



*Institute of Paper Science and Technology
Atlanta, Georgia*

IPST Technical Paper Series Number 793

Photoyellowing of Acetylated High-Yield Pulps
under Ambient, Oxygen, and Argon Atmospheres

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May 1999

Submitted to
The Tenth International Symposium on Wood and Pulping Chemistry
Yokohama, Japan
June 7-10, 1999

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PHOTOYELLOWING OF ACETYLATED HIGH-YIELD PULPS UNDER AMBIENT, OXYGEN, AND ARGON ATMOSPHERES

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ABSTRACT

The effect of oxygen pressure and chemical modification on the photoyellowing of lignocellulosic substrates during photoirradiation was investigated. The lignocellulosic substrates consisted of aspen (*Populus tremuloides*) handsheets derived from the chemithermomechanical pulping of aspen. The substrates were observed to undergo rapid photoyellowing under visible light conditions as a result of oxidation of the lignin. The phenol groups of lignin have been previously implicated to be responsible for initiating photoyellowing. The following studies support prior studies by demonstrating that protection of the phenol sites by acetylation attenuates photoyellowing, but does not entirely stop it. In fact, unlike previous studies, the irradiation experiments demonstrate that oxygen is not necessary during the early stages of photoyellowing. Its role, however, at relatively longer times is important and the photoyellowing phenomenon may therefore be a function of the oxidation of isolated leucochromophores unable to propagate a oxidative radical mechanism. Acetylation of the lignin clearly diminishes the kinetics of photoyellowing, but not noticeably at short times. The results suggest that at early times, a lignin radical mechanism presumably arising from excited state homolytic bond cleavage operates independently of oxygen concentration.

INTRODUCTION

Enhancing the production and efficient utilization of lignocellulosic products are issues of critical importance to both industry and society. Most industrial efforts chemically manufacture relatively costly, low-yield lignocellulosic products (e.g., kraft market pulp) whose production is accompanied by waste products that must be remediated. The mechanical manufacture of lignocellulosic product (mechanical pulp) is, however, high-yield while retaining most of the lignin, less expensive than kraft market pulp, and requires less waste product remediation. Although the production process is

relatively environmentally benign and generates a lower cost product, the lignocellulosic products tend to undergo severe photoyellowing as a function of light and/or heat exposure. Photoyellowing or brightness reversion, a discoloration due to chemical or photochemical oxidation, is cited as the principal reason for the limited commercial applications of mechanical pulps. Efforts to reduce or eliminate photoyellowing have received renewed attention in the last few years [1-5]. Most efforts have focused on understanding and mitigating the chromophore generation in lignocellulosics that occurs as a result of lignin absorbing near-UV spectral energy.

Lignin is a large biopolymer that displays highly polydisperse and amorphous character and comprises 20-25% of the mass of most mechanical pulps. Shown below in Figure 1 is a representative illustration of some of the common chemical linkages in lignin.

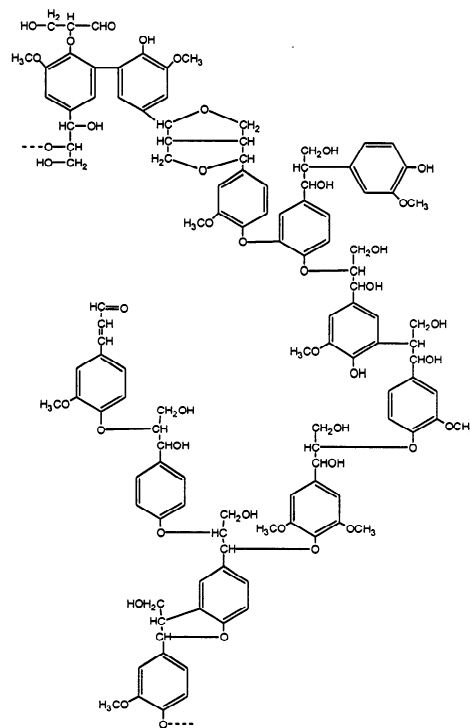


Figure 1. Structural representation for the common bonding patterns in lignin. Adapted from Adler (1977).

