Brightness Reversion of Mechanical Pulps VIII: Fate of Dienic Additives During Brightness Reversion of High-Yield Pulp

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ABSTRACT

The photostabilization mechanism of 1,4-dihydro-2-methylbenzoic acid was examined with a lignin model compound in solution and on BCTMP pulp. Photodegradation of 3,4-dimethoxy-α-(2'-methoxyphenoxy)-acetophenone (**1**), dissolved in benzene, was shown not to be influenced by the addition of the diene additive, suggesting that the additive does not influence the initial photochemistry of lignin model compound **1**. Product analysis indicated that the addition of the diene additive enhanced formation of 3,4-dimethoxyacetophenone, one of the principal products formed from photofragmentation of compound **1**. These results were attributed to hydrogen donation from the diene to the phenacyl radical. Photolysis of 1,4-dihydro-2-methylbenzoic acid impregnated on BCTMP test sheets revealed a gradual conversion of the diene additive into o-toluic acid; this reaction was attributed to a hydrogen donation mechanism.

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INTRODUCTION

Increased usage of mechanical pulp has many long-term benefits for the pulp and paper industry, including improved environmental and wood utilization practices. Unfortunately, the well-known photoreversion properties of mechanical pulp have limited the use of this valuable fiber source.[1] To address these challenges, several research groups have begun to establish the fundamental photochemical principles that contribute to brightness reversion of mechanical pulps. Model compound studies by Gierer and Lin[2] and others[3] demonstrated that phenacyl-α-O-aryl ether compounds were photo-labile and rapidly yellowed when irradiated with near-UV light. Castellan et al.[4] have shown that phenolic stilbenes, phenylcoumaran, monophenolic biphenyl, and biphenylmethane structures induced substantial yellowing upon irradiation with 300-400 nm light. Gellerstedt and Zhang[5] demonstrated that diguaiacylstilbenes, isolated from CTMP pulps, were photosensitive and rapidly yellowed under brightness reversion conditions. Other lignin functional groups shown to be photoreactive under the brightness reversion conditions include coniferyl alcohol,[6] hydroquinones,[7] and quinones.[8]

Along with an improved understanding of the lignin chromophores that initiate brightness reversion, recent research studies have begun to establish the nature of post-photolysis reactions that contribute to photoyellowing of wood fibers. A recent paper by Agnemo et al.[9] provided strong evidence for the intermediacy of hydroxyl radicals during brightness reversion of mechanical pulp. The authors suggested that hydroxyl radicals generated during the reversion process were major contributors to the photoyellowing of mechanical pulps. In contrast to these results, Fisher et al.[10] have demonstrated that hydroxyl radicals and superoxide radicals, generated from radiolysis of an aqueous N_2O solution, can bleach CTMP. Research efforts by Schmidt and Heitner[11] have illustrated that a benzyl ketyl free radical-

induced process could also contribute to the overall photoyellowing process.

As our understanding of the fundamental mechanisms of brightness reversion improves, so does our ability to design new photostabilizing agents for mechanical pulp. Two classes of additives that have shown promising results are UV absorbers[12] and free radical scavengers.[13] To-date the most effective UV absorbers for mechanical pulps are benzophenone and triazole-based structures. Free-radical scavengers that have been shown to be effective photostabilization agents include thiols, thioethers, ascorbic acid, and formates. Unfortunately, none of these additives has successfully addressed all of the requirements necessary for commercial applications.

Recently, we demonstrated that derivatives of 1,4-cyclohexadiene and related unsaturated systems were moderately effective in retarding the overall rates of photoyellowing of mechanical pulps.[14] Based upon fundamental considerations, the photostabilizing effects of these additives were attributed to the radical scavenging mechanism shown in Figure 1. This paper summarizes our initial investigations of the chemical mechanism that contributes to the photostabilization effect of 1,4-dihydro-2-methylbenzoic acid, one of the more effective photostabilizing diene-additives that we recently reported.[14]

EXPERIMENTAL

Materials and General Methods

1,4-Dihydro-2-methylbenzoic acid, o-toluic acid, 3,4-dimethoxyacetophenone, and guaiacol were purchased from a commercial source and used as received. All solvents used in solution photolysis were spectrophotometric grade and used as received. Commercial sources of hardwood BCTMP (bleached chemithermomechanical pulp) with average

