

Hydrolysis of the Amorphous Cellulose in Cotton-Based Paper

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Hydrolysis of cellulose in Whatman no. 42 cotton-based paper was studied using gel permeation chromatography (GPC), electrospray ionization-mass spectrometry (ESI-MS), and uniaxial tensile testing to understand the course and kinetics of the reaction. GPC results suggested that scission reactions passed through three stages. Additionally, the evolution of soluble oligomers in the ESI-MS data and the steady course of strength loss showed that the hydrolysis reaction occurred at a constant rate. These findings are explained with a more detailed description of the cellulose hydrolysis, which includes multiple chain scissions on amorphous segments. The breaks occur with increasing frequency near the ends of amorphous segments, where chains protrude from crystalline domains. Oligomers unattached to crystalline domains are eventually created. Late-stage reactions near the ends of amorphous segments produce a kinetic behavior that falsely suggests that hydrolysis had ceased. Monte Carlo simulations of cellulose degradation corroborated the experimental findings.

Introduction

Reactions of native cellulose have been studied for many years because of their importance to the durability of paper and textiles,¹ the synthesis of cellulosic derivatives,² and more recently, biomass conversion³ and polymer reinforcement.^{4,5} Of these areas, the stability of cellulose paper has attracted the most interest due to its importance in the preservation of library and archival materials^{6,7} and in industrial applications such as transformer insulation.^{8,9} Cotton-based papers have been widely studied because they provide an ideal material with which to explore fundamental cellulose properties and degradation reactions. Many advances have already been made in the understanding of cellulose reactions and of the fundamental relation between cellulose supramolecular structure and physical properties.

Degradation of cotton-based paper under normal aging conditions is primarily the result of the breaking of cellulose molecules through hydrolysis.^{10,11} The reaction is catalyzed by acid and requires the ready availability of water. In homogeneous conditions, hydrolysis of cellulose occurs randomly, with equal probability of attack at any link along the cellulose chain. In the solid state, however, hydrolysis is not random along the entire length of the chain. Because the compact organization of crystalline domains does not permit penetration of water and acid catalysts or the separation of chain fragments following bond breaking, hydrolytic degradation occurs only within the amorphous domains.

While the fundamental chemistry and mechanisms of heterogeneous hydrolysis in native cellulose fibers have been well established, details of the process remain elusive.^{12–14} As with most polymer reactions, cellulose hydrolysis has been probed mainly through measurement of scission reaction kinetics, which are derived from measurements of molecular weight changes. Simple models accurately describe the early stages of degrada-

tion. However, when the average molecular weight of the material approaches that of the microcrystalline cellulose, the so-called “leveling-off degree of polymerization” (LODP), models begin to fail. Studies persist that analyze chain-breaking kinetic results in terms of the hydrolysis rate approaching zero as the LODP is reached¹² even though the reason for such a deceleration is not made clear.

The major obstacle to a more detailed kinetic analysis of heterogeneous cellulose hydrolysis is the incomplete understanding of the nature of the amorphous domains in cellulose.^{15,16} While the crystalline phase can be investigated directly with various X-ray or particle scattering techniques, the amorphous cellulose can only be observed indirectly. Measurements of accessibility¹⁷ or reactivity^{18,19} only provide the amount of amorphous material relative to the crystalline phase, and studies of cellulose hydrolysis have suggested that only a portion of the amorphous phase is accessible for this reaction.¹⁸ Spectral changes due to mechanical strain²⁰ serve to verify the existence of tie chains but are imprecise probes of their nature. The descriptions of such basic features as the concentration of tie chains and their segment length are still lacking. A more refined kinetic model of cellulose hydrolysis can only be developed as a more detailed picture of the amorphous phase emerges.

This paper re-examines the hydrolytic deterioration of cellulose in aging cotton paper in order to gain insight into the course of the hydrolysis reaction in the amorphous phase. Using acid vapor exposure as well as prolonged oven-aging, very extensive degrees of reaction are explored using gel permeation chromatography (GPC) for molecular weight measurements, electrospray ionization-mass spectroscopy (ESI-MS) for solvent-soluble oligomer production, uniaxial tensile testing for physical strength measurements, and Monte Carlo computer simulations for the kinetics of the hydrolysis reaction. From these results, the course of the hydrolysis and the nature of the amorphous tie chains are inferred. The apparent changes in the kinetic rate of the reaction are analyzed to verify the realm within which the simple kinetic model of random chain-breaking is appropriate and the point in the degradation when that simple analysis no longer tracks the degradation accurately. This investigation

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provides a more complete picture of amorphous cellulose in cotton fibers and its degradation.

Experimental Section

Samples of pure cotton cellulose paper (Whatman no. 42) were studied. This paper was made from cotton linters that were acid-washed during manufacture to remove residual metal ion impurities. A cold-extract pH of the paper was measured to be 4.7 according to TAPPI 509-88. These papers were studied as supplied from Whatman.