Stilbene, coniferaldehyde, and conjugated phenyl units are primarily responsible for the absorbance of near-UV light. β -O-aryl linkages comprise approximately 55% of the total interunit linkages between the phenylpropanoid monomeric units of lignin. Model compound research by Schmidt and Heitner has concluded that the predominant mechanism responsible for chromophore generation occurs by homolytic cleavage of the β -O-aryl linkages as shown in Figure 2 [6].

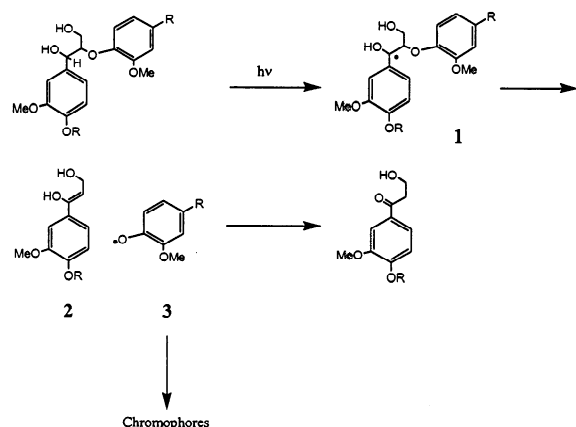


Figure 2. Mechanism of β -O-Aryl cleavage of arylglycerol- β -arylethers.

The first step, radical abstraction of a benzylic proton by an $n \rightarrow \pi^*$ excited carbonyl state generates a ketyl radical (1) that proceeds to undergo β -O-4 cleavage to leave an acetophenone enol (2) and a phenoxy radical (3). The reactive intermediate, 3, is strongly believed to participate in oxidation reactions generating o-quinones and other chromophoric compounds. O-quinones are also known to act as photosensitizers for continued chromophore formation in lignocellulosic samples as shown by studies in our lab [7].

The importance of atmosphere on chromophore generation is currently an unresolved issue. Various reports implicate the necessity of oxygen for photoyellowing, whereas other reports show that it is not necessary [8, 9]. Oxygen has been suggested to enhance radical reactions through radical coupling reactions with phenoxy groups generating hydroperoxy and alkylperoxy radicals that culminate in the generation of quinones [10]. Figure 3 illustrates a suggested reaction sequence.

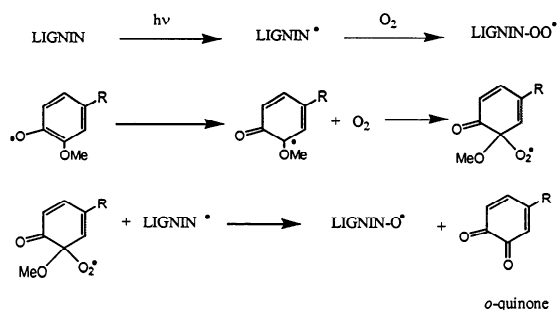


Figure 3. Potential involvement of oxygen in the photoyellowing response of mechanical pulps.

Not long ago, researchers discovered that photoyellowing could be partially inhibited by reducing the number of phenoxy forming hydroxyl groups [11]. Our group continued research into the potential of mini-

mizing photoyellowing by acetylating the hydroxyl functionalities of the phenol moieties in lignin [12-14]. By eliminating a potential avenue for phenoxy radical generation, the work demonstrated that the photoyellowing phenomenon was substantially reduced. The thrust of the present work centers on the effect of oxygen on the efficiency of photoyellowing of mechanical pulps as a function of both oxygen concentration and acetylation.

EXPERIMENTAL

Methods

Handsheets were prepared from industrial hardwood bleached chemithermomechanical pulp (CTMP) using standard literature procedures [15]. Acetylation was accomplished by placing the handsheets in a preheated glass vessel containing excess technical grade acetic anhydride and heating at either 80 and 110°C from 3 to 480 minutes to obtain different degrees of lignin acetylation. After the reaction time was completed, the handsheets were immersed in deionized water to terminate the acetylation, thoroughly rinsed, and pressed at 400 kPa pressure in a press plate for five minutes. They were dried for 24 hours and conditioned at 23°C and 50% relative humidity before the studies.

