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The Effect of Hydroxyl Radical Generation on Free-Radical Activation of TMP Fibers*

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The purpose of this work was to study the mechanisms involved in free radical activation of thermal mechanical pulp (TMP) fibers with the ultimate goal of developing methods for bonding wood fiber without the use of traditional adhesives. The generation of hydroxyl radicals in a mediated Fenton system was studied using electron spin resonance (ESR) spin-trapping techniques and indirectly through chemiluminescence measurement. The activation of TMP fibers was also evaluated by ESR measurement of free phenoxy radical generation on solid fibers. The results indicate that low molecular weight chelators can improve Fenton reactions, thus in turn stimulating the free radical activation of TMP fibers. However, it was also shown that excessive and prolonged free radical treatment may cause the destruction of fiber phenoxy radicals. In conclusion, this study demonstrates the potential for application, but also the complexity of free radical chemistry in biological materials, especially with regard to the chelation of transition metals and the interaction between free radicals.

KEY WORDS: Hydroxyl radical; phenoxy radical; TMP fibers; Electron Spin Resonance.

INTRODUCTION

Traditional methods for the manufacture of fiberboard involve the application of thermosetting resins to lignocellulosic fibers. The fibers are then formed into a mat, with the mat then being hot pressed into a fiberboard panel. Wood scientists have conducted studies to determine if the 'autobonding' of wood fibers without synthetic resins can be achieved [1–3]. Most of these autobonding processes are based on the generation of radicals on the surface of fibers so that the fiber can be pressed into boards without additional adhesives. The adhesion effect is likely due to phenoxy radicals formed on the fiber surface that may facilitate hydrogen bonding, the coupling of phenoxy radicals, or the reactions of fiber radicals with other reactive groups present in the fibers during hot pressing [4–7].

Several methods have been explored to generate free radicals on the surface of fibers. One is to treat wood fibers with phenoloxidases such as laccases and peroxidases [5–9]. Alternately, free radicals have also been generated by γ-irradiation or with Fenton's reagent [10]. Improved mechanical strength and thickness swell of fiberboards has been observed in boards made from fibers treated with enzymes or Fenton reagent [9,10]. It has been reported that the enhanced auto adhesion between wood fibers is associated with increased laccase-generated phenoxy radicals [7,8]. However, the mechanism of free radical generation and interaction during the fiber treatment is still unclear.

In previous research, we demonstrated that an extracellular low molecular weight chelator of benzoquinone or catecholate derivation may play an

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important role during Fenton chemistry based, non-enzymatic wood decay processes [11,12]. We found that the low molecular weight chelators could assist in the redox cycling of iron, which then in turn enhances the production of hydroxyl radicals via Fenton chemistry. However, efforts to quantify the oxygen based free radicals in a model Fenton system have been difficult due to the extremely unstable nature and short life-time of the hydroxyl radical. In a previous study, electron spin resonance (ESR) and ESR spin-trapping techniques were used to directly study iron chelation, hydroxyl radical generation, and the involvement of other oxygen-based free radicals [13]. Chemiluminescence was observed during the Fenton or mediated Fenton reaction as well [14] and attributed to hydroxyl radical production. In our current research, ESR and chemiluminescence analysis were used to study the various parameters which will affect free radical (phenoxy radicals and oxygen based radicals) generation during a chelator-mediated Fenton treatment of TMP fibers.

MATERIALS AND METHODS

Materials

Wood Fibers

Three types of wood fibers were tested: Ponderosa pine (*Pinus ponderosa*) Thermomechanical Pulp (TMP) fiber (MC ~10%) obtained as a gift from Louisiana Pacific Corporation in Missoula, MT; Aspen (*Populus tremuloides*) TMP fiber (MC ~10%); and southern yellow pine (*P. taeda*) TMP fiber (MC ~70%) obtained from the USDA Forest Products Laboratory in Madison, WI.

Chemicals

$FeCl_2$, $FeCl_3$, $CuCl_2$, H_2O_2, 2,3-dihydroxybenzoic acid (2,3-DHBA), acetic acid, and sodium acetate were purchased from Sigma-Aldrich. Purified 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) was obtained from the National Biomedical EPR center in Milwaukee, WI.

Determination of Radical Activity by Chemiluminescence Measurement

Reaction mixtures contained specified amounts of Fenton reagents and/or 2,3-DHBA to allow a comparison of radical production in Fenton chemistry with and without a reducing chelator added. Reactions were conducted in pH 5.0 acetate buffer, and H_2O_2 was added to the system last to trigger the reaction. The chemiluminescence measurement was conducted continuously in a liquid scintillation counter (TriCarb 1400) using the chemiluminescence protocol [14].