Solvents used were distilled water, 12 M hydrochloric acid (HCl), and HPLC grades methanol and *N,N*-dimethylacetamide (DMAc), respectively. DMAc was stored over a 4 Å molecular sieve that had previously been dried for 4 h at 250 °C. Lithium chloride (LiCl) was reagent grade (99+%) and was used after drying at 105 °C.

Paper samples were hydrolyzed in one of two ways. To dissolve the amorphous phase leaving only microcrystalline cellulose,^{21–24} two samples of Whatman 42 paper, an untreated one as well as one that had been aged for 5024 h at 90 °C, 50% RH, were each suspended in a closed vessel over 12 M hydrochloric acid (HCl) at room temperature for 96 h. To create cellulose hydrolyzed to a lesser degree, untreated papers were aged in a Blue M oven at 90 °C and 50% relative humidity (RH), using the residual acidity of the paper to act as catalyst for the hydrolysis. For this oven-aging treatment, 8 in. × 8 in. samples were arranged in stacks of 40 sheets between 9 in. × 9 in. glass plates. This stack configuration retained some volatile degradation products generated during the oven-aging that might otherwise escape from free-hanging sheets.²⁵ Three individual sheets were removed from the stack at various time points, ranging from 144 h to 11688 h of oven-aging. For chemical analysis, specimens were taken from the center of an aged sheet.

A modification of the solvent exchange protocol developed by others^{26–29} was used to prepare paper samples for GPC analysis. A 40–50 mg paper sample was soaked in 5 mL of water in a volumetric flask for 24 h. The water was then filtered out, and the sample was stirred two times in methanol for 1 h, followed by filtration. This procedure was repeated using DMAc. Finally, the sample was dissolved in 5 mL 8% (w/v) LiCl/DMAc, stirred continuously for 24 h at room temperature, and then stored at 4 °C for 7 days. On the day of analysis, sample solutions were diluted to 0.0625% (w/v) cellulose in a 0.5% (w/v) LiCl/DMAc solution. Although the solutions appeared clear and free of suspended particulates, they were still filtered with a 0.45 μm Teflon Acrodisc syringe filter before injection.

Molecular weight distributions (MWDs) of the dissolved paper samples were measured using a Waters 2695 separations module coupled to a Waters 2414 refractive index detector and Empower software, database version 5.0. Separations were carried out using three Waters HR Ultrastaygel columns, HR5, HR4, and HR3, held at 70 °C. The refractive index detector was set to its highest temperature, 50 °C. The mobile phase was 0.5% (w/v) LiCl/DMAc and flowed at a rate of 1 mL/min. An autosampler was used to inject 125 μL aliquots of sample solution into the GPC. Eight pullulan standards covering the range of molecular weights were dissolved in the 0.5% LiCl/DMAc solvent and analyzed to generate a calibration curve. Averages of three injections of each sample solution were used to determine the MWD and weight-average molecular weight (M_w).

Soluble residues were extracted from 4 g portions of aged paper samples placed in a Petri dish to which 10 mL of water was added and allowed to evaporate. The extraction procedure was repeated in the Petri dish with 10 mL of methanol and then again with the same amount of DMAc. After the final extraction, the solid residue left in the Petri dish was removed, transferred to a vial, and dissolved in water to make approximately 500 pmol/μL solutions for analysis. To make that concentration, it was assumed that the molar mass of the residue was equivalent to glucose, 180 g/mol. Mass spectra were acquired using a ThermoFisher LCQ quadrupole field ion trap mass spectrometer with an electrospray ionization source and Excaliber 1.3 software. Samples

Table 1. Measured Weight-Average Molecular Weight (M_w), Degree of Polymerization (DP), Polydispersity (PD), and Dry and Wet Tensile Strengths of Whatman 42 Paper during Aging at 90 °C and 50% RH

hours aged	M_w (g/mol)	DP	PD	sheet strength (N/m)			
				dry	error	wet	error
0	170000	1050	3.3	3410	70	460	10
144	130000	780	3.2	3180	60	470	30
840	74000	460	3.0	2650	130	380	20
1608	61000	380	3.1	1820	50	230	30
2424	56000	350	3.1	1520	60	180	10
3192	51000	310	3.2	1350	70	120	10
4296	50000	310	3.0	1190	30	93	11
6360	48000	290	3.1	1100	100	65	6
7320	47000	290	3.1	1090	60	63	7
11688	47000	290	3.2	890	40	53	4

were introduced at a flow rate of 5 μL/min. Data were collected in positive ion mode. Full scans were collected over a mass range of 150–2000 Daltons (Da), and 20 microscans were collected per scan. Spectra were an average of at least 40 scans.

