Effect of Paper-making Additives on Biodegradation of Lignocellulosic Fibers

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The biodegradation kinetics of paper materials with various chemical additives was studied, focusing on their potential tunability. Paper materials with additives, including retention aid, hydrophobic agent, and wet and dry strength agents, were explored in two forms: disintegrated fiber and paper form. Using the Gompertz equation, biodegradation kinetics were modeled to calculate the lag phase, initial biodegradation rate, and ultimate biodegradation extent. All paper materials showed higher biodegradation extents than microcrystalline cellulose (MCC) due to the highly biodegradable nature of hardwood bleached pulp. Disintegrated paper materials exhibited similar lag phase values and ultimate biodegradation to MCC regardless of treatment, while punched paper materials showed noticeable differences, suggesting that fiber disintegration plays a critical role in initiating biodegradation. Hydrophobic and wet strength treatments, such as alkyl ketone dimer (AKD) and wet-strength agents (PAE), respectively, significantly increased the lag phase, but their ultimate biodegradation extent remained intact. These findings highlight that the biodegradability of paper materials can be preserved even after chemical treatments, underscoring their environmentally friendly potential.

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Keywords: Aquatic biodegradation; Lignocellulose; Paper wastes; Paper additives

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INTRODUCTION

Paper, a sheet-form material composed of pulp or other fibrous substances, has been used for various purposes since ancient times. It has served as a significant medium for records and communication over time, evolving alongside the progress of civilization. In recent decades, the expansion of distribution industries and e-commerce has significantly increased the use of paper for packaging purposes. Notably, paper is considered an environmentally friendly and biodegradable material, leading many industries to adopt it as a sustainable alternative.

Paper additives are incorporated during the papermaking process to enhance the quality of paper or impart specific properties depending on its intended purposes and applications. Typical additives include retention agents, sizing agents, and wet- and dry-strength agents. During papermaking, these additives interact with pulp fibers, altering the properties of fiber surfaces.

The biodegradation of paper materials containing additives has been studied for decades (Kanie *et al*. 2005; Cerpakovska *et al*. 2010; Ahmed *et al*. 2018; Sandak *et al*.

2015, 2019; Korpela *et al*. 2023; Perdoch *et al*. 2023). For instance, cationic starch and resinous adhesives have been found to increase susceptibility to microorganism colonization on paper materials (Sandak *et al*. 2015). Even paper treated with hydrophobically silanized starch showed improved biodegradability, despite being resistant to biodegradation before water exposure (Perdoch *et al*. 2023). Similarly, natural fillers such as bran particles have enhanced the biodegradability of paper materials (Sandak *et al*. 2019). Conversely, Ahmed *et al*. (2018) found that inks in newsprint delayed and disturbed the composting of newsprint in a compost environment.

The impact of wet-strength agents has also been reported: they impede the biodegradation of paper, although the paper lost 90% of its weight after 60 days (compared to 30 days for untreated paper) (Kanie *et al*. 2005). Paudel *et al*. (2022) investigated the effects of wet-strength and sizing agents on the biodegradation of paper-based seeding pots, finding that while initial weight loss varied, the overall extent of biodegradation was similar between pots with and without additives. However, conflicting results have been found; chemical crosslinking agents that increase the wet strength of kraft paper have also been shown to enhance its resistance to biodegradation (Korpela *et al*. 2023).

To the best of the authors' knowledge, a comprehensive study comparing the impact of various additives on the biodegradation kinetics of paper materials under controlled conditions has not been conducted. Most studies have analyzed biodegradation by tracking weight loss (Sandak *et al*. 2019) or changes in functional groups on the paper surface (Sandak *et al*. 2015). Furthermore, these studies typically focused on single types of paper additives, such as wet-strength agents (Kanie *et al*. 2005) or dry strength agents (Kanie *et al*. 2005; Sandak *et al*. 2015).

Biodegradation kinetics are particularly important when both durability and biodegradability are required. For example, food packaging materials or paper-based seedling pots need to be stable during their service time, and paper towels must be durable while in use. Since cellulose and hemicellulose in paper materials are readily biodegradable (Kwon *et al*. 2021), paper materials with additives in many studies have shown biodegradation extents over 90% (Kanie *et al*. 2005; Sandak *et al*. 2019). However, additives appear to affect the lag phase before biodegradation initiation and/or the rate of biodegradation. Therefore, understanding how additives influence the biodegradation kinetics of lignocellulosic fibers is crucial for controlling the durability and biodegradability of paper products.

The objective of this study was to understand the effect of additives on the biodegradation kinetics of pulp fibers. This is the first study to compare different additives under controlled conditions and thoroughly analyze their biodegradation kinetics. The results will provide valuable information for manufacturers to control the durability and biodegradability of paper products.

EXPERIMENTAL

Materials

Once-dried hardwood bleached pulp (HW) sourced from a Southeast United States mill was supplied in dry-lap form from the pilot plant of the Department of Forest Biomaterials, North Carolina State University. The fiber length and width of the pulp fiber were 0.86 mm and 19.0 μm, respectively (measured by Fiber Quality Analyzer, OpTest Equipment Inc., Canada). Alkyl ketene dimer (AKD, sizing agent), polyamide

epichlorohydrin resin (PAE, wet strength agent), and cationic polyacrylamides (C-PAM, retention aid) were provided by Solenis LLC (DE, USA) and were used as received. Cationic starch (CATO® 237, Ingredion, IL, USA) was utilized as a dry strength agent. Inorganic mineral salts for aquatic biodegradation experiments included potassium dihydrogen phosphate (KH_2PO_4), dipotassium hydrogen phosphate (K_2HPO_4), disodium hydrogen phosphate dihydrate ($Na_2HPO_4 \cdot 2H_2O$), ammonium chloride (NH_4Cl), magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), and iron III chloride hexahydrate (FeCl3·6H2O). These salts were purchased from Sigma-Aldrich (USA) and used as received. Potassium hydroxide, used as a CO_2 absorber for biodegradation experiments, was also used as received (Fisher Scientific, USA). Microcrystalline cellulose (MCC, Acros organics™, USA; particle size 50 μm) was the reference material.