Photo-reversion chemistry
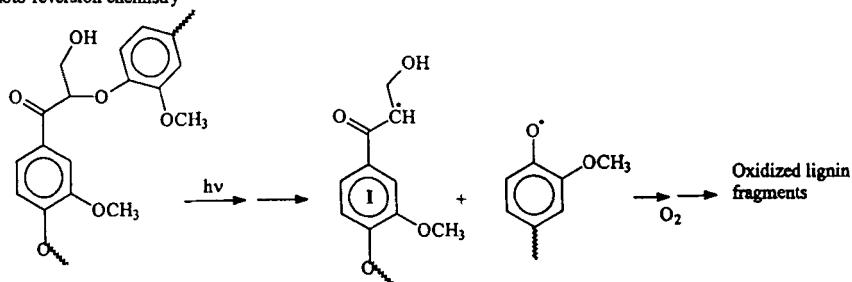
Photo-stabilization chemistry

R: is either initial radical from photolysis reaction (I) or a post-photolysis radical that could include hydroxy or peroxy type structures.
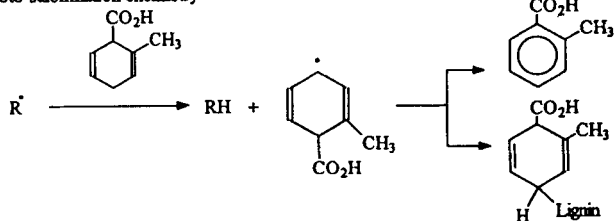
FIGURE 1:   Proposed photostabilization mechanism for 1,4-dihydro-2-methylbenzoic acid.

TAPPI brightness values of 82.8 and bleached softwood kraft pulp (TAPPI brightness of 87.8) were employed for the solid-state photolysis experiments. The BCTMP pulp was manufactured from aspen and spruce using sodium sulphite for chemical pretreatment and DTPA, hydrogen peroxide for bleaching.   Routine ^1H NMR spectra were recorded on a Bruker DMX 400, typically in deuterochloroform with tetramethylsilane as internal standard. Quantification of photoproducts was accomplished on a Hewlett Packard 5890 gas chromatograph equipped with an HP-17 capillary column and flame ionization detector. Routine GC-MS data were obtained with an HP-5890 Series 2 gas chromatograph coupled to an HP-5971A mass selective detector.

TABLE 1: Relative Proportion of Starting Material Remaining After Irradiation.

Irradiation Period, h.	Exp. 1: Lignin Dimer 1	Exp. 2: Lignin Dimer 1 + Diene	
	Dimer 1, %	Dimer 1,%	Diene,%
0.5	39	36	19
1.00	15	13	16
2.0	8	5	15

Solution Photolysis Studies

Benzene solutions of **1** (0.01 M) and **1** (0.01 M) containing 1,4-dihydro-2-methylbenzoic acid (0.01 M) were deoxygenated by purging with solvent-saturated nitrogen[15a] for 20 minutes prior to photolysis [Note: compound **1** was prepared following the procedure described by Adler[15b] uncorrected mp=88.0-89.5°C, Lit. 90-92°C, ^{1}H NMR of **1** agreed with results reported by McCarthy[15c]]. Irradiations were performed at 30 °C in Pyrex tubes using an Oriel 1000 W solar simulator that uses a xenon-arc lamp and were fitted with an air-mass 1.5 global filter to model average wavelength distribution in the continental United States. Samples were uniformly and simultaneously photolyzed on a merry-go-round apparatus. For studies where products were monitored over specific time intervals, aliquots were removed at 0.5-, 1-, and 2-h intervals. After the prescribed irradiation period, the solvent was removed and the photolysis products were redissolved in methylene chloride and spiked with 1,2,3-trimethoxybenzene as internal standard. Quantification of the major products formed as a result of the initial homolytic rupture of the β-O-aryl ether bond from lignin model **1**, 3,4-dimethoxyacetophenone (DMAP) and guaiacol, was accomplished by gas chromatography. These results are summarized in Table 1 and Figures 2 and 3.

% Dimethoxyacetophenone Formed*
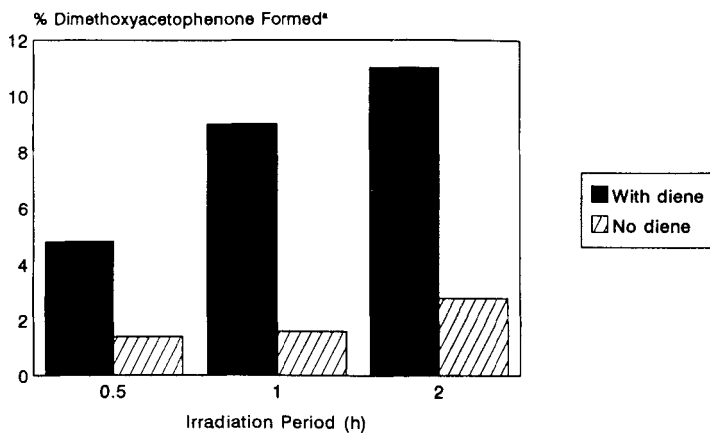
*calculated relative to starting material