An Instron 4443 with pneumatic grips and controlled by Series IX software was used to measure the tensile strength of samples in uniaxial tension. Tests were conducted at 23 °C and 50% RH after conditioning the paper samples at those conditions for 24 h. The ASTM standard test method ASTM D828-97 was followed with several exceptions. Clamps used to hold paper samples were composed of two flat surfaces. The gauge length was modified to 40 mm. The sample width was 15 mm, and the length was 100 mm. Samples were pulled at 25.4 mm/min. Paper samples that had been oven-aged for short times were cut to the 15 mm width using a specimen cutter. Paper samples aged for long times were too fragile to be cut in the specimen cutter, so they were measured and cut with a razor blade and metal ruler. For papers aged for short times, a 500 N load cell was used. Those aged for longer times were tested using a 50 N or 10 N load cell depending on the expected failure stress. Tensile strengths reported were the stress at break normalized to sample cross-sectional area and data were the average of the results for 10 strips taken from the same sample sheet. Dry strengths were measured on sheets as conditioned in the constant environment. Wet strengths were measured after saturating the paper sample with water for 1 min prior to mounting in the Instron.

Results

Molecular weight analysis of unaged and thermally aged cotton cellulose samples showed that oven-aging the cotton paper caused chain scission reactions to occur, decreasing the average molecular weight over time (Table 1). Select MWDs for the paper samples are shown in Figure 1. Unaged Whatman 42 paper exhibited a monomodal MWD with $M_w = 170000$ (DP = 1050). For aging times up to 3192 h, the average molecular weight decreased steadily to $M_w = 51000$ (DP = 310). After that time, reduction in the molecular weight slowed significantly, decreasing only 20 DP units over the subsequent 8500 h of aging.

Starting at 840 h of aging, in addition to the large peak in the MWD of the oven-aged cellulose, a shoulder developed in the low molecular weight region. This shoulder is indicated with an arrow in Figure 1 on the chromatograms of samples aged for 2424 and 11688 h. Once the shoulder appeared in the chromatograms, its intensity slowly increased with further aging, however its elution time did not shift with continued oven-aging.

The nature of the shoulder in the low molecular weight region was examined two ways. First, an unaged Whatman 42 paper was exposed to acid vapors, which effectively eliminated the amorphous phase, leaving an molecular weight distribution

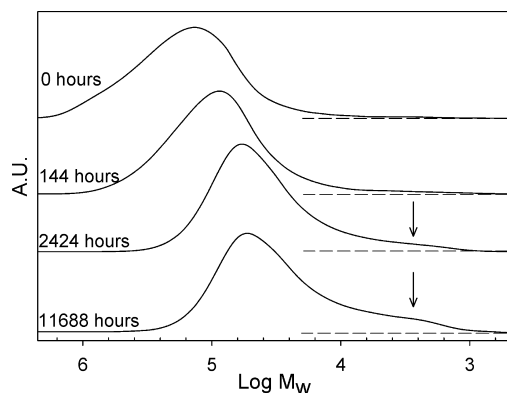


Figure 1. Molecular weight distributions of cellulose in Whatman 42 papers before and during oven-aging at 90 °C and 50% RH. Curves vertically offset for clarity.

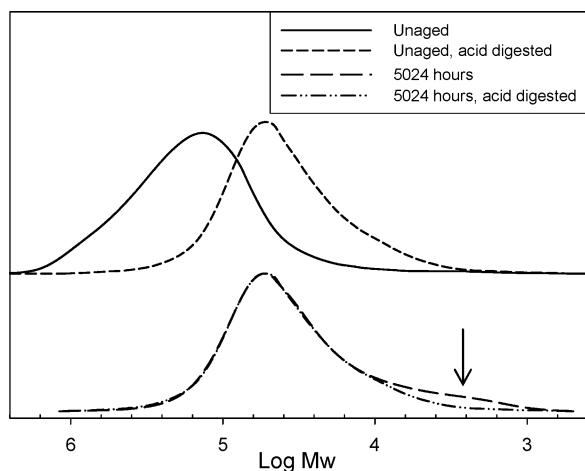


Figure 2. Molecular weight distributions of unaged, unaged and acid-digested, 5024 h aged, and 5024 h and acid-digested cellulose in Whatman 42 papers.

comprised only nonhydrolyzable crystals.^{21–24} If the shoulder in the MWD was related to the crystalline phase of the cellulose, the acid treatment would reproduce the shoulder in the GPC chromatogram that was observed in the thermally aged samples.

The top portion of Figure 2 shows an overlay of the unaged and unaged then acid-digested Whatman 42 GPC chromatograms. The MWD of the acid-digested paper was monomodal with $M_w = 60000$ (DP = 370). No shoulder was observed in the acid-soaked sample, indicating that the shoulder observed in thermally aged samples was not part of the crystalline phase.