The acetyl content for a handsheet was determined by mechanical disintegration of the handsheet, hydrolysis with 5 mL of 1N sodium hydroxide, filtration, and a water rinse after 18 hours (30 minutes vacuum step during base treatment). The resultant acetate from base hydrolysis of the acetyl groups was quantified by HPLC analysis using propanoic acid as an internal standard. The acetyl content in the work is a percentage of dry handsheets. The low acetyl content that was thus measured is 4.6%, whereas the high is 7.3%.

Acetyl contents were also determined after all irradiation and were found to minimally change ($\pm 0.2\%$) from their original unirradiated values. The largest changes were observed for the handsheets irradiated under ambient conditions: reductions of acetyl content of 0.2% for the control, 0.4% for the low acetyl content, and 0.5% for the high acetyl content.

Substrate Irradiation

All handsheets that were used were rectangular two dimensional strips cut to measure approximately 12 x 70 mm and were placed inside home-built O-ring sealed quartz vessels having a stopcock to a vacuum line. The quartz vessels were mounted in a merry-go-round apparatus that was then placed inside a Rayonet photochemical reactor (Model RMA-400) outfitted with eight 575 nm "cool white" fluorescent lamps (each rated at 8 watts).

The handsheet atmosphere was either laboratory ambient air or ultra-high purity research grade (99.999%) argon or oxygen. All vessels were thoroughly vacuum degassed (<1 mTorr) for 30 minutes and

backfilled with a stream of the desired atmosphere. The cycle was repeated in triplicate and a positive head pressure of gas was maintained by attaching a thick-walled balloon to the vessels. The temperature inside the vessels never fluctuated more than 1 degree from 25°C. The samples were allowed to remain in the dark for 30-60 minutes after turning off the lamps.

Optical Measurements/UV-VIS

A Technidyne Brightmeter (Model S-5) was used to measure the brightness of the handsheets. All values were calibrated according to the brightness from a commercially accepted standard [17]. The UV-VIS spectra were recorded on a Perkin-Elmer Lambda 19 DM spectrophotometer equipped with a diffuse brightness and transmittance accessory (Labsphere RSA-PE-90). The accessory is an optical bench that includes double beam transfer optics and six-inch diameter (154 mm) integrating sphere. Using an SRS-99-010-7890 standard, background corrections were collected. All experiments were conducted with the underlying assumption that the scattering coefficients were the same since the handsheets were obtained from the same source. The absorbance (Abs) of the samples were calculated from the diffuse brightness by applying the following expression derived from the Beer-Lambert Law: $Abs = -\log(\text{Diffuse Reflectance})$. All spectra were averaged from a set of three to four measurements and are displayed as the difference spectra between an irradiated and non-irradiated sample.

RESULTS AND DISCUSSION

Most of the prior work in our laboratory with handsheets was done under ambient conditions in a merry-go-round apparatus housed in a Rayonet photochemical reactor. The results unequivocally demonstrated a brightness stabilizing effect through the introduction of acetylated sites in the handsheets [18]. The studies used light sources of different wavelengths, namely 350, 419, and 575 nm, to observe the influence of different radiation energies on the photoyellowing of acetylated aspen (*Populus tremuloides*) handsheets. This report focuses on the results obtained with the 575 nm wavelength. These irradiation wavelengths did affect chromophore generation as illustrated by the UV-VIS spectra in Figure 4.