Determination of Hydroxyl Radical by ESR Spin-Trapping

The formation of free hydroxyl radicals during a Fenton or mediated Fenton reaction was studied using ESR spin-trapping techniques. The purpose of the ESR spin-trapping measurement was to study the correlation between fiber radical generation and the free hydroxyl radical concentration in the system. Hydroxyl radicals were generated by a Fenton type system in a reaction mixture consisting of Fe^{2+} or Cu^{2+}, 2,3-DHBA, and hydrogen peroxide. The spin trap (DMPO) was used to trap hydroxyl radicals. The reaction mixture was then rapidly introduced into an aqueous flat cell and ESR observations were begun. ESR spectra were recorded at room temperature. The yield of the free hydroxyl radicals was determined by the formation of characteristic DMPO-OH spectrum (Fig. 1).

All of the spin trap experiments in this work investigated the generation of hydroxyl radicals by measuring the initial DMPO-OH adduct formation. To study the hydroxyl radical activities over time, DMPO was added to the Fenton system after incubation for a specified time. The ESR measurement was conducted immediately after the addition of DMPO.

Determination of Fiber Radical Activity by ESR Measurement

Fiber Radical Formation

TMP fibers were treated with the Fenton-chelator reagents at 5% consistency. Model chelator (2,3-DHBA) was added to enhance the Fenton reaction and to produce a sustained production of hydroxyl radicals as outlined previously [12, 13]. The temperature of the suspension was 25°C, and the pH was adjusted to 4.5 using 20 m*M* acetate buffer. A range of reagent concentrations was studied. H_2O_2 was added last to trigger the reaction in a complete Fenton system. As most of the radical formation was obtained during the first 30 min treatment (see "Results and Discussion"), a 30 min treatment time was used in our ESR experiments involving quantification of radicals unless otherwise stated. If

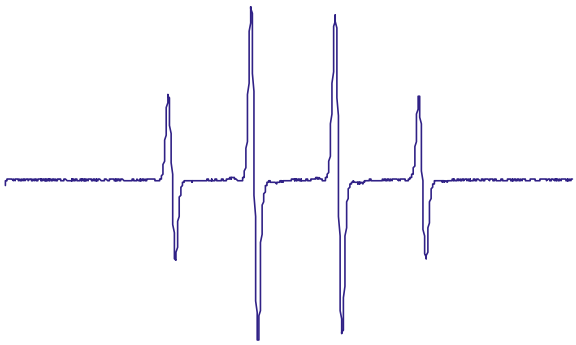

Fig. 1. Typical ESR spectrum of a DMPO-OH spin adduct.

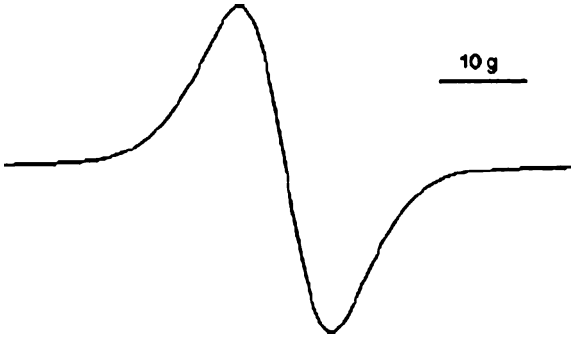

Fig. 2. Typical ESR spectra of phenoxy radicals on solid state fibers.

not otherwise discussed, each treatment as summarized below was conducted in duplicate, and the final integration results were averaged.

Effect of Wood Type on Radical Formation

Three different fiber species were tested in this work as outlined above. The relative radical concentration of untreated, Fenton treated, and mediated Fenton in the treated fibers was measured and compared.

Effect of Chelator, Fenton Reagent and Treatment Time on Fiber Radical Formation

In order to study the effect of the chelator, Fenton reagent and treatment time on the formation of fiber radicals, the ponderosa pine TMP fiber was treated with Fenton and the chelator mediated Fenton system at room temperature at 5% consistency for a time period from 15 to 120 min.

Effect of Metal Type on Fiber Radical Formation

The effect of two transition metals (Fe^{2+} and Cu^{2+}) on fiber radical formation was investigated. Ponderosa pine TMP fiber was treated with either the Fenton system or the chelator-mediated Fenton system at room temperature, and at 5% consistency for 30 min. The metal compounds used were $FeCl_2$ and $CuCl_2$.

Stability of Fiber Radicals

The stability of fiber radicals over time was assessed by treating fibers first with the Fenton or mediated Fenton system and then aging at room temperature or in a 100°C oven. The treated fibers were kept in standard ESR tubes during aging and were exposed to the atmosphere.