Further support for the identification of the low MW shoulder as a residue of amorphous cellulose was provided in a second investigation. A sample that previously showed evidence of the shoulder in its chromatogram, a 5024 h aged sample, was exposed to acid vapors. The MWDs of the cellulose after oven-aging and following subsequent acid exposure are shown in the bottom half of Figure 2. Acid vapor exposure left the high molecular weight peak essentially unchanged, while the low molecular weight shoulder was eliminated. Hence, the shoulder that developed during oven-aging was a product of degradation reactions; further, the shoulder that developed was comprised of hydrolyzable amorphous cellulose.

Another method to probe amorphous phase degradation products of cellulose was to examine the solvent-extractable material of oven-aged Whatman 42 paper samples using ESI-MS. Mass spectra of residues taken from samples aged for various times are shown in Figure 3. These spectra showed the

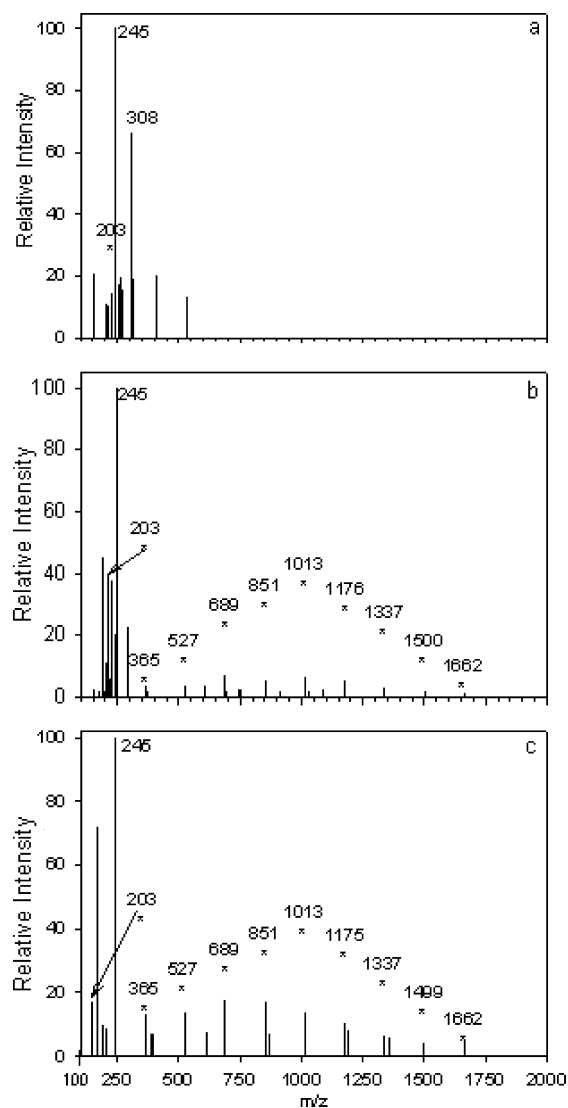


Figure 3. ESI-mass spectra of the solvent-extracted residues from Whatman 42 papers aged at 90 °C, 50% RH for: (a) 144 h, (b) 2424 h, (c) 3636 h.

presence of a number of compounds, including Na^+ -adducts of glucose and of cellulose oligomers up to DP = 10. The sodium adducts of glucose (m/z 203), cellobiose (m/z 365), cellotriose (m/z 527), cellotetraose (m/z 689), cellopentoise (m/z 851), cellohexose (m/z 1013), celloheptose (m/z 1175), cellooctose (m/z 1337), cellononose (m/z 1500), and cellodecose (m/z 1662) are indicated with stars on the mass spectra in Figure 3. These oligomers were observed in extracts from all but the least aged sample (144 h), where only the Na^+ -adduct of glucose was identified. As aging progressed, it was possible to observe increasing amounts of the aforementioned oligomers.

The effect of amorphous phase degradation on the physical behavior of Whatman 42 paper was probed. The tensile strength of the sheets decreased with oven-aging (Figure 4). The dry tensile strength of the sheet, a summation of intra- and intermolecular bonding, began at 3410 N/m, decreased exponentially to 1350 N/m at 3192 h of aging, and had a calculated exponential decay of $18.3 e^{-0.0003t}$ with an $r^2 = 0.97$. After 3192 h, the strength decreased progressively more slowly to a value of 890 N/m at 11688 h. The wet tensile strength showed similar behavior to the dry strength behavior. Wetting the paper served to eliminate bonding between fibers, permitting intramolecular bonding alone to be analyzed.³⁰ At the start

