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BRIGHTNESS REVERSION OF MECHANICAL PULPS.
X. PHOTOREVERSION FIBER TOPOCHEMISTRY

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ABSTRACT

The topochemistry of thiol-photostabilization of hardwood BCTMP (bleached chemithermomechanical pulp) was investigated by scanning electron microscopy (SEM). Employing advanced SEM methods, the location of unextractable sulfur across the fiber wall was determined for post-photolyzed BCTMP fibers. These studies illustrate that thio additives remove chromophores across the fiber wall.

INTRODUCTION

Predicted shortages in wood supply and increasing wood costs have stimulated research on the use of high-yield mechanical pulps and over the past decade, dramatic improvements have been achieved in the manufacturing and product quality of mechanical pulps. Perhaps the greatest hindrance to further usage of these pulps is their well-known brightness reversion properties.¹

Future commercial applications depend significantly on the development of new, cost-effective photostabilization technologies for mechanical pulps. In response to these challenges, a variety of researchers have explored new methods of hindering brightness reversion. Studies performed by Gellerstedt,² Fournier de Violet,³ Kringstad,⁴ Janson,⁵ Davidson,⁶ and Cook⁷ have explored the effectiveness of several substituted hydroxybenzophenone and benzotriazole derivatives at retarding brightness reversion. Unfortunately, the amounts of additive required to significantly photostabilize high-yield pulps are cost-prohibitive. The use of polymeric additives has been extensively explored by Hortling⁸ and continues to show promising results. Radical scavenging agents such as ascorbic acid,⁹ formate salts,¹⁰ thiols,¹¹ and bisethylene thioethers¹² have also been found to retard brightness reversion, but none of these additive technologies has addressed all of the challenges of the marketplace.

Despite the lack of a commercially suitable product, from a broader perspective, the application of photostabilization additives onto mechanical pulps has significantly advanced our ability to hinder the photoyellowing process. Interestingly, the technological requirements for photostabilizing mechanical pulps by additives remain poorly understood compared with the extensive experimental data available for plastics and related man-made polymers. To address these issues, our research group has been involved in studying the photostabilization mechanisms of known brightness stabilization additives. This article summarizes our recent investigations on determining the topochemistry of brightness stabilization across a fiber wall. The issue of whether brightness reversion is a surface-localized phenomenon or occurs throughout the fiber has not, to date, been fully established. The topochemistry of reversion is an important issue for future developments of photostabilization technologies because, if reversion is a surface-dominated effect the application of antioxidants could be restricted to the fiber surface. On the other hand, if reversion occurs

throughout the fiber wall, the application of antioxidants to a fiber would require diffusion of the additive throughout the fiber. This report summarizes our investigations of this challenging issue.

RESULTS AND DISCUSSION

Recently, our research group has demonstrated that thiol additives, applied onto BCTMP fibers, slowly become incorporated into the fiber when photolyzed and cannot be removed under exhaustive (*i.e.*, Soxhlet) extraction conditions with dichloromethane.¹³ Furthermore, we have previously reported¹⁴ that the extent of sulfur incorporation into the fiber directly correlates with the efficiency of the photostabilization additive and the irradiation period.

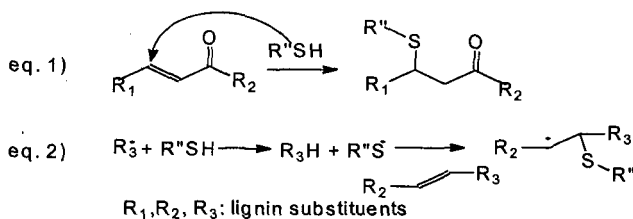
To further explore this phenomenon, we treated BCTMP fibers with thio-glycerol and photolyzed them with black lamps (λ_{max} :350 nm) for an extended time period with vigorous stirring. During the photolysis, samples of BCTMP were removed, brightness values were determined, and the samples were exhaustively solvent extracted and submitted for elemental analysis. The results of these analysis are summarized in Table 1. The initial incorporation of sulfur into the pulp, prior to irradiation, is most likely the result of Michael-type addition reactions leading to thio-bleaching of the pulp. The increased sulfur incorporation after photolysis is consistent with Cole's hypothesis that thio-additives retard brightness reversion, in part, by a Michael-type addition reaction to lignin chromophores (see eq. 1).¹² However, in a recent paper Gellerstedt¹⁴ has demonstrated that thiol additives might become attached to lignin by way of a radical scavenging mechanism (see eq. 2). Further studies are needed to explore these two mechanistic pathways and how they contribute to sulfur incorporation in mechanical pulp.