Solid Fiber Preparation and ESR Measurement of Fiber Radicals

After a specified treatment and exposure period the fiber suspension was placed in a freezer. The frozen samples were then lyophilized for 5–9 h depending on the sample size, and approximately 100 mg of lyophilized fiber was evenly packed into a ϕ3 mm quartz ESR tube for measurement. The ESR spectra were recorded at room temperature on a Bruker EMX ESR spectrometer in the X-band range using a microwave frequency of ~9.8 GHz. If not otherwise discussed, the spectra were measured with a microwave power of 2 mW, a modulation frequency of 100 kHz, and modulation amplitude of 1 G. Since the intensity of the signal is proportional to the radical concentration, the relative concentration of phenoxy radicals within or at the surface of lyophilized fibers can be obtained by double integration of the first-derivative ESR signal. Figure 2 shows a typical ESR spectrum of phenoxy radicals observed in this work.

RESULTS AND DISCUSSION

Determination of Radical Activity by Chemiluminescence Measurement

Figure 3 illustrates the chemiluminescence produced by the Fenton and mediated Fenton systems. The data clearly show that chemiluminescence emission in the neat Fenton system lasted for less than 5 min, but the emission in the 2,3-DHBA mediated Fenton system was sustained for a much longer period. The shape of the curves for the neat and

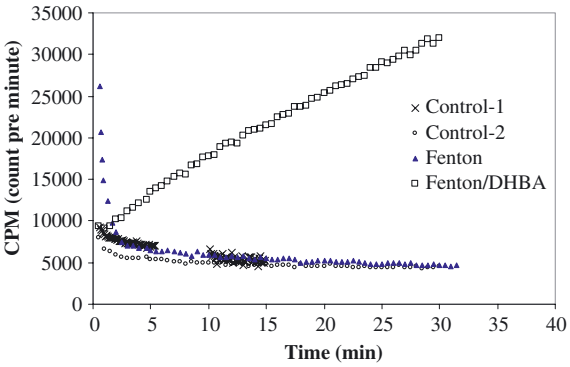

Fig. 3. Chemiluminescence of Fenton and mediated Fenton systems. Experimental condition: pH 5.0 buffer 20 m*M*, Fe(II) 1 m*M*, H_2O_2 5 m*M*, DHBA 1 m*M*.
Control-1: buffer;
Control-2: H_2O_2, buffer;
Fenton: Fenton, with iron and H_2O_2 only;
Fenton/DHBA: mediated Fenton, with iron, H_2O_2 and DHBA.

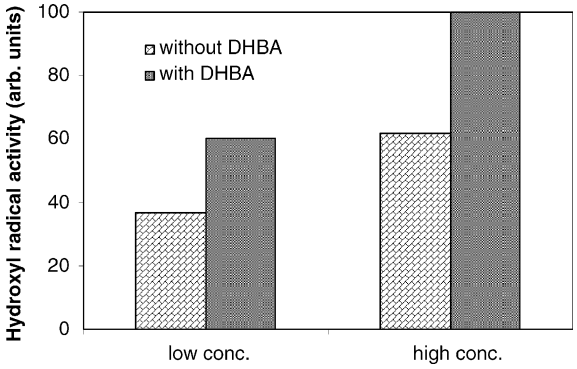

Fig. 4. Relative formation of hydroxyl radical measured as the DMPO-OH spin adduct.
The samples contained:
Low conc.: DMPO 10 m*M*, buffer 20 m*M*, Fe_2Cl_2 0.1 m*M*, H_2O_2 0.5 m*M*, (DHBA 0.1 m*M*);
High conc.: DMPO 10 m*M*, buffer 20 m*M*, Fe_2Cl_2 1 m*M*, H_2O_2 5 m*M*, (DHBA 1 m*M*).

mediated systems is also different. The neat Fenton system quickly reaches a peak level of chemiluminescence that rapidly declined. The 2,3-DHBA mediated system continues to increase suggesting a sustained production of long-lived as opposed to short-lived radicals. It has previously been reported that the chemiluminescence observed is directly associated with free hydroxyl radical activity in the Fenton system [14], however, our work suggests that, in the presence of ligands such as 2,3-DHBA, longer lived radicals may be produced in addition to the hydroxyl radical, resulting in the chemiluminescence pattern observed. The interpretation of chemiluminescence data from the mediated Fenton reaction may be more complex than initially reported [14]. It is difficult, using chemiluminescence data alone, to differentiate between the continued generation of hydroxyl radicals associated with the Fenton system and the possible generation of longer lived radicals which may also be associated with the mediated Fenton system.