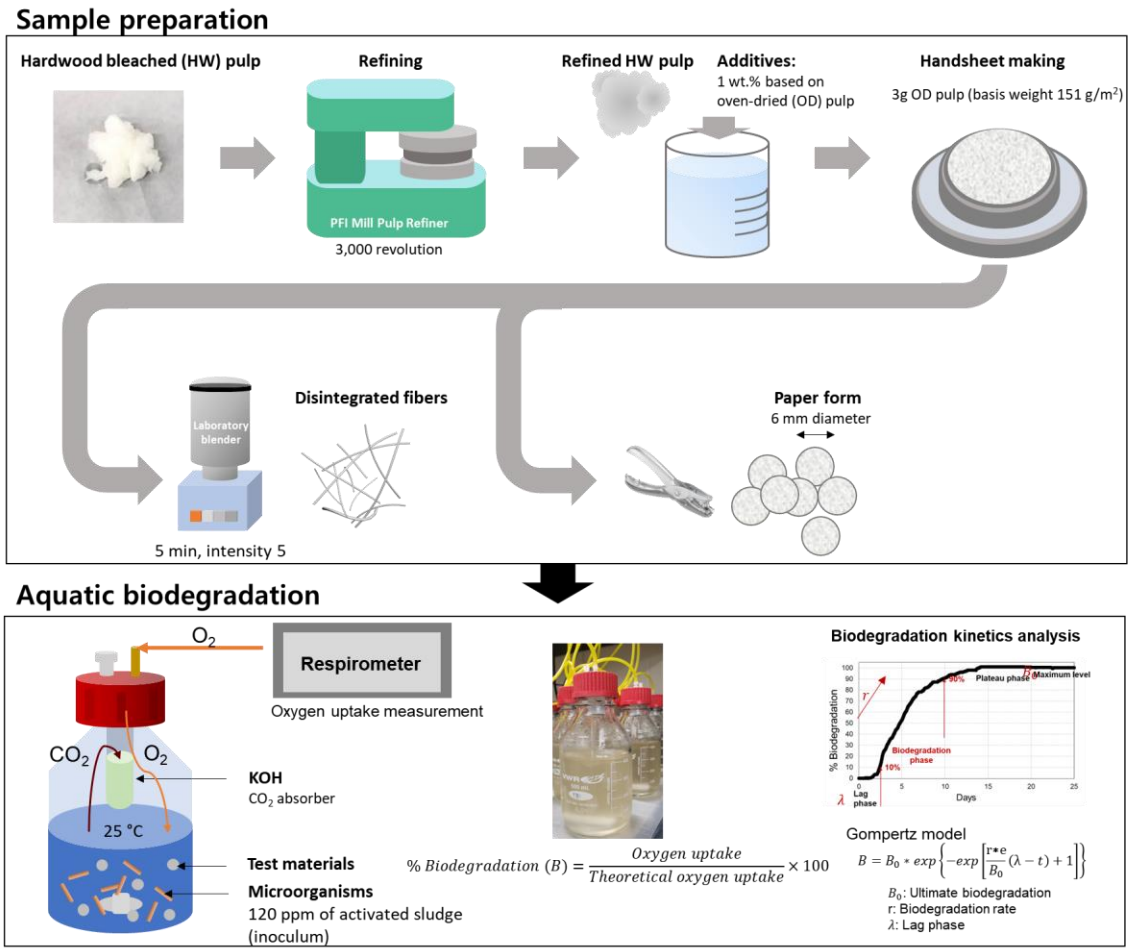


Fig. 1. Experimental scheme of sample preparation and aquatic biodegradation

Sample Preparations

The paper samples for biodegradation experiments were prepared as illustrated in Fig. 1. Hardwood pulp was dispersed at 1.2% consistency using a pulp disintegrator (Testing Machine Inc., New Castle-DE, USA) for 5 min at 3,000 rpm. The pulp was then thickened to 10% consistency using filter paper and a vacuum pump and subsequently refined with a PFI mill refiner for 3,000 revolutions (the Norwegian Pulp and Paper Research Institute, Oslo, Norway (TAPPI 248 Sp-00 2000)) for 3,000 revolutions. The

refined pulp was blended with the additives (1% based on oven-dried pulp weight) using a pulp disintegrator for 5 min. Handsheets were formed using a TAPPI handsheet former, following the TAPPI standard method (TAPPI 205 Sp-02 2006). The basis weight of the formed handsheet was 151 g/m^2. The handsheets were dried under conditions of 50% relative humidity and 23 °C. To cure the additives to the fibers in the handsheets, an additional curing step was performed at 115 °C overnight.

Two different forms of paper samples were prepared. Disintegrated fiber forms were produced using a laboratory blender (Waring, CT, USA) at intensity 5 for 5 min. Paper form samples were prepared using a paper hole punch, producing punched paper with a diameter of 6 mm.