TABLE 1

Sulfur Incorporation into Hardwood BCTMP Fibers^a Impregnated with 5% Thioglycerol, Photolyzed, and Soxhlet Extracted with Dichloromethane.

% Thioglycerol on Pulp	TAPPI Brightness	Irradiation ^b time, h	C:H:S ^c
0	81.4	0	44.23 : 6.38 : 0.00
5	84.6	0	43.75 : 6.40 : 0.07
5	79.9	12	43.61 : 6.31 : 0.11
5	76.8	24	43.60 : 6.35 : 0.16
5	75.5	60	43.69 : 6.36 : 0.19

^aBCTMP pulp from a commercial mill employing hydrogen peroxide for pretreatment and as a bleaching stage; ^birradiated pulp fibers with eight RPR-3500 A lamps; ^cC:H:S ratio determined by elemental analysis after extended Soxhlet extraction.



Despite uncertainties associated with the exact mechanism by which sulfur is incorporated into pulp fibers, we realized that the sulfur incorporation mechanism could become a unique tool in determining the topochemistry of reversion by employing SEM techniques. To accomplish this goal, the irradiated thioglycerol-treated BCTMP fibers, reported in Table 1, were imbedded in epoxy, ultramicrotomed, mounted on a TEM grid, and analyzed using SEM-EDS.

Generally, five equidistant x-ray spectra were collected per scan and five scans were collected per fiber per slice. The starting point for each analysis was adjacent to the lumen and the end point was adjacent to the outer cell wall. Each

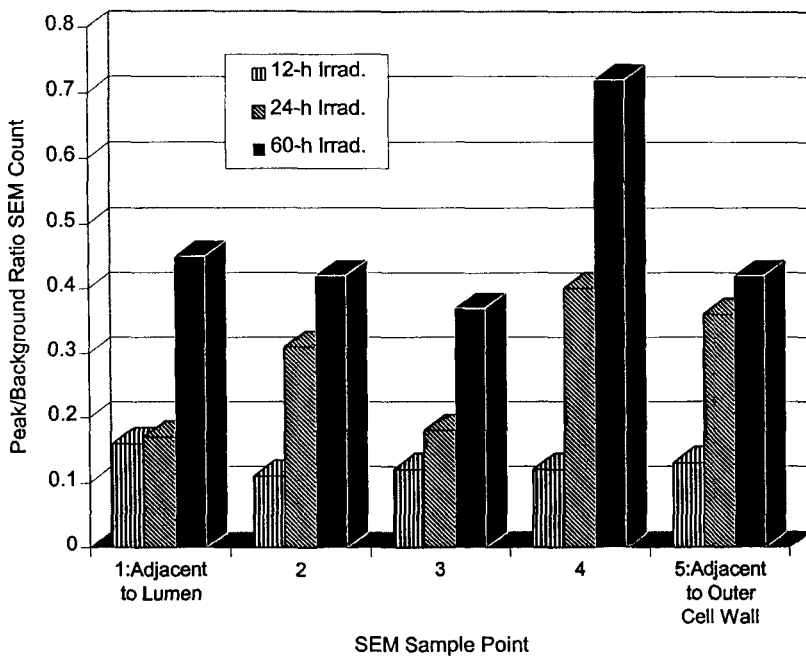


FIGURE 1. Spatial distribution of unextractable sulfur in post-photolyzed thioglycerol-treated BCTMP fibers analyzed by SEM-EDS. In the SEM-EDS analysis, the fiber was sampled at five equidistant locations from the lumen to the outer cell wall. See experimental section for further detail.

analysis was repeated on three fiber sections. The results of these studies are summarized in Figure 1.

After 12 h of irradiation, the SEM-EDS analysis detected sulfur incorporation across the fiber wall with a slight enrichment on the inner and outer cell wall. Nonetheless, approximately 50% of the sulfur was present in the inner portions of the fiber as determined by the SEM-EDS analysis. Further photolysis resulted in greater sulfur incorporation that was again distributed throughout the fiber wall. The SEM studies provide a clear description of the topochemistry of

CONCLUSIONS

Studies presented in this report indicate that sulfur incorporation during brightness reversion is not a surface-dominated effect and occurs throughout the fiber wall. Although the results presented in this article are applicable only to chromophores that react with thioglycerol under the experimental conditions employed, it is likely that these results are representative of the topochemistry of antioxidants in general. Additional studies will be needed to confirm this latter issue especially as it applies to the photoaging of paper under ambient conditions.