Determination of Hydroxyl Radical by ESR Spin-trapping

Figure 4 compares the formation of hydroxyl radicals under different experimental conditions as measured by the ESR spin-trapping technique. As shown, treatment with a higher concentration of Fenton reagent led to greater hydroxyl radical formation, and the addition of DHBA also boosted the formation of hydroxyl radicals. In Fig. 4, under the "high conc." condition, the Fenton reagent solution was 10 times greater in concentration than the "low conc." condition. However, the hydroxyl radical formation in the "high conc." treatment was only twice that of the "low conc." treatment. This is probably due to the faster decay rate of hydroxyl radicals in "high conc." treatments. Alternatively it may be attributed to the order of chemical addition during measurement since DMPO was added to the system last and, as hydroxyl radical formation and decay is extremely rapid, some of the hydroxyl radicals may well have been decayed prior to DMPO addition.

The effect of different metal species on hydroxyl radical generation was also investigated in this study. Figure 5 shows the effect of H_2O_2 and DHBA on the formation of hydroxyl radicals in the presence of copper. It appears that Cu^{2+} and H_2O_2 alone produce detectable amounts of hydroxyl radicals. However, comparing the same concentration of Fe^{2+} and H_2O_2, the hydroxyl radicals produced in Cu^{2+}/H_2O_2 system was only about 6% the radicals produced in Fe^{2+} based Fenton system (data not shown). Pecci *et al.* [15] gave a likely explanation of the hydroxyl radical generation with Cu^{2+} and excessive H_2O_2, which are presented in the following reactions (Eqs. (1)–(3)).

$$Cu^{2+} + H_2O_2 \rightarrow Cu^{+}O_2H + H^{+}, \quad (1)$$

$$Cu^{+}O_2H + H_2O_2 \rightarrow Cu^{+} + O_2 + \cdot OH + H_2O_2, \quad (2)$$

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + \cdot OH + OH, \quad (3)$$

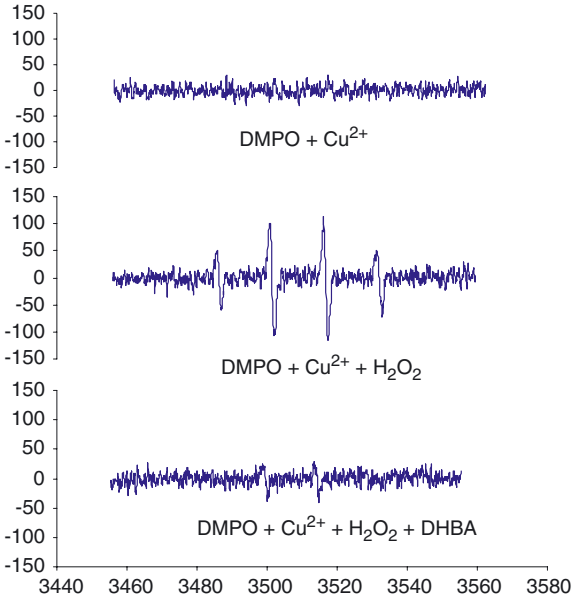

Fig. 5. Relative formation of hydroxyl radical measured as the DMPO-OH spin adduct. Experimental conditions: DMPO 10 m*M*, pH4.5 acetate buffer 20 m*M*, $CuCl_2$ 1 m*M*, H_2O_2 5 m*M*, DHBA 0.5 m*M*.

Where Eq (2) is similar to the Haber–Weiss reaction [16] and Eq (3) is the copper-driven Fenton reaction. Figure 5 also shows that the formation of hydroxyl radicals was inhibited by the addition of 2,3-DHBA, which may be due to the formation of the DHBA/Cu^{2+} complex, thus preventing the further reduction of Cu^{2+} by H_2O_2. Alternatively, 2,3-DHBA may be oxidized to form semiquinone radicals. Formation of the semiquinone would effectively prevent further reduction of transition metals and therefore limit the production of hydroxyl radicals.