Characterization

The characteristics of raw materials and prepared paper materials were investigated in terms of cellulose crystallinity and surface properties, including surface morphology and water contact angle.

The cellulose crystallinity index of MCC and HW pulp fibers was determined using an X-ray Diffractometer (Rigaku SmartLab X-Ray Diffractometer, Japan). Samples were scanned over a range of 5° to 45° at a scanning speed of 0.01°/s. The crystallinity index (CrI) was calculated using the following formula (Eq. 1) (Segal *et al*. 1959; Xu *et al*. 2012; Yoshida *et al*. 2008),

$$CrI\ (\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

where I_{200} represents the peak intensity at 200 (θ = 22.5°), and I_{am} represents the minimum intensity between the 200 and 110 peaks (θ = 18.5°).

The surface and cross-section of the paper materials were characterized using Scanning Electron Microscopy (SEM, JCM-6000Plus Versatile Benchtop SEM, JEOL, Japan). The fiber cross-section was obtained using a razor blade.

The water contact angle was measured using an SEO Phoenix 300 (SEO, Korea) and analyzed with ImageJ (National Institutes of Health, USA).

Aquatic Biodegradation

Aquatic biodegradation of paper materials was investigated following an ISO standard method (ISO 14851 2019) (Fig. 1) and procedures detailed in previous studies by the authors' research group (Kwon *et al*. 2021, 2023; Zambrano *et al*. 2021). A closed respirometer (RSA PF-8000, Respirometer System and Applications, LLC., USA) tracked the oxygen uptake from the test flask by measuring the pressure drop caused by oxygen consumption. The extent of biodegradation (B, %) was calculated based on the ratio of oxygen uptake to the theoretical oxygen demand (ThOD) of the test materials (Eq. 2). The ThOD for each test material was calculated based on its elemental composition, analyzed with a Perkin Elmer PE2400-Series II, CHNS/O analyzer (MA, USA) (Eq. 3).

$$B\ (\%) = \frac{Oxygen\ uptake\ (\frac{mg}{g} material)}{ThOD\ (\frac{mg}{g} material)} \times 100 \quad (2)$$

$$ThOD\ (\frac{mg}{g} material) = 16 \times 10 \times (\frac{2}{12} C + \frac{H}{2} - \frac{O}{16}) \quad (3)$$

(C, H, O: elemental composition (%))

Each test flask was filled with 400 mL of test medium and 100 mg of test materials. The test medium was prepared with a solution of mineral salts and inoculum to simulate freshwater conditions. Solutions in Table 1 were added to deionized water as follows: 20 mL of A, and 2 mL each of B, C, and D solutions were added to 2 L of deionized water and stirred for 5 min. Activated sludge from the Neuse River Wastewater Treatment Plant (USA) was used as the inoculum. Inoculum was added to the test flask with the mixture of mineral salt solutions and deionized water to achieve 120 ppm suspended solids in 400 mL of test medium. The pH of the test medium was adjusted to 7 using hydrochloric acid and sodium hydroxide.

Four milliliters of potassium hydroxide were added in a glass tube and placed in the test flask to absorb carbon dioxide emitted by microorganisms, allowing oxygen to be supplied by the pressure drop in the closed test flask. The test flask was connected to the respirometer with an oxygen supply and stabilized for one week before adding the test materials. Two repetitions were conducted for each test material. The test flasks were stirred constantly at 300 rpm in a temperature-controlled room at 25°C in the dark. The biodegradation experiment was conducted until all the biodegradation curves reached their plateau.

Table 1. Solution of Mineral Salts and their Concentration

Solution	Mineral Salt	Concentration (g/L)
A	KH_2PO_4	8.5
	K_2HPO_4	21.8
	$Na_2HPO_4.2H_2O$	33.4
	NH4Cl	0.5
B	$MgSO_4.7H_2O$	22.5
C	$CaCl_2.2H_2O$	36.4
D	$FeCl_3.6H_2O$	0.25

Biodegradation Kinetics

The biodegradation extents were fitted to the Gompertz model (Eq. 4) to analyze the biodegradation kinetics (Cho *et al*. 2011; Kwon *et al*. 2021, 2023; Lay *et al*. 1997),

$$B = B_0 * exp\left\{-exp\left[\frac{r^{*}2.71828}{B_0}(\lambda - t) + 1\right]\right\} \quad (4)$$

where B_0 is ultimate biodegradation (%), r is initial biodegradation rate (%/day), λ is the lag phase (day) before the initiation of biodegradation, and t is the time (day).

The ultimate biodegradation represents the potential biodegradation extent when the biodegradation period (t) is considered very long (calculated as the limit of an infinite period). However, it is important to note that the calculation herein results from a defined period of observation. The lag phase is the period before the initiation of biodegradation (when the biodegradation extent reaches 6.6% of its maximum rate), and the initial biodegradation rate is the maximum rate before reaching a plateau (Kwon *et al*. 2021). This model has been confirmed as an appropriate fit for biodegradation data in previous research (Lay *et al*. 1997; Cho *et al*. 2011; Kwon *et al*. 2021, 2023; Zambrano *et al*. 2021).