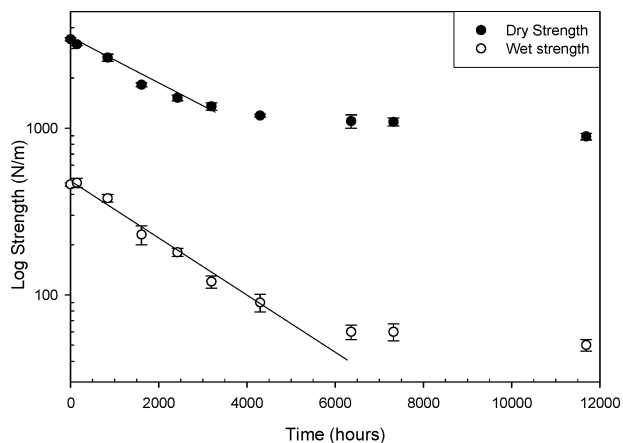


Figure 4. Changes in measured dry and wet strength of Whatman 42 papers during thermal aging at 90 °C and 50% RH: (●) dry strength. (○) wet strength.

of oven-aging, the wet tensile strength was only 460 N/m. Oven-aging reduced that value to 53 N/m after 11688 h. The wet strength decreased according to an exponential function (Figure 4) for the first 6360 h. The calculated exponential decay for that period was $\text{strength} = 2.5 e^{-0.0003t}$ with an $r^2 = 0.97$.

Discussion

Polymer degradation reactions are typically investigated by examining the kinetics of the chain-breaking. This is typically done using any of a number of equations that utilize changes in molecular weight averages for model polymer MWDs. A common formula that has been used for cellulose reactions is:

$$N = (M^0/M) - 1 \quad (1)$$

where N is the calculated number of breaks per original chain, and M^0 and M are the average molecular weights (or degrees of polymerization) for the ensemble at the start of the reaction and after some degradation has occurred, respectively. This equation is strictly true only if the number-average molecular weight (M_n) or degree of polymerization (DP_n) is used.³² However, the weight-average molecular weight (M_w) or degree of polymerization (DP_w) can also be used provided the polydispersity does not change. According to the measured polydispersities shown in Table 1, that value stayed relatively constant during the oven-aging. Chain breaks have been calculated from the measured M_w for the cellulose and are shown during the oven-aging treatment in Figure 5.

This kinetic view of cellulose degradation from thermally accelerated hydrolysis has been observed in a prior study.¹² The picture presented is usually interpreted as a degradation reaction occurring with an initial period of rapid hydrolytic attack on amorphous chain segments, a late period of extremely slow chain-breaking as hydrolytic attack occurs to crystal ends and surfaces, and an intermediate period of transition between the initial and late rates. While this view does tend to conform to fundamental notions of hydrolytic reaction in a semicrystalline polymer, the kinetic course of the degradation has also been used to argue for the existence of sites on cellulose chains of greater or lesser reactivity^{30,31} and the cessation of hydrolysis once the final slow rate has been established.

There are a number of reasons for skepticism of a picture of hydrolysis that slows and ultimately stops during the oven-aging. It is well-known that large decreases in MW can be achieved

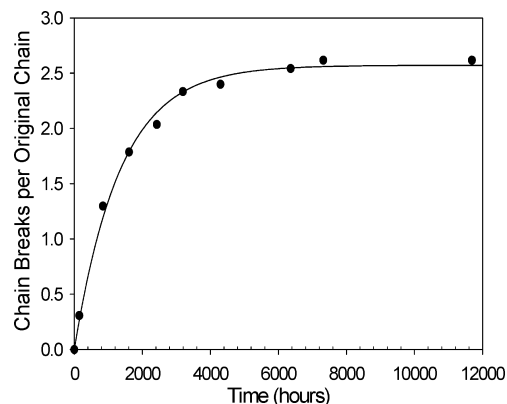


Figure 5. Apparent chain breaks using conventional approach to calculating degradation from GPC M_w data.

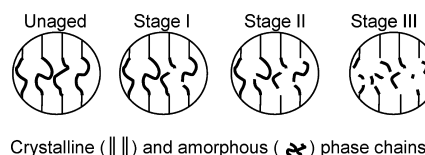


Figure 6. Model illustrating the stages in hydrolytic degradation of semicrystalline cellulose.

with relatively few numbers of chain breaks. It is possible that all available links have been broken by the time the calculated kinetic rate has decreased to its very small late stage value. If that were the case, however, one would expect the amorphous segments to have been completely reduced to glucose. Yet for the oven-aged papers, glucose was not the only breakdown product observed. For those samples, there was also evidence in the GPC MWDs and in the extractable residues analyzed by ESI-MS of higher MW oligomers. These oligomers demonstrate that not all the available cellulose links had been reacted, and the acid vapor exposures of the oven-aged papers show that further hydrolysis of these fragments can indeed occur.