Most notably, the near-UV wavelength irradiation (350 nm) generated a spectrum consisting of a peak at 370 nm with a broad shoulder at a maximum of 415 nm. The other irradiation wavelengths (visible) gave rise to spectra displaying peaks at approximately 370 nm that extended into the visible. Clearly two chromophores are being generated, perhaps in differing proportions as a function of the source irradiation. Not that the visible irradiation spectra do not eliminate the possibility of a band at 420 nm. Although NMR data provides practically no evidence for the correlation of photoyellowing

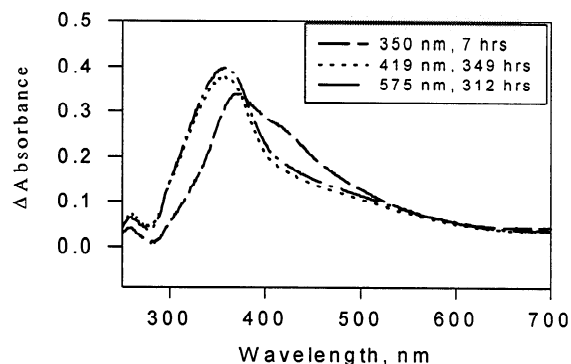


Figure 4. Difference absorbance spectra of hydrogen peroxide bleached aspen CTMP as a function of wavelength and time.

to chromophore identity, model studies have shown that methoxylated *para*-quinones and *ortho*-quinones are partly responsible for absorbance bands at 360 and 420, respectively [15]. We were able to show conclusively that various composite levels of lignin acetylation attenuated the kinetics of chromophore formation accounting for photoyellowing. Clearly, the same signature bands corresponding to a photoyellowing phenomenon were observed, albeit reduced in magnitude. As a natural extension of the previous work, it was decided to control the atmosphere surrounding the handsheets during the irradiation and follow the UV/VIS spectra as a function of irradiation time. Various conflicting literature reports have appeared on the role of oxygen during photoyellowing. Leary has stated that oxygen is essential for the photoyellowing phenomenon to occur [8, 11]. Other work, however, has shown that the role of oxygen in the photoyellowing process is more ambiguous, and in some cases, atmosphere appears to play no significant role [9].

The present work has investigated the effect of atmosphere (argon, oxygen, and ambient) on the photoyellowing of unacetylated, low, and high level acetylated aspen handsheets. Figure 5 shows a typical

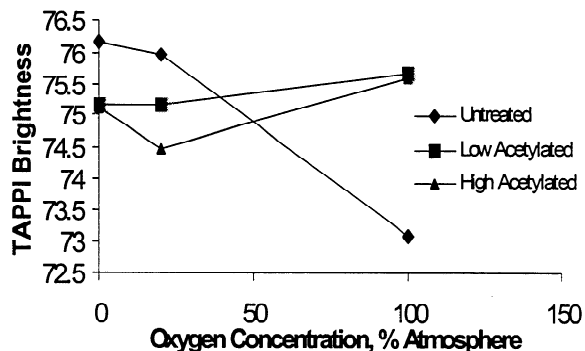


Figure 5. Change in brightness of handsheets as a function of acetylation and atmosphere after 18 hours of irradiation at 575 nm.

profile for the handsheets of TAPPI brightness versus oxygen concentration after 18 hours irradiation at 575 nm. Not surprisingly, the unacetylated handsheet has a stronger photoyellowing response in an enriched oxygen environment as compared to the acetylated sheets. Interestingly, the small gains in brightness by the acetylated sheets may be indicative of enhanced oxidation of the important contributing chromophoric structures. Although, the changes at 18 hours of irradiation are amenable to a relatively simple interpretation based on acetylation level, a profile of the changes over the 18 hours shows some parallel trends that are somewhat more difficult to interpret.

Shown in Figure 6a-c are the changes of brightness as a function of time for unacetylated, low, and high-acetylated handsheets in argon (a), ambient (b), and oxygen (c) atmospheres:

