difference in the production process, in the case of some applications of paper, it significantly reduces the visual qualities of the product, and thus its quality, which is particularly important in the case of hygienic paper.

5. Conclusions

Wet strength agents play a critical role as additives in the paper industry due to their ability to enhance the mechanical properties of paper products when exposed to water, which was confirmed by the analyses performed. Moreover, the performed research showed that wet strength resin added in the right amount to recycled pulp before paper is made can make the final product also have a higher strength in a dry state, up to about 46%. The appropriate addition of an agent also reduces the porosity and roughness parameters of the recycled paper, which greatly enhances sanitary paper's functional values, aesthetic qualities, and market value. In summary, the results of this paper intend to show information about the data on the correlation between the wet strength agent and the usable properties of the wastepaper. By understanding and leveraging these correlations, additives can effectively enhance the water resistance properties of paper and improve its overall durability and performance. Therefore, the usability of this data provides significant support for the sustainable production of sanitary paper and the conducted research provides a solid foundation for further analysis on this topic.

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References

1. Wohlert, M.; Benselfelt, T.; Wågberg, L.; Furó, I.; Berglund, L.; Wohlert, J. Cellulose and the role of hydrogen bonds: Not in charge of everything. *Cellulose* **2022**, *29*, 1–23. [CrossRef]
2. Dankovich, T.; Gray, D. Contact angle measurements on smooth nanocrystalline cellulose (I) thin films. *J. Adhes. Sci. Technol.* **2011**, *25*, 699–708. [CrossRef]
3. Lee, D.; Owens, V.N.; Boe, A.; Jeranyama, P. *Composition of Herbaceous Biomass Feedstocks*; South Dakota State University Publication: SGINC1-07, Brookings, SD: Washington, DC, USA, 2007.
4. Goudarzi, A.; Lin, L.T.; Ko, F.K. X-ray diffraction analysis of kraft lignins and lignin derived carbon nanofibers. *J. Nanotechnol. Eng. Med.* **2014**, *5*, 021006. [CrossRef]
5. Hubbe, M.; Douglas, J.; Wei, S. Contact angles and wettability of cellulosic surfaces: A review of proposed mechanisms and test strategies. *BioResources* **2015**, *10*, 8657–8749. [CrossRef]
6. Chen, Y.R.; Sarkanen, S. X-ray powder diffraction analyses of kraft lignin-based thermoplastic polymer blends. In *Characterization of Lignocellulosic Materials*; Hu, T.Q., Ed.; Wiley Online Library: Hoboken, NJ, USA, 2009; pp. 301–315.
7. Ganicz, T. Perspektywy rozwoju technik hydrofobizacji papieru. *Przeg. Pap.* **2021**, *77*, 53–61. [CrossRef]
8. Hubbe, M. Paper's resistance to wetting—A review of internal sizing chemicals and their effects. *BioResources* **2007**, *2*, 106–145.
9. Alava, M.; Niskanen, K. The physics of paper. *Rep. Prog. Phys.* **2006**, *69*, 669–723. [CrossRef]
10. Wulz, P.; Waldner, C.; Krainer, S.; Kontturi, E.; Hirn, U.; Spirk, S. Surface hydrophobization of pulp fibers in paper sheets via gas phase reactions. *Int. J. Biol. Macromol.* **2021**, *180*, 80–87. [CrossRef] [PubMed]
11. Borch, J.; Lyne, M.; Mark, R.; Habeger, C. *Handbook of Physical Testing of Paper*; Marcel Dekker Inc.: New York, NY, USA, 2002.
12. Andersson, C. New ways to enhance the functionality of paperboard by surface treatment—A review. *Packag. Technol. Sci.* **2008**, *21*, 339–373. [CrossRef]
13. Espy, H. The mechanism of wet-strength development in paper: A review. *Tappi J.* **1995**, *78*, 90–99.
14. Francolini, I.; Galantini, L.; Rea, F.; Di Cosimo, C.; Di Cosimo, P. Polymeric wet-strength agents in the paper industry: An overview of mechanisms and current challenges. *Int. J. Mol. Sci.* **2023**, *24*, 9268. [CrossRef] [PubMed]
15. Yang, D.; Stimpson, T.C.; Soucy, J.; Esser, A.; Pelton, R.H. Increasing wet adhesion between cellulose surfaces with polyvinylamine. *Cellulose* **2019**, *26*, 341–353. [CrossRef]
16. Pelton, R.; Hong, J. Some properties of newsprint impregnated with polyvinylamine. *Tappi J.* **2002**, *1*, 21–26.
17. Kurita Europe GmbH. Innovative Wet Strength Technology Giluton. Available online: https://d3pcsg2wjq9izr.cloudfront.net/files/5206/download/724596/042018_WetStrengthTechnology-shortcut.pdf. (accessed on 21 April 2024).
18. Wågberg, L.; Björklund, M. On the mechanism behind wet strength development in paper containing wet strength resins. *Nord. Pulp Pap. Res. J.* **1992**, *8*, 53–58. [CrossRef]
19. Ntifafa, Y.; Ji, Y.; Hart, P.W. Polyamidoamine epichlorohydrin (PAAE) wet-strength agent: Generations, application, performance, and recyclability in paperboard and linerboard. *BioResources* **2024**, *19*. [CrossRef]
20. Keim, G. Cationic Thermosetting Polyamide-Epichlorohydrin Resins and Process of Making Same. U.S. Patent 2,926,154, 23 February 1960.
21. Diack, A.J. Wet Strength Innovations for Regulatory Compliances, World Pulp & Paper—The International Review for The Pulp and Paper Industry. 2015; pp. 39–44. Available online: http://www.remproductions.co.uk/flipbook-4/files/inc/08dba1d5ec.pdf (accessed on 22 April 2024).
22. Wet Strength Resin Technology and its Benefits for Paper Industry. Available online: https://balajichemsolutions.com/wet-strength-resin-technology-and-its-benefits-for-paper-industry/ (accessed on 9 March 2024).
23. The Many Benefits of Wet Strength Resins. Available online: https://www.paperindustryworld.com/many-benefits-wet-strength-resins/ (accessed on 15 March 2024).
24. Żywice Syntetyczne Wodoutrwalające. Available online: https://tsc.com.pl/oferta/dzia%C5%82-chemikali%C3%B3w/chemikalia/zywice-syntetyczne-wodoutrwalajace?switch=true (accessed on 9 March 2024).
25. Siqueira, E.J. Polyamidoamine Epichlorohydrin-Based Papers: Mechanisms of Wet Strength Development and Paper Repulping. Available online: https://theses.hal.science/tel-00952991/document (accessed on 27 April 2024).
26. PN-EN 643:2014-03. Available online: https://sklep.pkn.pl/pn-en-643-2014-03e.html (accessed on 13 February 2024).
27. Małachowska, E.; Lipkiewicz, A.; Dubowik, M.; Przybysz, P. Which wastepaper should not be processed? *Sustainability* **2023**, *15*, 2850. [CrossRef]
28. *ISO 5263-1:2004*; Pulps, Laboratory Wet Disintegration, Part 1: Disintegration of Chemical Pulps. ISO: Geneva, Switzerland, 2004.
29. *PN-EN ISO 5269-2 (2007)*; Masy Włókniste—Przygotowanie Arkusików Laboratoryjnych do Badań Fizycznych—Część 2: Metoda Rapid-Kothen. Polish Committee for Standardization: Warsaw, Poland, 2007.
30. *ISO 536:2019*; Paper and Board, Determination of Grammage. ISO: Geneva, Switzerland, 2019.
31. *ISO 187:2022*; Paper, Board and Pulps, Standard Atmosphere for Conditioning and Testing and Procedure for Monitoring the Atmosphere and Conditioning of Samples. ISO: Geneva, Switzerland, 2022.
32. *ISO 8791-2:2013—TMI 58-27*; Paper and Board, Determination of Roughness/Smoothness (Air Leak Methods), Part 2: Bendtsen method. ISO: Geneva, Switzerland, 2013.
33. *ISO 5636-3:2013—TMI 58-27*; Paper and Board, Determination of Air Permeance (Medium Range), Part 3: Bendtsen method. ISO: Geneva, Switzerland, 2013.