To study hydroxyl radical activity over time, two Fenton system based samples with iron were prepared and their hydroxyl radical production was measured over time (Fig. 6). As shown in Fig. 6, the amount of detected hydroxyl radicals decreased rapidly over time. It is consistent with Fig. 3 that for the neat Fenton system, the detectable free hydroxyl radical activity was sustained for less than 1 min. In contrast, the hydroxyl radical formation in the DHBA mediated Fenton system lasted longer with continued detectable free hydroxyl radical generation after 15 min of incubation. The reciprocal radical concentration (Fig. 6, inset) as a function of time indicated that radical decay proceeded through a second-order reaction. Compared to Fig. 3, Fig. 6 shows that hydroxyl radical activity in the mediated Fenton system decreased over time, where in Fig. 3

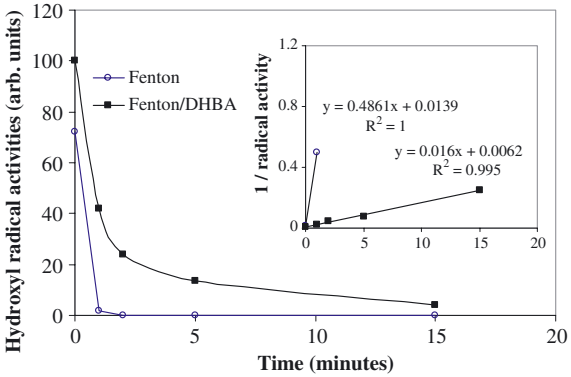

Fig. 6. The formation of hydroxyl radicals over time in Fenton and mediated Fenton reactions. DMPO was added to the system just before each measurement. Experimental conditions: DMPO 10 m*M*, pH 5.0 buffer 20 m*M*, $FeCl_2$ 0.1 m*M*, H_2O_2 0.5 m*M*, (DHBA 0.1 m*M*).

the chemiluminescence-emission for the mediated Fenton system increased at least for the first 30 min. This would be consistent with the oxidation of a portion of the 2,3-DHBA in the system while at the same time, the remainder of the ligand in solution would function to reduce metals with the two reactions occurring simultaneously. Goodell *et al.* [12] have suggested that the oxidative breakdown of 2,3-DHBA by hydroxyl radical may provide a source of electrons to cycle semiquinone forms of the molecule back to the hydroquinone state. This would explain the non-stoichiometric increase in iron reduction by DHBA, and also help to explain the increased hydroxyl radical production at the same time that other longer-lived radical species are formed as observed in the chemiluminescence study. The differences between the mediated Fenton reaction data in Figs. 3 and 6 may also be explained by the differences in the techniques used to detect radical activity. Whereas the chemiluminescence method detects all radicals, the ESR spin trap method is specific for hydroxyl radicals. Because the hydroxyl radicals are short-lived, not all of them will react with the DMPO spin trap in solution, and the ESR method therefore, underestimates the amount of these radicals produced in the system.

Determination of Fiber Phenoxy Radicals by ESR Measurement

In the following sections, the effect of Fenton reagent concentration, treatment time, and fiber species on phenoxy radical formation in the fibers is presented. Since in this study, the intent of treatment

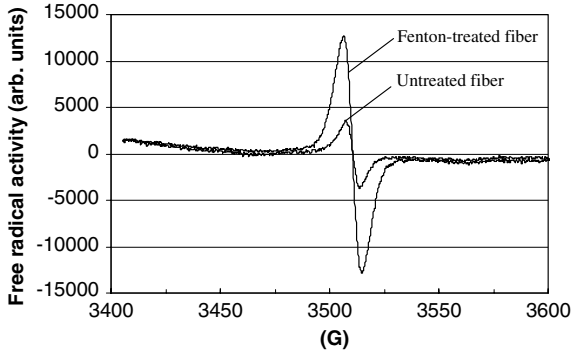

Fig. 7. A typical ESR spectra of Fenton-treated and untreated fiber. Ponderosa pine TMP fibers were treated at room temperature at 5% consistency for 30 min with following chemicals: 20 m*M* acetate buffer; 10 m*M* H_2O_2; 2 m*M* $FeCl_2$.

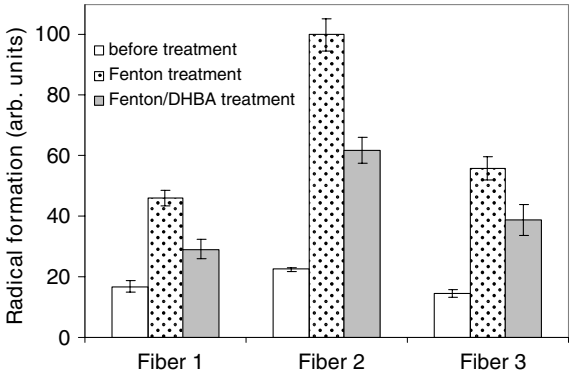

Fig. 8. Relative radical concentration of TMP fiber before and after a neat Fenton, and a mediated Fenton treatment. Fiber 1: Ponderosa pine softwood TMP; Fiber 2: S. yellow pine TMP; Fiber 3: Aspen TMP. The treatment was conducted at room temperature at 5% consistency for 30 min. The chemical concentrations (based on final mixture volume) were: 20 m*M* acetate buffer; 20 m*M* H_2O_2; 5 m*M* $FeCl_2$; and 2mM DHBA (mediated Fenton treatment).