FIGURE 2:   Formation of 3,4-dimethoxyacetophenone from the photolysis
            of lignin model 1 with and without 1,4-dihydro-2-methylbenzoic
            acid.
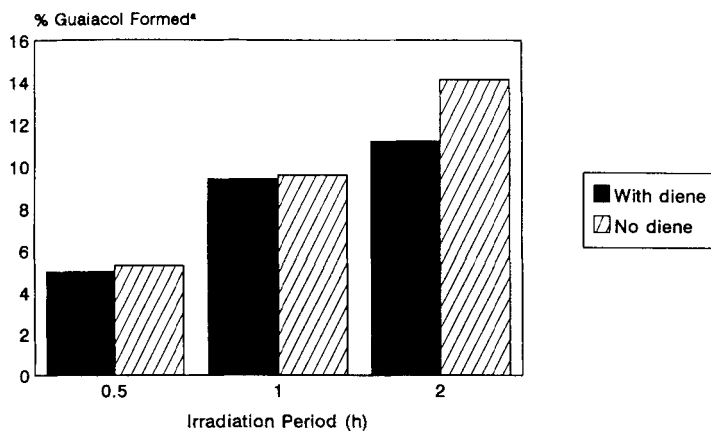
% Guaiacol Formed*

*calculated relative to starting material

FIGURE 3:   Formation of guaiacol from the photolysis of lignin model 1
            with and without 1,4-dihydro-2-methylbenzoic acid.

Photolysis of 1,4-Dihydro-2-methylbenzoic Acid on Pulp

The photolysis studies of 1,4-dihydro-2-methylbenzoic acid on BCTMP and fully bleached softwood kraft pulp followed a standardized experimental protocol. Prior to preparing the testsheets, the pulp was soxhlet-extracted with acetone to remove low molecular weight components. Previous studies[16] have demonstrated that removal of pulp extracts ensures accurate determination of additive application levels, simplifies analysis of the postphotolysis extracts, and does not influence the overall brightness reversion properties. BCTMP test sheets were prepared following TAPPI procedure T 218, and initial TAPPI brightness values were measured. The test sheets were then impregnated with a 3% application of 1,4-dihydro-2-methylbenzoic acid (wt additive/wt pulp). After application, the handsheets were air dried, and TAPPI brightness values were re-recorded. The handsheets were then placed on a merry-go-round and irradiated in a Rayonet photochemical reactor with eight phosphorous blacklight lamps for periods of 20, 40, 80, and 160 min. After photolysis, brightness values were measured, and the handsheets were Soxhlet-extracted with chloroform overnight under argon. The extracts were concentrated, dried under high vacuum, and analyzed by ^{1}H, ^{13}C NMR, and GC/MS spectrometry. Analysis of the extracts from the photolyzed BCTMP pulp indicated that it contained a mixture of 1,4-dihydro-2-methylbenzoic acid and o-toluic acid. The exact amounts of material isolated and percent composition are summarized in Table 2.

RESULTS AND DISCUSSION

In contrast to our understanding of the fundamentals of brightness reversion, few studies have explored the photostabilization mechanisms for

Table 2: Characterization of 1,4-Dihydro-2-methylbenzoic Acid Photolyzed
on BCTMP Test Sheets.

Irradiation Period/min[a]	% Photostabilization Effect[b]	% Additive recovery	Diene:o-toluic acid[c]
0	--	93.0	65:1
20	42	92.1	11.1:1
40	48	92.4	3.5:1
80	55	91.1	2.16:1
160	33	87.4	1:17

[a]test sheets irradiated with blacklight lamps; [b]% photostabilization= 100 x [(Δin TAPPI brightness of control test sheets) - (Δ in TAPPI brightness of treated handsheets)]/(Δin TAPPI brightness of control test sheets); starting brightness values for the control test sheets averaged 82.8, the treated test sheets averaged brightness values of 84.0; [c]ratio of 1,4-dihydro-2-methylbenzoic acid to o-toluic acid was determined by measuring peak intensities at δ 8.10 (H-6 of o-toluic acid) and δ 3.56 (H-1 of the diene) ppm; the starting material contained ca. 1% o-toluic acid.

known brightness stabilization agents.   Schmidt and Heitner[16] have examined the effect of treating wood fibers with ascorbic acid on photoyellowing. Investigations by Sumimoto,[17] Gellerstedt,[18] and Pan[19] have begun to define the fundamental mechanisms that contribute to the photostabilization effects observed for thio additives.   Although many aspects of brightness reversion need further analysis, we believe that investigations of the photostabilization mechanisms of known brightness stabilization agents will provide valuable knowledge for the design of novel, more effective photostabilization technologies for mechanical pulp.