RESULTS AND DISCUSSION

Characteristics of Paper Materials with Additive

The cellulose crystallinity of the hardwood pulp fibers was investigated with XRD analysis, compared to MCC, which is the reference material used for biodegradation experiment. As shown in the normalized XRD spectra in Fig. 2, the HW pulp showed less distinct crystalline peaks (2θ=22.5 for 200 plane, and 2θ= 16.0 for 110 plane) and more prominent amorphous hump (2θ=18.5°) compared to MCC. The crystallinity calculated based on the XRD spectra was 85% for MCC and 66% for HW pulp, agreeing with the previous study (Carrillo-Varela *et al*. 2019). MCC is produced by hydrolytic depolymerization of cellulose to isolate the crystalline regions (Abdelwahab *et al*. 2012; Zarmpi *et al*. 2017; Zhao *et al*. 2022). Thus, the higher crystallinity of MCC is reasonable considering its manufacturing process, which involves breaking down the amorphous (non-crystalline) regions of cellulose fibers.

The surface and cross-sectional images of paper materials with different additives are shown in Fig. 3. Overall, the surface and cross-sectional structures of the paper materials did not exhibit significant differences based on the type of additives used. No local aggregation or flocculation of additives was observed, confirming the controlled preparation of the paper materials. In the cases of C-PAM and PAE, there was some local fiber entanglement, but it was not particularly pronounced.

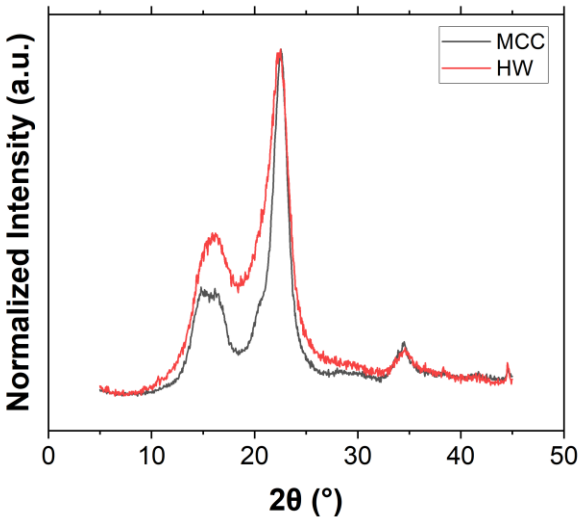


Fig. 2. Normalized XRD spectra of MCC and HW pulp

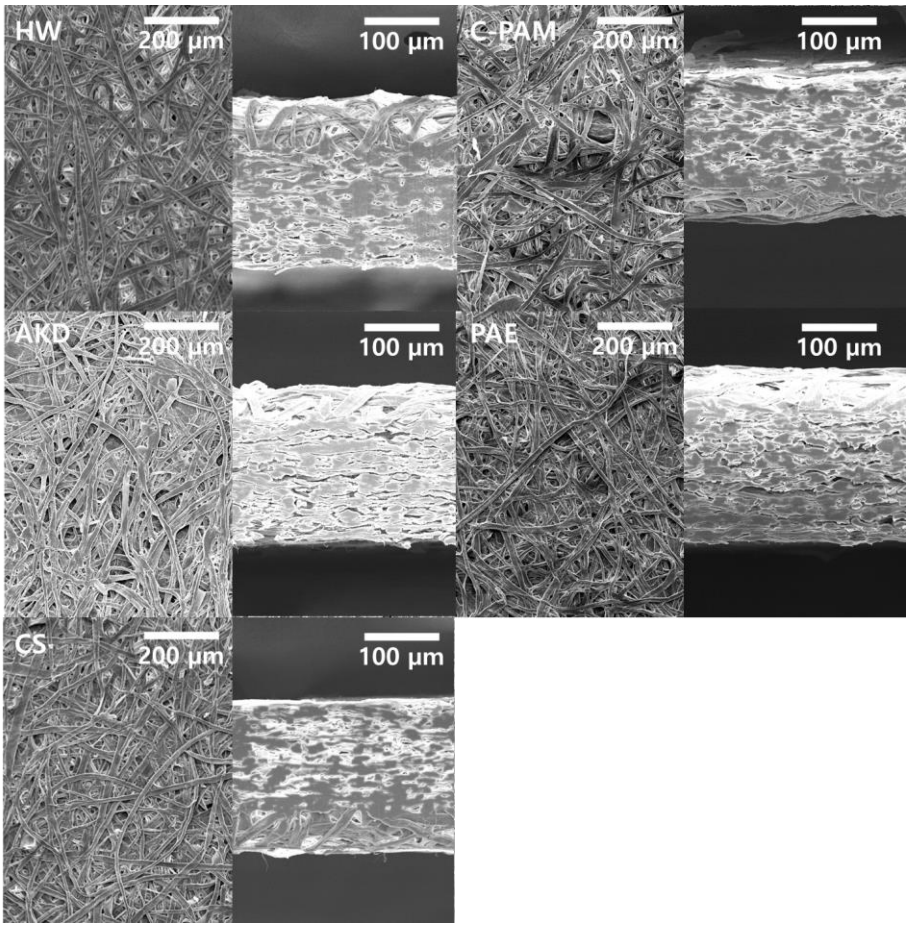


Fig. 3. SEM images of paper materials (left: top-side surfaces at 100x magnification; right: cross-sections at 200x magnification, cut by a razor blade)