* For all the figures presented in this work, if not otherwise indicated all error bars represent the actual data range of the two duplicates.

ultimately is to produce fiberboard at a specified time after the treatment of fibers, an important aspect of this research was to monitor the stability of the fiber radicals over time as well.

The ESR spectra of untreated and treated solid fibers show a signal with no hyperfine structure due to the heterogeneous natural of the solid fiber (Fig. 2). In this work, the characteristic *g*-values of the ESR spectra of treated and untreated fibers were similar to those reported for phenoxy radicals [7, 17].

Figure 7 shows a typical ESR spectra for Fenton-treated and untreated fibers. The increase of the ESR signal intensity is due to the formation of phenoxy radicals after Fenton treatment. It is difficult to accurately quantify the radical activity of heterogeneous organic compounds such as fibers, since there are many side reactions and radical couplings, which can affect the radical concentration. Therefore, in the following studies, the quantification of all free radical activity is presented as arbitrary units relative to the concentrations of free radicals in other samples.

The three different fiber species outlined in the previous section were also tested in this work. Phenoxy radicals were observed (Fig. 8) in all three types of untreated fiber, with Fiber 2 (southern pine TMP) having a slightly higher radical concentration. The radicals present in the untreated fiber were probably induced by mechanical stress during TMP production, or by UV radiation [7]. Figure 8 also shows that significantly increased radical formation was detected in all fiber types following Fenton-based treatment.

Among the three TMP fibers, Fiber 2, the southern pine TMP, shows the greatest relative radical formation after treatment. The fiber radical content of Fibers 1 and 3 was increased only moderately by the Fenton treatment. More investigation is necessary to study the exact effect of wood species on fiber radical formation.

We also observed that under the current treatment conditions (relatively high concentrations of Fenton reagents), the mediated Fenton treatment resulted in less fiber radical formation compared to the neat Fenton treatment (Fig. 8). It is possible that excessive and prolonged hydroxyl radical formation associated with the addition of DHBA interfered with the formation of fiber radicals (see concentration effects below).

The relative concentrations of ponderosa pine TMP fiber radicals after different treatments are compared in Fig. 9. It shows that excessive hydroxyl radical may actually inhibit the formation of fiber radicals. For example, the Fenton reagent concentration in treatment Cond 2 is only one-quarter of the chemical concentration used in the treatment Cond 4. However, compared to Cond 4, the fiber radical formation in Cond 2 is almost doubled for neat Fenton treatment and tripled for the mediated Fenton treatment.

Figure 9 also shows that the effect of the chelator (2,3-DHBA) on fiber radical formation depends highly on the Fenton reagent concentration. With high dosages of Fenton's reagent (Cond 3 and Cond 4), treatments with DHBA led to less fiber radical formation than the treatments without DHBA. This may be due to the excessive generation of hydroxyl

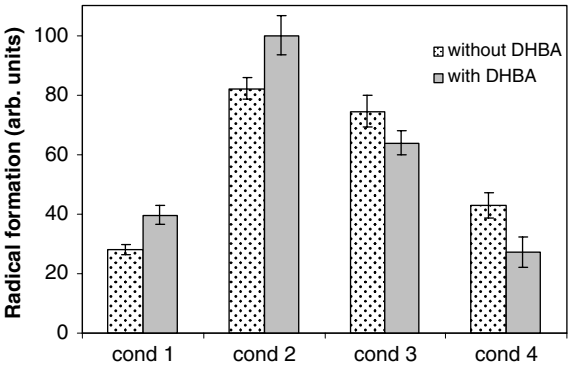

Fig. 9. Effect of treatment conditions on fiber radical formation. The treatment was conducted at room temperature at 5% consistency for 30 min. The chemical dosage used in each treatment was as follows:
Cond 1: 20 m*M* acetate buffer, 0.5 m*M* H_2O_2, 0.2 m*M* $FeCl_2$, (0.1 m*M* DHBA);
Cond 2: 20 m*M* acetate buffer, 5 m*M* H_2O_2, 1 m*M* $FeCl_2$, (0.5 m*M* DHBA);
Cond 3: 20 m*M* acetate buffer, 10 m*M* H_2O_2, 2 m*M* $FeCl_2$, (1 m*M* DHBA);
Cond 4: 20 m*M* acetate buffer, 20 m*M* H_2O_2, 5 m*M* $FeCl_2$, (2 m*M* DHBA).