34. *ISO 2470-1:2016*; Paper, Board and Pulps, Measurement of Diffuse Blue Reflectance Factor, Part 1: Indoor Daylight Conditions (ISO brightness). ISO: Geneva, Switzerland, 2016.
35. *PN-EN ISO 1924-2:2010*; Papier i Tektura—Oznaczanie Właściwości Przy Działaniu Sił Rozciągających—Część 2: Badanie Przy Stałej Prędkości Rozciągania (20 mm/min). ISO: Geneva, Switzerland, 2010.
36. Andreasson, B.; Wågberg, L. 7. On the mechanisms behind the action of wet strength and wet strength agents. In *Paper Products Physics and Technology*; De Gruyter: Berlin, Germany, 2009.
37. Su, J.; Mosse, W.K.J.; Sharman, S.; Batchelor, W.; Garnier, G. Paper strength development and recyclability with polyamideamine-epichlorohydrin (PAE). *BioResources* **2012**, *7*, 913–924. [CrossRef]
38. Xing, Q.Q.; Zhao, C.S.; Han, W.J. Manufacture and application of PAE as wet strength agent. *Adv. Mat. Res.* **2012**, *557–559*, 1070–1073. [CrossRef]
39. Zhang, S.; Zhao, D.; Hou, C.; Zhang, N.; Yang, M.; Liu, L. A Novel Development and Application of Self Crosslinking Strengthening for Polyamide Epichlorohydrin (PAE) Resin in Polyacrylonitrile (PAN) Sheet. In Proceedings of the 21st International Conference on Composite Materials, Xi'an, China, 20–25 August 2017.
40. Liang, S.B.; Ning, X.; Fu, Q.-J.; Liu, Q.; Yao, C.L. The use of a PAE/bentonite binary system to improve the wet strength of paper. *BioResources* **2020**, *15*, 8449–8458. [CrossRef]
41. Husić, E.; Botonjić, Š. Effect of addition of wet-strength agent on tensile strength of paper. *JST&M* **2023**, *3*, 30–35.

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