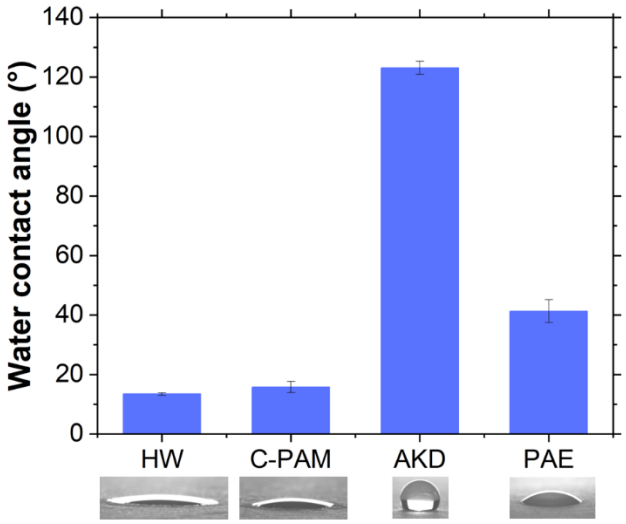


Fig. 4. Water contact angle of paper materials with different treatment

The surface properties of the paper materials were analyzed using water contact angle (WCA) measurements, with the results presented in Fig. 4. The paper material treated with CS was not available to measure the water contact angle, as the water drop spread too

quickly to be analyzed. The HW sample exhibited the lowest WCA, with the water drop being quickly absorbed into the structure in less than 1 second. The C-PAM sample displayed a similar WCA to the HW sample, but the water drops remained on the surface for a longer period, indicating better surface coverage. The AKD sample showed the highest WCA, averaging 123°, followed by the PAE sample, which averaged 41°. This suggests that the AKD and PAE samples have more hydrophobic surfaces compared to the HW and C-PAM samples.

Aquatic Biodegradation of Paper Materials with Additives

Aquatic biodegradation of paper materials was investigated using two different forms: disintegrated fibers and punched paper. Except for the type of material, all other conditions, including temperature, amount of test materials, and stirring conditions, were kept constant. Microcrystalline cellulose (MCC), a well-known biodegradable material, was used as a reference. The validity of the experiments was confirmed by the biodegradation extent of MCC (73% and 72%), which aligns with the ISO test method requirement that the biodegradation extent of reference material should exceed 60% at the end of the test.

Figure 5 shows the biodegradation extent of disintegrated fibers over time, with detailed results presented in Table A1 in the Appendix. The final biodegradation extents of all disintegrated paper fibers were higher than that of MCC, confirming their biodegradability regardless of chemical treatment. The initiation of biodegradation was similar to MCC, but the initial biodegradation rate was faster, likely due to the high biodegradability of hardwood pulp fibers (HW). The biodegradation curve for disintegrated HW paper showed a higher final biodegradation extent and a faster initial rate compared to MCC. The mechanical disintegration likely increased the surface area available for microbial activity, even with the presence of chemical additives.

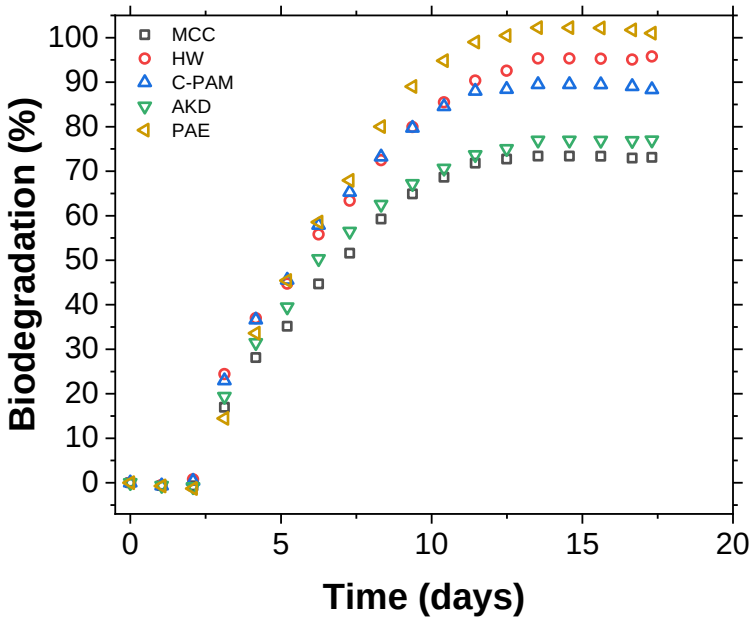


Fig. 5. Aquatic biodegradation result of disintegrated paper materials with additives

The biodegradation of non-disintegrated paper materials was also investigated to compare with the disintegrated forms. The paper materials were cut into circular shapes with a 6 mm diameter to avoid entanglement. The biodegradation results are illustrated in Fig. 6. Similar to the disintegrated samples, all punched paper materials showed higher final biodegradation extents than MCC. However, the lag phase and initial biodegradation rate varied depending on the treatment, with some conditions (e.g., AKD and PAE) showing lower initial slopes. The lag phase and initial biodegradation rates will be further discussed in the next section.