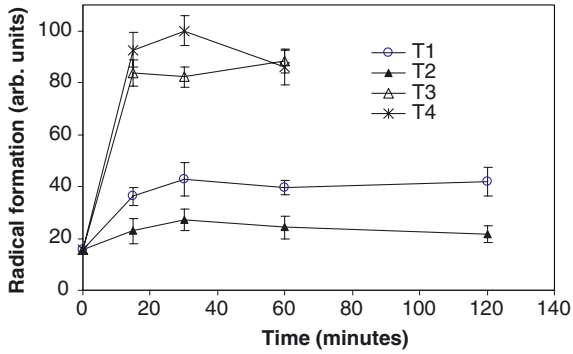

Fig. 10. Effect of treatment time on fiber radical formation in ponderosa pine TMP fiber. The treatment was conducted at room temperature at 5% consistency for the specified periods of time. The chemical dosage used in each treatment was as follows:
T1: 20 m*M* acetate buffer, 20 m*M* H_2O_2, 5 m*M* $FeCl_2$;
T2: 20 m*M* acetate buffer, 20 m*M* H_2O_2, 5 m*M* $FeCl_2$, and 2 m*M* DHBA;
T3: 20 m*M* acetate buffer, 5 m*M* H_2O_2, 1 m*M* $FeCl_2$;
T4: 20 m*M* acetate bufferm, 5 m*M* H_2O_2, 1 m*M* $FeCl_2$, and 0.5 m*M* DHBA.

radicals by the mediated Fenton reaction, which may contribute to the destruction of fiber radicals. In contrast, the addition of DHBA in the treatments with the lower dosage of Fenton's reagent actually increased the formation of fiber radicals (Cond 1 and Cond 2).

Figure 10 shows the effect of treatment time on fiber radical formation. In both the neat and chelator-mediated Fenton systems, fiber radicals were formed during the first 15 min of the treatment, with the maximum radical formation being reached after around 30 min of treatment. It also presents additional evidence suggesting that excessive hydroxyl radical production could cause fiber radical destruction.

These results suggest that hydroxyl radicals cause the formation of phenoxy radicals through the depolymerization and oxidation of lignocellulose compounds during Fenton type treatment. However, hydroxyl radicals are also responsible for the destruction of fiber radicals. For the treatments with low Fenton reagent load, the majority of the hydroxyl radicals probably participate in the fiber radical forming reactions. The addition of DHBA leads to an increase in the formation of hydroxyl radicals and this in turn leads to the increased formation of fiber radicals. For the treatments with high Fenton reagent load, the greater number of hydroxyl radicals produced probably causes the destruction of fiber phenoxy radicals.

Figure 11 shows the comparison of fiber radical formation between samples treated with different metals (Fe^{2+} and Cu^{2+}). Unlike the samples treated with the Fe^{2+} based Fenton system, there is only a very limited amount of fiber radical generated after the Cu^{2+} based treatment. This is probably due to reduced hydroxyl radical formation in the Cu^{2+} based Fenton-like reaction. Under the specified experimental conditions, the addition of DHBA

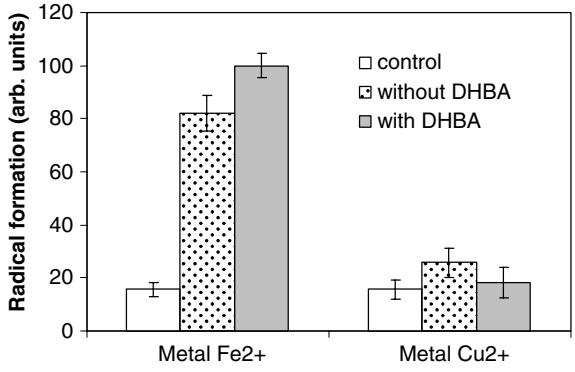

Fig. 11. Relative phenoxy radical concentration of fibers before and after treatments involving different transition metals. Ponderosa pine TMP fiber was treated at room temperature at 5% consistency for 30 min. The chemical concentrations (based on final mixture volume) were: 20 m*M* acetate buffer; 5 m*M* H_2O_2; 1 m*M* metal (Fe^{2+}/Cu^{2+}); and/or 0.5 m*M* DHBA.