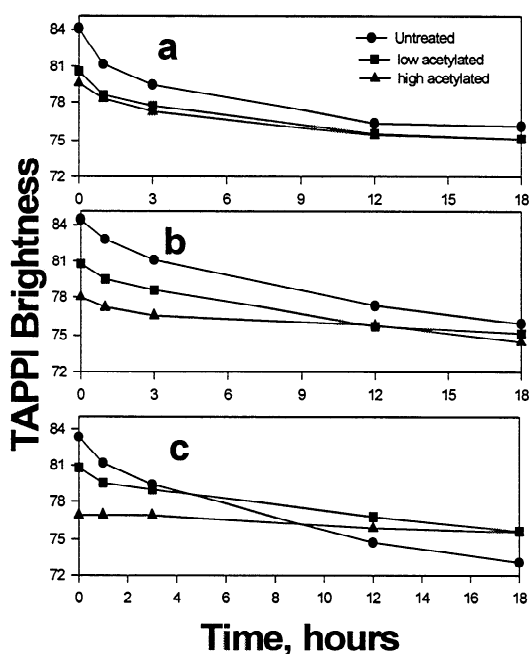


Figure 6. Brightness values for untreated, low, and high acetylated handsheets as a function of atmosphere: (a) argon, (b) ambient, (c) oxygen.

In general, the handsheets exhibit biphasic kinetics, possessing a very fast initial drop in brightness that levels off to a slow phase. The rapid initial phase is almost certainly a consequence of the availability of "reactive" leucochromophore molecules whose photochemical changes can strongly affect the relative brightness at 457 nm according to Kubelka-Munk Theory. Kubelka-Munk essentially relates the scattering coefficient to the fraction of chromophores on a two-dimensional surface. As the chromophore level reaches a minimum threshold level, the gains in reflectance become exponential due to

the lack of linearity in the absorbance. At approximately a level of 30-40% remaining total chromophores, the change in the absorbance begins to fail to correlate linearly with the fraction of chromophores being measured. The later changes in brightness are certainly a larger bulk phenomenon, and can be clearly seen for the unacetylated sheet to depend on the atmosphere. At lower oxygen pressures, the reflectance changes are less pronounced than at higher oxygen pressures over long irradiation times.

The acetylated sheets demonstrate that acetylation impedes chromophore development throughout the irradiation, sustaining brightness at longer times. Low and high doses of acetylation do not drastically impact the overall effect of enhanced brightness, perhaps indicating that a certain number of leucochromophores are acetylated and any further changes are not strongly observed in brightness changes. In fact, the photoyellowing response is not as sensitive to differing oxygen pressures as expected. Again, this result may be a consequence of the relative inertness of the handsheets due to fewer active leucochromophores or the photoyellowing response does not correlate well to the oxygen pressure.

To assess accurately the origin of the photoyellowing changes observed, UV-VIS diffuse reflectance spectroscopy was employed. The technique is a very well established and accepted spectroscopic technique for probing complex photochemical changes occurring in lignocellulosic handsheets. Figure 7 illustrates spectra of unacetylated sheets in various atmospheres at prolonged visible irradiation (18 hours). Notice that the spectral distributions of peaks are very similar (a major peak at 360 nm with a shoulder at 420 nm) strongly suggesting that similar chromophoric structures are developing. Yet, the major difference is the protracted spectral shoulder for the oxygen atmosphere samples that does not substantially develop in the oxygen-free environment. These chromophoric structures obviously absorb more strongly in the visible, suggesting increased conjugation or an enrichment of the chromophores in that spectral region for the higher oxygen pressure experiments. Although no formal identification of these structures can be made, model studies strongly implicate their quinoidic character [*vide supra*]. In all likelihood, the development of the chromophores is attenuated in oxygen-depleted environments, but their formation is not solely dependent on oxygen.

The mechanism that is shown in Figure 3 may not be the dominant mechanism in the lignocellulosic samples since oxygen is obviously not required to attain the photoyellowing phenomenon. The primary rationale for the existence of alternative mechanisms may likely be due to the limited effect of oxygen on chromophore development and distribution due to differences in chromophore concentration and localization. Figures 8a and 8b illustrate the kinetic formation of the *p*-quinones and