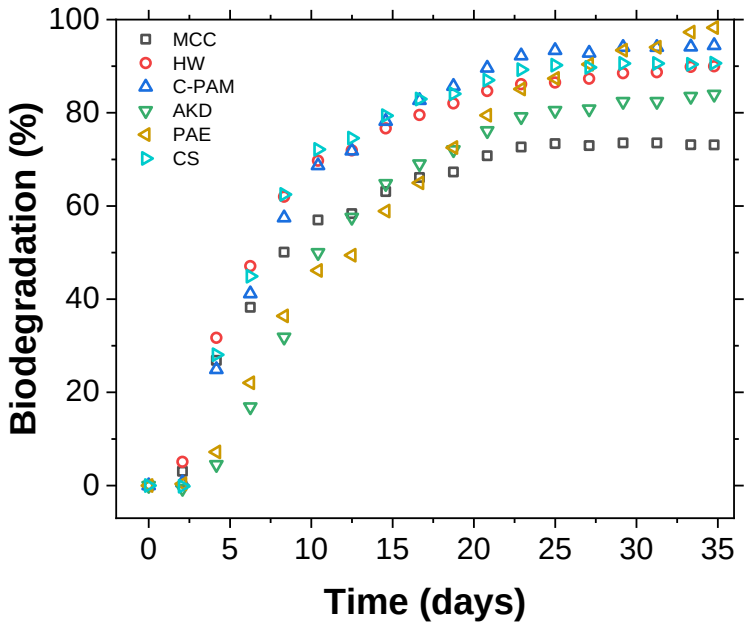


Fig. 6. Aquatic biodegradation result of punched paper materials with additives

Notably, under both conditions, the paper materials made with hardwood pulp (HW) exhibited a higher biodegradation extent, which could extend to other paper materials made from the same pulp but with different additives. This increased biodegradability can be attributed to the lower cellulose crystallinity of HW pulp compared to microcrystalline cellulose (MCC). As shown in the XRD spectra in Fig. 2, HW pulp has less distinct crystalline peaks and a more prominent amorphous hump compared to MCC, resulting in a lower crystallinity index. It is well known that crystallinity is closely related to the biodegradability of polymers, since tightly packed crystalline structures inhibit the access of microorganisms, possibly through the water medium in this study (Kwon *et al*. 2023).

The hemicellulose content in HW pulp also contributes to its biodegradability. HW pulp consists of 80% cellulose and 20% hemicellulose, with hemicellulose having a higher biodegradability and biodegradation rate than cellulose (Kwon *et al*. 2021). Therefore, the fibril structures of hemicellulose and cellulose together might provide better accessibility for microorganisms, leading to easier degradation. Additionally, HW pulp fiber has a high aspect ratio, with a length of 0.86 mm and a width of 19.0 μm, resulting in a surface area of 5.19 x 10^4 μm^2 per particle. In comparison, MCC has a diameter of 50 μm, giving it a surface area of 1.18 x 10^4 μm^2 per particle (assuming a cylindrical shape). Therefore, HW pulp fiber might provide easier access for microorganisms due to its higher surface area, facilitating their biodegradation activity. Moreover, since this research used highly

biodegradable HW pulp as the base material for paper preparation, paper materials made from different pulps, such as Kraft pulp, recycled OCC pulp or mechanical pulp, might exhibit varying biodegradability depending on the additive treatment (Korpela *et al*. 2023), which could be explored in future studies.

The high final biodegradation extent of all paper materials treated with different additives (compared to MCC) suggests that the biodegradability of highly biodegradable fibers, such as HW pulp fibers, remains intact even with the inclusion of chemical additives, including hydrophobic and wet-strength agents. This result emphasizes the environmentally friendly aspects of chemically treated paper materials and demonstrates their potential for various applications as biodegradable materials.

Biodegradation Kinetics of Paper Materials with Additives

The biodegradation kinetics of paper materials with additives were further analyzed for potential tunability. The kinetics were modeled using the Gompertz equation to calculate the lag phase, initial biodegradation rate, and ultimate biodegradation extent (Fig. 7). Differences in the lag phase and initial rate of MCC observed in Fig. 7 (a-d) are attributed to variations in the experimental conditions, likely due to differences in microorganism activity resulting from the collection times of the activated sludges (August for the former and October for the latter). Therefore, all analyses of the other paper material results were conducted by comparing them to the MCC results within each respective experiment.

For disintegrated paper materials (Fig. 7(a)), the lag phase values were similar to MCC regardless of treatment. However, the lag phases differed noticeably from MCC in the biodegradation of punched paper materials, suggesting that fiber disintegration plays a critical role in initiating biodegradation. The laboratory blender may efficiently disintegrate and cut fibers, exposing more untreated surfaces to the water medium and facilitating microbial activity.

Interestingly, hydrophobic treatments like AKD and wet-strength agents significantly increased the lag phase, more than tripling the lag phase of untreated HW paper in punched conditions. In aquatic biodegradation, water diffusion into the polymer chain is crucial, and increased hydrophobicity likely delays this process, thereby delaying biodegradation initiation (Perdoch *et al*. 2023). Notably, in the case of disintegrated paper, the increase of lag phase time for AKD treated was not significant like in the punched condition. This might be attributed to the exposure of the inner surface that was not covered by AKD, weakening the influence of the hydrophobic treatment. Additionally, hydrophilic treatments, such as C-PAM and cationic starch (CS), also delayed biodegradation initiation, possibly due to dense paper structures, as shown in Fig 3.

The initial biodegradation rate of HW samples was higher than that of MCC in both disintegrated fibers and punched paper materials. In both types of samples, AKD treatment slowed down the rate of biodegradation compared to neat HW paper. While PAE in the punched paper showed a slower biodegradation rate, PAE in the disintegrated paper showed a higher rate, suggesting that PAE affects the biodegradation of paper, but its impact diminishes once the paper is disintegrated. The CS condition showed a higher biodegradation rate than other conditions, despite having a longer lag phase than HW. In cross-sectional images in Fig. 3, the CS sample showed a denser and less porous structure. A denser structure might delay the initiation of biodegradation, but since starch is highly biodegradable, it could facilitate the biodegradation of pulp fibers (Sandak *et al*. 2015).