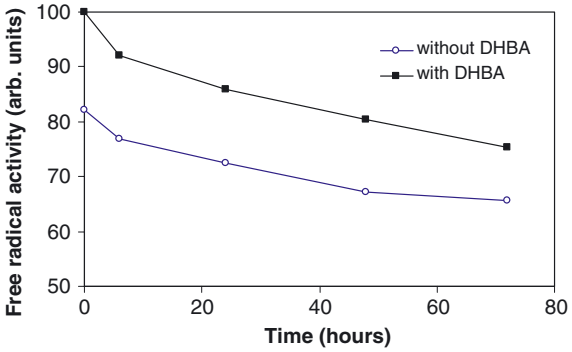

Fig. 12. Decay of radicals at room temperature in the Fenton treated or mediated Fenton treated ponderosa pine TMP fibers. The treatments were conducted at room temperature at 5% consistency for 30 min. The chemical concentrations (based on final mixture volume) were: 20 m*M* acetate buffer; 5 m*M* H_2O_2; 1 m*M* Fe^{2+}; 0.5 m*M* DHBA.

boosted the apparent fiber radical formation for the Fe^{2+} based treatment. However, no definitive effect of addition of DHBA in the Cu^{2+} based system was observed.

The stability of fiber radicals over time was assessed by treating fibers first with the Fenton or mediated Fenton system followed by aging at room temperature or in a 100°C oven to simulate material fabrication conditions. The treated fibers were kept in standard ESR tubes during aging and were exposed to the atmosphere. Figures 12 and 13 show the decay of fiber radicals over time at room temperature and at elevated temperature respectively. As shown in Fig. 12, at room temperature, the decay of radicals in the two fibers followed a similar pattern. After 72 h aging, about 20% of the fiber radicals for both treatments had decayed. As discussed in previous work, the decay likely involves coupling and disproportionation of fiber radicals [7]. Figure 13 shows the

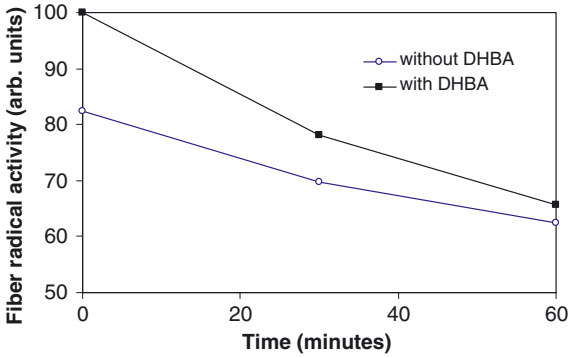

Fig. 13. Decay of radicals in fibers aged at 100°C. Fibers were from the same treatment illustrated in Fig. 12.

decay pattern of fiber radicals aged at 100°C for up to 60 min. It is apparent that the increased temperature greatly accelerates the rate of fiber radical decay. Approximately 30% of the fiber radicals decayed after only 60 min aging at 100°C vs. 0.5% to 1% fiber radical decayed after 60 min at room temperature. The results above also indicate that fiber radicals generated by the mediated Fenton treatment were more vulnerable to heat. Therefore, in fiberboard production, lower temperature and quicker processing time during fiber preparation may help keep the fiber radicals active.

CONCLUSION

The effect of different Fenton or mediated Fenton treatments on the generation of fiber phenoxy radicals, and on the formation of free hydroxyl radicals was studied using ESR techniques. Analysis of the radical generating mechanism in a 2,3-DHBA mediated Fenton system suggests that the ligand oxidizes to the semiquinone and promotes iron reduction. The reduced iron can then participate in Fenton reactions to produce hydroxyl radicals.

With regard to fiber radical generation, it was demonstrated that the fiber radical formation depends significantly on Fenton reagent type and concentration. High concentrations of Fenton reagents may actually cause the destruction of fiber radicals. The effect of wood type and treatment time on fiber radical formation was investigated as well and showed that different wood species responded differently to the Fenton based treatment, and a 30 min treatment time is optimal for most of the fibers. The stability study of fiber radicals reveals that the fiber radicals generated by Fenton treatment decay at a relatively slow rate at room temperature but decay rapidly when being heated, which indicates that the activated fibers should be kept at relatively low temperature to maintain fiber radicals activity in future fiberboard autobonding experiments.

FUTURE RESEARCH

The goal of this research was to explore the basic parameters which would affect the production of high quality fiberboard without the use of synthetic resins. It has previously been proposed that the phenoxy radicals present in activated fiber are responsible for enhanced interfiber bonding. To verify the relationship between fiber radicals and fiberboard physical properties, future research will focus on the manu-

facture of fiberboard from activated fibers, and the test of the physical properties of fiberboards produced.

The mechanism of fiber phenoxy radical formation is still not well understood. Gierer et al. [18] demonstrated the different pathways for formation of phenoxy radicals using lignin models. However, the effect of Fenton type treatment on natural lignin in the fiber requires additional study. The aim of the treatment ultimately will be to generate appropriate amounts of hydroxyl radicals in the correct microsites, to maximize fiber radical formation and minimize the fiber radical destruction.

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