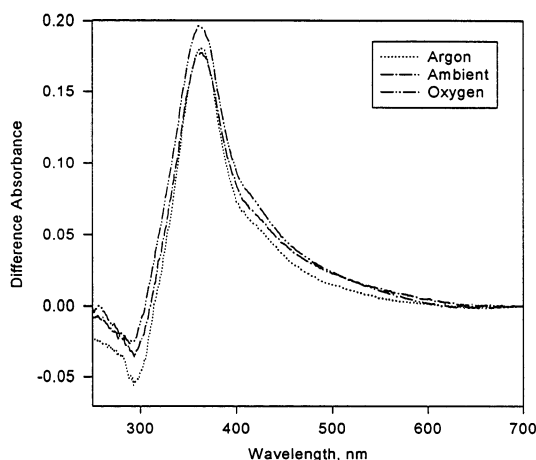


Figure 7. The UV-VIS diffuse reflectance spectra after 18 hours irradiation at 575 nm for an untreated handsheet as a function of argon, ambient, and oxygen atmospheres.

o-quinone structures that are partially responsible for the absorbance peaks located at 360 nm and 420 nm, re-

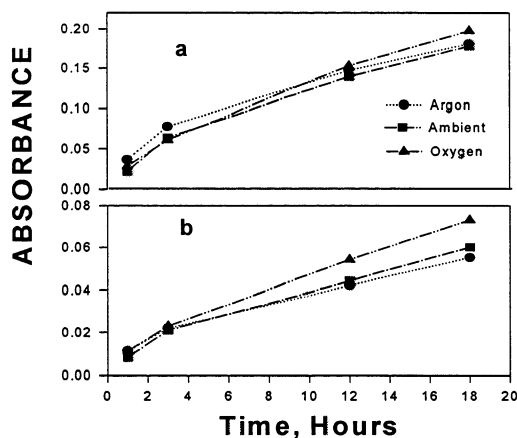


Figure 8. Absorbance changes at 360 nm (a), and 420 nm (b) for an unacetylated handsheet as a function of atmosphere.

spectively, as a function of time for an unacetylated handsheet. It is apparent that the kinetics of *p*-quinone generation is not affected by atmosphere, whereas the kinetics for *o*-quinone generation is enhanced as the atmosphere becomes enriched in oxygen. Indeed, the latter moieties have been suggested to be responsible for photoyellowing of lignocellulosics.

Another important observation that may partially account for the "slow" phase of brightness changes in the samples is the ability for the newly generated chromophores to act as filters. They can behave as internal filters to reduce the amount of light that impinges upon the reactive leucochromophores and shunt off the radical reactions that lead to chromophores. It is possible

that in the solid matrix, physical limitations are imposed on continued oxidation reactions despite the oxidizing ability of various reactive sites or the newly formed chromophores.

CONCLUSIONS

The preceding study demonstrates the utility of chemical modification of complex lignocellulosic aspen handsheets for hindering the photoyellowing phenomenon. It also describes the relative importance of atmosphere in the process, definitively demonstrating that oxygen is not the predominant propagator of the photoyellowing reactions. At short times, all handsheets respond similarly to the influx of light, but tend to display a brightness drop that levels off. The response at long times is critically dependent on the atmospheric component as evidenced clearly for unacetylated sheets. The latter result is perhaps mostly attributable to the relative preponderance of reactive leucochromophore sites. In acetylated samples, the number of reactive sites diminishes, and the response is not as sensitive to the atmosphere. We measured the change of acetyl sites in the samples gravimetrically and found that they did not statistically diminish, suggesting the relative robustness of the acetylated site. Oxygen may indeed accelerate photochemical changes for unacetylated pulps, but ostensibly at longer times, and may not play as significant a role as thought in the initial rapid photoyellowing phase of mechanical pulps. Further studies are underway to address the rapid initial kinetics of photoyellowing by evaluating the effect of various efficient radical traps and phenoxy protecting groups.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the United States Department of Agriculture for support (Agreement No. 96-35103-3800) as well as the member companies of the Institute of Paper Science and Technology. M.P. served as a Gunnar-Nicholson Postdoctoral Fellow in our laboratories during 1997-98 and currently serves as an assistant professor at Chalmers University of Technology.

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