The ultimate biodegradation extents are shown in Fig. 7 (e-f). Overall, all paper samples were found to be highly biodegradable compared to MCC, but the additives did affect their ultimate biodegradation, considering the differences in ultimate biodegradation compared to HW samples. While C-PAM treatment did not significantly change the ultimate biodegradation of HW pulp fibers, AKD decreased the biodegradability of HW fibers, although they still exhibited high ultimate biodegradation. The nitrogen content in PAE might facilitate the activities of microorganisms, as it is an important element for microbial growth, proliferation, and enzymatic activities (Prescott *et al*. 1999), which can accelerate biodegradation (Tanunchai *et al*. 2022). However, it is still unclear how microorganisms utilize the nitrogen in the PAE structure, and this aspect is beyond the scope of our research. Nevertheless, the results with PAE suggest that even if the paper was treated with the wet strength agent PAE, which could inhibit fiber disintegration in water, the paper could still be fully biodegradable once the fibers are disintegrated over a longer period, consistent with the previous reports (Kanie *et al*. 2005; Paudel *et al*. 2022).

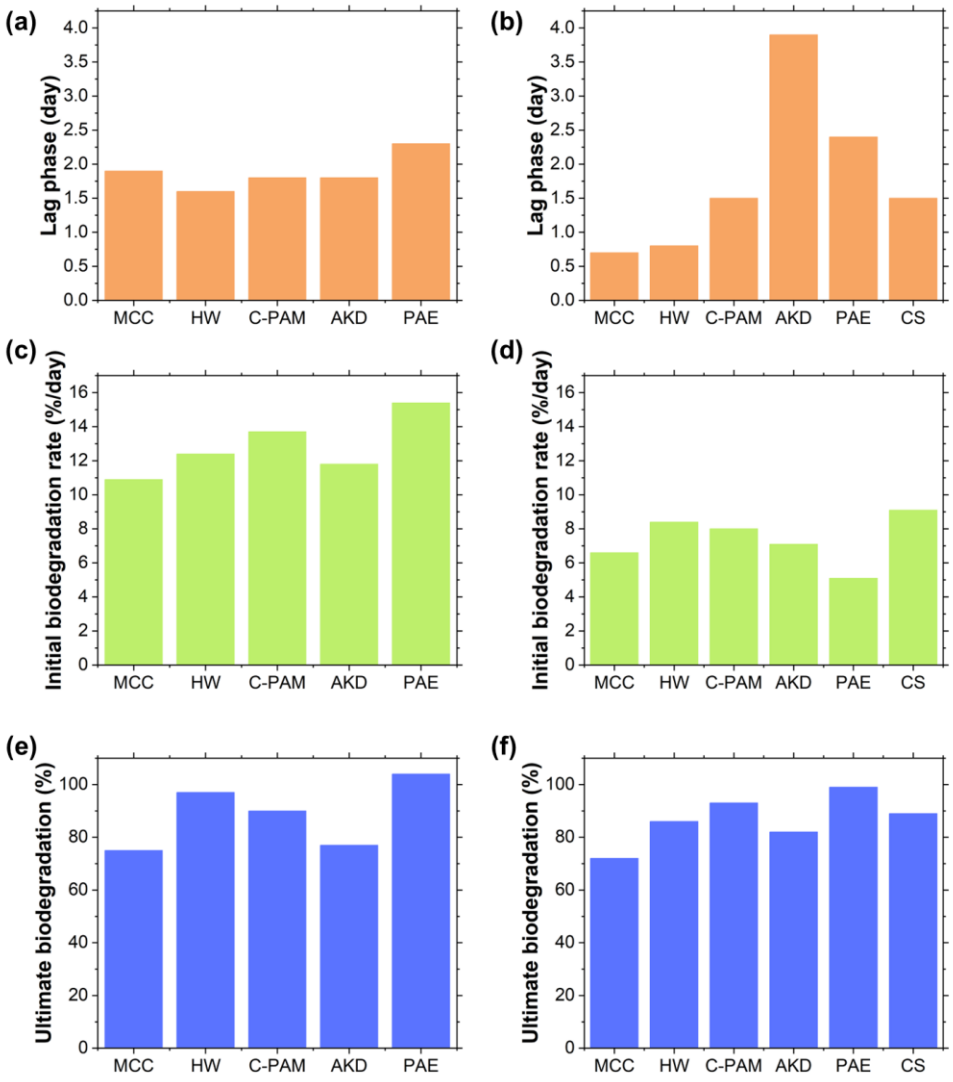


Fig. 7. Lag phase, initial biodegradation rates, and ultimate biodegradation extents of paper materials with different additive treatments. The lag phase is the period before the initiation of biodegradation. (a, c, e): disintegrated paper materials, (b, d, f): punched paper materials.

This research showed the effect of several papermaking additives on the biodegradability of paper materials in terms of their biodegradation kinetics, including lag phase, initial biodegradation rate, and ultimate biodegradation extent. Overall, while additives can change the initiation or rate of biodegradation, the biodegradability of paper materials remains intact even after hydrophobic or wet-strengthening treatment. These results demonstrate the potential for tuning the biodegradation and durability of paper materials with various additives, suggesting the feasibility of designing paper products that are durable during use but ultimately biodegradable at the end of their life.