Finally, the kinetic course of the strength loss is consistent with a first-order process having a single rate, at least up to the point when the strength value stabilizes at very long aging times. As has been observed by others in earlier studies,^{13,32,33} the loss of strength follows a roughly exponential course if the underlying chain-breaking occurs at a constant rate. In the present study, the wet tensile strength decreased exponentially up to 6360 h for the wet measurements; after that time, the strength stayed relatively constant (Figure 4b). This experimental finding indicates that the hydrolysis of the tie chains, which is reflected in the wet strength loss, probably occurred at a constant rate, at least up to 6360 h. Thus there seems to be little evidence of the hydrolysis rate decreasing during the intermediate transitional period.

The experimental observations and the kinetic analysis presented here can be explained with a new, more detailed structural model of the hydrolytic breakdown of the cotton cellulose that includes a more reasonable description of the progress of hydrolysis in the amorphous regions. Hydrolysis of the amorphous cellulose is expected to follow a course that passes through several stages, illustrated in Figure 6. As hydrolytic chain-breaking commences in the amorphous cellulose, each reaction results in the breaking of an amorphous tie chain (stage I, Figure 6). Assuming that the amorphous tie chains originally extend through crystalline segments, the broken chain fragment created will be at least one crystalline segment length shorter than the original chain length. As a result, a

significant reduction to the weight-average molecular weight will be observed.

Continued hydrolytic reaction in the amorphous phase results in the situation illustrated as stage II in Figure 6. In this stage, which is essentially a transition stage, the amorphous phase is composed of a decreasing number of unbroken tie chains as well as an increasing number of broken tie chains, which occur as dangling amorphous tie chain fragments emerging from crystalline segments. Unlike the reaction in stage I, which occurred predominantly on unbroken tie chains, hydrolytic attack in this stage will occur with increasing frequency on already broken amorphous tie chains. When the breaks occur at chains that are no longer intact tie chains, no loss of strength will result. Thus the strength will be lost progressively more slowly with further reaction: the strength loss will be first-order in the population of intact tie chains. The chain-breaking of already broken amorphous tie chains will occur near the ends of the amorphous chain segments. This will cause the reaction to become increasingly nonrandom, with degradation occurring on the amorphous chain segments dangling from the crystals while the chain lengths within the crystals are protected from hydrolytic attack. Because the chain-breaking is occurring near the ends of the amorphous tie chain fragments, the weight-average molecular weight will not decrease as rapidly as observed during stage I.

During stage II degradation, hydrolysis on the dangling amorphous tie chain fragments also produces fragments that are no longer connected to any crystalline segment. These fragments are free oligomers, the smallest of which may be extracted from the fibers. These two phenomena, the onset of nonrandom degradation and the generation of free oligomers, define stage II of the reaction.

After very extensive hydrolysis, stage III degradation is reached (Figure 6). Here, nearly all the tie chains have been broken so that the strength derived from the connectivity of the cellulose network is nearly gone. The once-broken amorphous tie chain fragments dangling from the ends of the crystalline segments continue to undergo chain-breaking, and the free oligomers created from multiply broken amorphous tie chains continue to react to form ever-smaller oligomers. Assuming that these amorphous segments are relatively short and in low abundance, little change in the average molecular weight will be observed because the molecular weight distribution will be dominated by the chains bound in the crystalline phase.

This picture provides an explanation for nearly all the experimental observations in the present study. Up to 144 h of oven-aging, the paper degraded according to stage I of the hydrolytic reaction. Changes in molecular weight and reduction of strength were large, as tie chains in the amorphous regions were broken. By 840 h of aging, the hydrolysis entered stage II. Free oligomers (the shoulder in the MWD measured by GPC and as the soluble fragments analyzed by ESI-MS) began to be produced, which indicated the tie chains were breaking more than once. The calculated kinetic rate also seemed to slow at this time. According to the model, this slower rate resulted from degradation occurring near the ends of the amorphous tie chain segments, where the amorphous fragments emerged from the crystals, which caused a smaller reduction of the average molecular weight. Finally, after approximately 6360 h of aging, the hydrolysis entered stage III. The calculated chain-breaking rate seemed to decrease to nearly zero, for the MWD was dominated by the unreactive crystalline cellulose. Hydrolysis

was still occurring on the remnants of the amorphous chain fragments emerging from the crystals and to the oligomers.

To gain support for the view that the course of hydrolysis in the semicrystalline cotton cellulose is constant, Monte Carlo modeling was undertaken to generate a reaction kinetics curve and to model the oligomer production and strength loss for degradation of a semicrystalline polymer assuming the kinetic rate was constant. For this simulation, a monodisperse ensemble of 100 polymer chains was created, with each chain having four crystalline segments 200 monomers long connected by three amorphous tie chain segments 25 monomer units long. This crystallite dimension and degree of crystallinity approximate those values measured in cotton cellulose undergoing hydrolytic attack.³⁴ Links within the amorphous phase were randomly broken, while those in the crystalline phase were not allowed to undergo chain-breaking. Neither interactions between the chains nor cross-linking was permitted. The results of the Monte Carlo simulations were an average of 10 runs of the simulation, with each run proceeding until 2000 breaks had occurred on the entire ensemble. This degree of degradation corresponded to the breaking of roughly 28% of the available links in the amorphous chain segments.