Our general approach to investigating the mechanisms of known photostabilization agents for mechanical pulp employs a combination of lignin model compound studies and photoreversion studies of pulp. The photostabilization effects of 1,4-dihydro-2-methylbenzoic acid were initially explored in a benzene solution with lignin model compound 1. A series of dilute benzene solutions of compound 1, with and without 1,4-dihydro-2-methylbenzoic acid, were irradiated under nitrogen with near-UV light. During the photolysis experiments, aliquots were removed and analyzed by photodegradation of model compound 1 was not significantly influenced by the presence of the diene additive (see Table 1). This result suggests that the photostabilization effects of the diene additive occur after the initial photolysis reaction. As anticipated, the addition of the additive did have a substantial effect on the relative amounts of 3,4-dimethoxyacetophenone (see Fig. 2) formed during photolysis.

Studies by Vanucci et al.[3b] have shown that a variety of products are formed from the photolysis of model compound 1 with the phenacyl and guaiacoxy radicals being the key intermediates that then undergo a host of secondary radical-based reactions. If 1,4-dihydro-2-methylbenzoic acid acts as a radical scavenging agent during reversion, it should readily quench the acetophenone radical by a hydrogen donation mechanism (see Fig. 1) since it is well-known that doubly allylic systems are prone to loss of a hydrogen atom.[21] Although we are uncertain about the site of initial hydrogen abstraction from the diene additive (i.e., H-1 or H-4), steric considerations suggest that H-4 is more likely to be abstracted. Following this initial hydrogen abstraction, the cyclohexadiene radical could undergo several subsequent radical-based reactions, including donation of a second hydrogen atom yielding o-toluic acid. Presumably, re-aromatization would be a driving force in this to case, and, indeed, small amounts (2-3% conversion from diene) of this aromatic acid were detected in the complex photolysis product mixture.

Interestingly, the diene additive appears not to influence the formation of guaiacol, during the photolysis experiments (see Fig. 3). Presumably, this comes about in part, because of the inherent stability of the phenoxy radical thereby reducing the likelihood of radical abstraction from the diene additive.

Solid-State Photolysis Studies

Although the model compound studies suggested that the diene additive retarded photoreversion by a radical scavenging mechanism, differences in solution-phase and solid-state (i.e., pulp) chemistry could be significant and impact the overall mechanism(s) of stabilization. To explore this issue, we applied 1,4-dihydro-2-methylbenzoic acid to BCTMP and cellulose test sheets and irradiated these samples for extended time periods. A comparison of the rates of photoyellowing for BCTMP test sheets treated with and without the diene additive indicated that the treated handsheets exhibited reduced rates of brightness reversion upon irradiation with the phosphorous blacklight source (see Table 2).

After irradiation, the treated test sheets were soxhlet extracted with chloroform under argon, and the extracts were characterized by GC/MS and NMR spectrometry. The MS and NMR studies indicated that the product mixture contained only the starting diene and o-toluic acid as summarized in Table 2. Control experiments demonstrated that impregnation, drying, and extraction of the diene additive from BCTMP handsheets did not lead to formation of o-toluic acid, therefore, suggesting that the formation of o-toluic acid occurred as a result of reactions initiated during the brightness reversion process. Although the formation of o-toluic acid is indicative of a radical scavenging process, the decreased mass recovery after prolonged photolysis suggests that additional chemical processes occur that prevent total recovery of the additive.

To ensure that the results reported in Table 2 could be attributed to photo-initiated lignin reactions occurring in BCTMP test sheets, the photolysis experiments were repeated with fully bleached kraft pulp for 160 min.   After photolysis, the test sheets were Soxhlet-extracted, and the extracts were characterized by GC/MS and NMR spectrometry.   These studies demonstrated that the photolysis extracts contained only the starting diene and o-toluic acid. NMR analysis indicated that the photolysis extracts contained 9% o-toluic acid and 91% starting diene (92% additive recovery). In comparison, the BCTMP test sheets impregnated with 1,4-dihydro-2-methylbenzoic acid afforded 94% o-toluic acid after 160 minutes of irradiation.   These results are consistent with an oxidative induced dehydrogenation mechanism for the diene additive during photolysis of mechanical pulps. Presumably, on cellulose, the small amounts of o-toluic acid formed during photolysis arise by a slow autoxidation process.

CONCLUSIONS

The results of the studies presented in this paper suggest that 1,4-dihydro-2-methylbenzoic acid retards reversion, in part, by acting as a hydrogen source for reactive lignin-based radicals.   Other pathways of stabilization for the diene may include radical coupling reactions and other oxidative reactions. Experiments designed to clarify these photostabilization pathways are currently being conducted.

ACKNOWLEDGMENTS

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