CONCLUSIONS

1. The biodegradation kinetics of paper materials with various additives were successfully modeled using the Gompertz equation, providing insights into the lag phase, initial biodegradation rate, and ultimate biodegradation extent.
2. Disintegrated paper materials exhibited similar lag phase values to microcrystalline cellulose (MCC) regardless of treatment, while punched paper materials showed noticeable differences, suggesting that fiber disintegration plays a critical role in initiating biodegradation.
3. Hydrophobic and crosslinking treatments, such as AKD and wet-strength agents, PAE, significantly increased the lag phase, indicating that increased hydrophobicity delays water diffusion into the polymer chain and thus delays biodegradation initiation. Notably, AKD also slowed down the initial biodegradation rate. However, their ultimate biodegradation extent remained intact.
4. The research demonstrates that the biodegradability of paper materials can be maintained even after chemical treatments, highlighting the environmentally friendly potential of using paper materials with various additives for different applications.

ACKNOWLEDGMENTS

Not applicable.

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APPENDIX

Table A1. Final Biodegradation and Results of Kinetic Analysis of Paper Materials

Sample		Final biodegradation (%)		Lag phase (day)	Initial biodegradation rate (%/day)	Ultimate biodegradation (%)
Disintegrated	MCC	73	±0	1.9	10.9	75
	HW	96	±8	1.6	12.4	97
	CPAM	88	±6	1.8	13.7	90
	AKD	77	±16	1.8	11.8	77
	PAE	101	±5	2.3	15.4	104
Punched	MCC	72	-	0.7	6.6	72
	HW	90	±12	0.8	8.4	86
	CPAM	94	±0	1.5	8.0	93
	AKD	84	-	3.9	7.1	82
	PAE	98	±3	2.4	5.1	99
	CS	91	±29	1.5	9.1	89

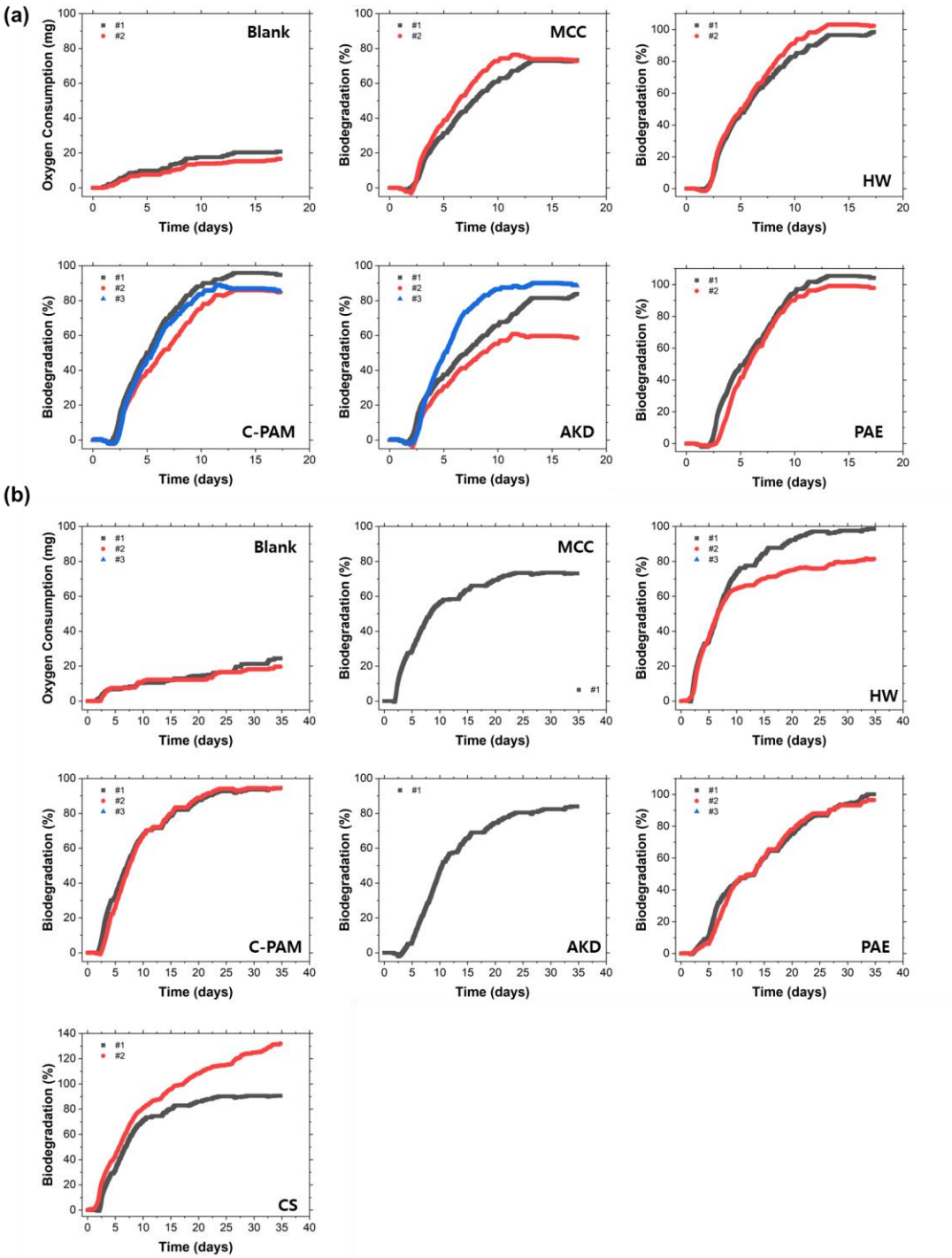


Fig. A1. Individual results of each material. (a): disintegrated fibers, and (b): punched paper.