For this simulation, after a number of chain breaks were performed on the ensemble, the weight average degree of polymerization (DP_w) of the ensemble was determined and eq 1 was used to calculate the apparent progress of the degradation. The kinetic curve was generated assuming that equal numbers of chain breaks occurred during each time period, i.e., the reaction rate was constant throughout.

The kinetic behavior generated from the simulated steady chain-breaking is shown in Figure 7a. The simulation demonstrated that even when the degradation rate was constant, three stages of degradation resulted. This result corroborated the structural model proposed above. In the initial stage, the chain-breaking calculated from the DP_w of the ensemble showed a roughly linear time dependence. At an intermediate stage, the simulation began to show a slowing in the kinetics of chain-breaking. With very extensive degradation, the calculated chain breaks showed that essentially no hydrolysis was occurring. It is clear from the simulation that the distortion of the underlying constant reaction rate is a result of the increasingly nonrandom reaction localized nearer the amorphous tie chain ends. This pattern would result in the polydispersity of the ensemble changing so that the validity of 1 no longer holds. The experimental GPC results did not indicate such a change in polydispersity. However, this may be a consequence of the poor ability of GPC analysis to accurately track low molecular weight fragments, which are crucial to accurate determinations of M_n . Furthermore, it is apparent that the low MW material in the experimental MWD is present in only very small quantities relative to the crystalline fraction, a reflection of the high crystallinity of cotton cellulose.

This Monte Carlo simulation suggests that, for highly crystalline native celluloses, experimentally measured MWDs may not indicate when the polydispersity has changed due to the generation of low molecular weight fragments as the reaction becomes nonrandom. Thus, one must exercise caution, using only the early stage I results to determine hydrolysis rates for eq 1 may only be valid during this period. Reaction rates derived from later periods in the kinetic curve may be distorted by the progressively more nonrandom course of the reaction.

The simulation was also used to examine the production of free oligomers during the degradation from the multiple breaking of amorphous tie chains. Figure 7b shows that two populations

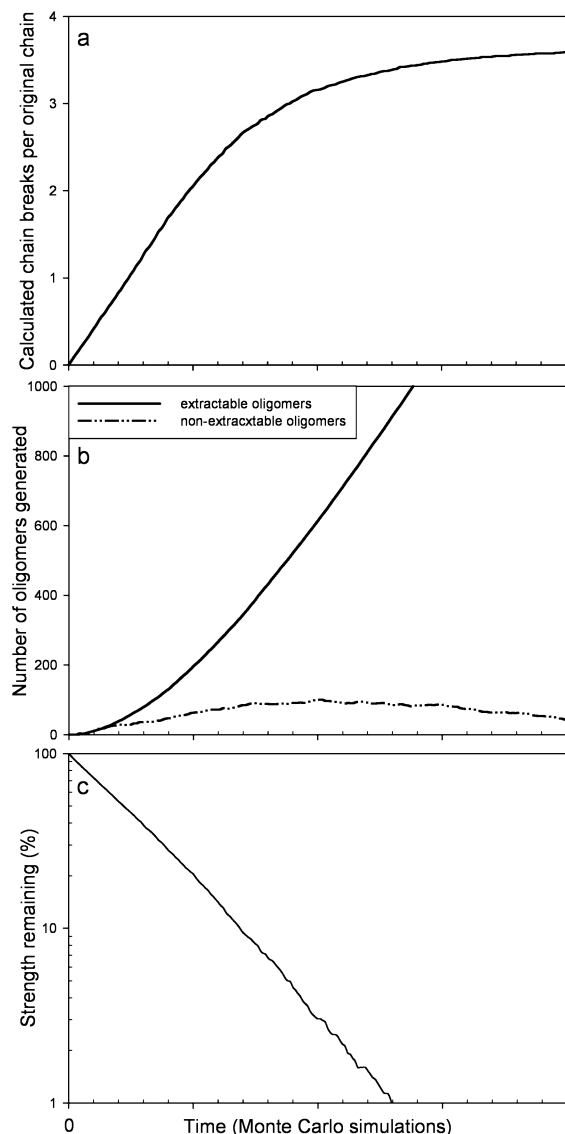


Figure 7. Results of Monte Carlo simulations. (a) Chain-breaking kinetics calculated from weight-average DP of the ensemble; (b) generation of extractable (DP = 1–10) and nonextractable (DP = 11–25) free oligomers; (c) changes in strength, calculated from the percent of unbroken tie chains for ensemble experiencing chain-breaking at a constant rate with time.