EXPERIMENTAL

Materials

All chemicals, including thioglycerol, Epox 812, dodecyl succinic anhydride, nadic methyl anhydride, and N,N-dimethylbenzylamine were obtained commercially and used as received. Commercial hardwood BCTMP (93% yield) prepared from aspen, using hydrogen peroxide for both the chemical pretreatment and bleaching, was employed for all studies in this report. All pulp samples were disintegrated using only glass or Teflon-coated labware to prevent metal contamination. After disintegration, the pulp was Soxhlet-extracted with acetone for 24 h and then allowed to air dry for 24 h in a controlled 50% humidity environment. Previous studies have demonstrated that this mild extraction procedure¹³ does not influence the brightness reversion properties of mechanical pulp but does simplify additive reversion studies.

Accelerated Photoreversion Studies

BCTMP fibers (30 g, o.d.) were impregnated with a methanolic solution of thioglycerol (1.5 g in 1000 mL), stirred for 2 h, and then concentrated under

reduced pressure. After complete solvent removal, the dry BCTMP fibers (33.0 g, o.d.) were added to a glass vessel and photolyzed in a Rayonet Photochemical Reactor equipped with eight RPR 3500 A lamps (λ_{max} 350 nm). During photolysis, the pulp was vigorously stirred with a Teflon mechanical stirrer. The reaction flask was maintained at a temperature of 25-30°C with the aid of a cooling fan. Pulp samples were withdrawn after 12, 24, and 36 h of irradiation. Samples of the pulp were used for preparing handsheets following TAPPI procedure T 218. Brightness measurements were accomplished following TAPPI standard procedure T 452. Typically ten measurement were made per handsheet and brightness values for each handsheet varied less than 5% suggesting that the individual fibers were homogeneously irradiated during the photolysis experiment.

Sulfur Incorporation Studies

Sulfur incorporation into pulp fibers was monitored by elemental analysis of the pulp after exhaustive Soxhlet extraction. Prior to analysis, the fibers were Soxhlet-extracted with acetone for 24 h, and this was followed by a second Soxhlet extraction using CH_2Cl_2 for 24 h. The fibers were then dried under reduced pressure and submitted to Galbraith Laboratories, Knoxville, TN, for C:H:S analysis.

SEM-EDS Sample Preparation

Pulp fibers were passed through a modified Millipore funnel that yielded a small plug of oriented fibers. The fiber plug was then freeze-dried and imbedded in Epox 812 resin using coffin-shaped molds. The Epox 812 resin was prepared by mixing Epox 812, dodecenyl succinic anhydride (6.44 g), nadic methyl anhydride (7.05 g), and N,N-dimethylbenzylamine (7.05 g); after stirring for 5 minutes additional N,N-dimethylbenzylamine (0.9 mL) was added and the

thiol additive incorporation into pulp fibers under brightness reversion conditions. The mixture was stirred vigorously. The imbedded fiber molds were then placed in a vacuum oven set at 35°C, (60 torr) for 1 h to infiltrate the fibers. The resin was cured by placing the molds in an oven at 60°C for 18 h.

The imbedded fiber samples were sectioned on an ultramicrotome (50-400 nm thick) and mounted on a 150-mesh high transmission TEM grid. The grids were then blotted and coated with a thin layer of carbon.

SEM-EDS Sulfur Analysis

The fiber cross sections were examined by scanning electron microscopy-energy disperse spectroscopy (SEM-EDS), and only fibers free of defects were tested. Automated beampoint analysis was initiated adjacent to the lumen and the end point was adjacent to the outer cell wall. Generally, five equidistant x-ray spectra were collected per scan and five scans per fiber were performed; a total of three fiber sections were examined per photo-aged sample. The x-ray spectra were processed by determining the gross and net counts of the sulfur ka (k alpha) peak using the automated integration function of the spectrometer.

A JEOL JSM-6400 with a Link exL energy spectrometer was employed for the SEM-EDS analysis. The EDS had a 40° incline and was operated in the beryllium window mode. The accelerating voltage was 15 kV; the sample tilt was 20°; the working distance was 39 mm.

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