of oligomers were tracked in the simulation. One group comprised the smaller oligomers, DP = 1–10, which were meant to represent the fragments that could be extracted and analyzed by ESI-MS. The larger oligomers, DP = 11–25, were meant to represent those fragments that would be retained in the GPC analysis and would appear as the low MW material in the MWD. Figure 7b shows that small oligomer products were produced very early in the simulated degradation, for these can be created from virtually every broken tie chain fragment and their concentration steadily increased throughout the reaction. The higher oligomers, which can only be produced from long amorphous tie chain fragments, were not produced in significant quantities until many amorphous tie chains had been broken. This trend was observed in this experimental study. The first soluble fragment observed was glucose, after 144 h of oven-aging, which also agrees with prior studies that have reported the detection of glucose in papers that were oven-aged for only a relatively short time.^{35,36}

According to the Monte Carlo simulation, the abundance of the nonextractable oligomers, which were observed as the

shoulder on the MWD measured in the GPC analysis, should increase to a low level and then slowly decrease as hydrolysis breaks these fragments into smaller products (Figure 7b). During the oven-aging experiment reported here, only the slow emergence of the low molecular weight fraction in the MWD was observed. The predicted decline of these oligomers was not observed, perhaps because the oven-aging had not progressed to the extent necessary to observe the further reaction of this material. It was only with extensive hydrolysis by exposure to acid vapors that the nonextractable oligomers were seen to disappear as they degraded to form extractable residues, which were then lost during the sample workup for the GPC analysis.

The Monte Carlo simulation also permitted the prediction of the loss of strength in the semicrystalline material, which is a function of the number of amorphous tie chains.³⁷ By tracking the decrease in the total surviving tie chain segments as degradation proceeded, the loss of strength was predicted, shown in Figure 7c. For chain-breaking occurring at a constant rate in this simulation, the strength loss was roughly exponential with time, as indicated by the linear relationship on the semilogarithmic plot. This was consistent with the notion that chain-breaking was first-order in the remaining intact tie chains, with reaction at links on intact tie chains being progressively less likely to occur as the population of those tie chains decreases. This single exponential time dependence for the strength loss was also observed in the experiment (see Figure 4), at least for the first few thousand hours of oven-aging.

The nonzero strength levels reached for the very degraded paper were not predicted by the Monte Carlo analysis. This could indicate that the residual strength derives from interactions between chains, which were not allowed in the simulation. At this very late stage of degradation, there is little fiber strength from the few surviving tie chains, as the fiber comprises essentially nonhydrolyzable crystals and free oligomers. Thus the fiber, which once a series of crystals held together by amorphous tie chains, van der Waals forces, and hydrogen bonding must now be held together only by the attractive forces between the crystalline domains, perhaps mediated by the surrounding free oligomers. Because the strength is no longer derived from tie chains, further hydrolytic reaction, which will occur predominantly to the free oligomers, will not significantly reduce the strength. Thus the attractive forces that impart strength to very degraded paper may be the same as those that lend cohesion to other assemblages of crystalline cellulose such as pressed pharmaceutical tablets.³⁸

Conclusions

This study provided a more detailed picture of the course of hydrolysis of cellulose molecules in cotton fibers composing Whatman 42 paper. A model of hydrolytic degradation proceeding in stages that included multiple reactions to cellulose chains described the measured molecular weight changes in the GPC and the observed evolution of free, low molecular weight oligomers in the ESI-MS. In stage I, amorphous tie chains were broken once, causing a large decrease to the measured DP, accompanied by strength loss from the breaking of tie chains. In stage II, amorphous chains started to be broken a second time nearer the end of amorphous segments, causing smaller changes to the calculated DP and generating small amounts of free oligomers. The continued breaking of intact tie chains during this stage caused the strength to continue to decrease. During stage III degradation, minimal changes to the calculated DP were observed, for most of the hydrolytic reaction occurred on the very short amorphous segments protruding from the

crystals and to the free oligomers. According to the developed model, the strength should continue toward zero. However, experimental measures showed the strength leveled off to a small but persistent value, which indicated a transition to cohesive strength originating from attractive forces between cellulose crystals rather than from tie chains in the amorphous phase.

This examination of aging cotton cellulose paper provided evidence to support a simple view that cellulose hydrolysis occurred at a constant rate throughout the oven-aging. Hence, the calculated chain breaks beyond stage I was likely incorrect and was due to inaccurately determined DP. Kinetic analysis of changes in hydrolysis rates during later stages of degradation may prove difficult, because while the overall hydrolysis rate seems to be roughly constant, the reaction, which occurs predominantly to intact amorphous tie chains in the earliest stage, eventually transitions to attack on links in free oligomers. However, it may still be accurate to describe the hydrolysis reaction intact of amorphous tie chains as slowing, according to the exponential time dependence characterizing the first-order reaction of the intact tie chains.

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