

Graft Copolymerization of Polyfurfuryl Alcohol and Cellulose

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SYNOPSIS

Viscosity of polyfurfuryl alcohol (PFA) and addition of hydroquinone exert a strong positive effect on grafting polyfurfuryl alcohol to cellulose fiber with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ oxidant in an aqueous slurry at pH 2. Composition of the atmosphere and the nature of acids used to adjust pH does not influence the reaction, with the exception of phosphoric acid, which negatively influences polymer loading. Conducting the reaction in nonaqueous media inhibits grafting. $\text{K}_2\text{S}_2\text{O}_8$, $\text{Ce}(\text{SO}_4)_2$, and $\text{K}_2\text{Cr}_2\text{O}_7$ perform as well as $\text{H}_2\text{O}_2/\text{Fe}^{2+}$, whereas H_2O_2 /thiourea dioxide, H_2O_2 /thiourea, NH_4VO_3 , KMnO_4 , and KNO_3 give inferior polymer loads; Mn^{3+} /acetylacetonate and azobisisobutyronitrile are ineffective. A small improvement in polymer loading is obtained by gradual addition of the oxidant to the reaction slurry.

INTRODUCTION

In an earlier paper, we demonstrated that treating an aqueous slurry of polyfurfuryl alcohol (PFA) and cellulose fibers with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ oxidant at 90°C gave a grafted product, with polymer loading increasing with time to 68% after 60 min of treatment.¹ Under the same conditions, monomeric furfuryl alcohol (FA) gave mainly a mixture of free cellulose and cross-linked PFA.

Investigation of various reaction parameters indicated that a decrease in reaction temperature or an increase in volume of the aqueous phase decreased both polymer loading and grafting efficiency. Increase in cellulose consistency also decreased the polymer loading, while it slightly increased the grafting efficiency; this was explained by distribution of the same amount of grafted polymer over an increased amount of cellulose fibers. Increase in concentration of H_2O_2 , Fe^{2+} , or both gave curves with the polymer loading going through a maximum, most likely resulting from an interplay of the first- and the second-order terms in the reaction-rate equations. Varying pH (from 1 to 6) gave a maximum

polymer loading at pH 2, sharply decreasing toward higher pH values, most likely due to precipitation of the Fe^{3+} catalyst.

Pretreatment of cellulose with the oxidant prior to addition of PFA resulted in no grafting, whereas pretreatment of PFA prior to addition of cellulose produced a grafted product. This indicates that oxidation produces long-lived active sites in PFA, but not in cellulose.

In this report, we present the results of our examination of the influence of additional reaction parameters on polymer loading and grafting efficiency, which include viscosity of PFA, addition of polyhydroxyphenolic compounds, lignin content of cellulose, nature of the added acids, and composition of the atmosphere, nature of solvents and oxidants, and rate of addition of the oxidant.

EXPERIMENTAL

Unless otherwise stated, the grafting procedure used was as described in our previous paper with pH = 2.0; temp = 90°C ; grafting reaction time = 60 min; $\text{Fe}^{2+} = 0.01 \times 10^{-3}$ mol; $\text{H}_2\text{O}_2 = 35.0 \times 10^{-3}$ mol; PFA = 2.5 g; and total aqueous volume = 100 mL.¹

Thermomechanical pulp (60% western hemlock and 40% white fir, passed through secondary refinery) was supplied by Boise Cascade Corporation.

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The pulp was extracted with ethanol/benzene and ethanol and then with water according to TAPPI standard T12 os-75.² The extracted fibers were stored in a plastic bag at +4°C and had a Klason lignin content of 30%, determined using the USDA-Forest Products Laboratory procedure.³ Pulp samples of varying lignin content were then prepared by delignification using the chlorite method⁴ with varying amounts of chlorite.

PFA of melt viscosities 1,700, 4,400, 15,000, and 41,000 cps was supplied by Werner G. Smith, Inc., Cleveland, OH. All four samples were used for determining the relationship between PFA viscosity and polymer loading. In all other experiments, PFA of melt viscosity 1,700 cps was used. Because of the lower viscosity of PFA used, the polymer loadings and grafting efficiencies were generally appreciably lower than reported in our previous paper,¹ where PFA of higher viscosity was used. All reagents were analytical grade and were used without further purification.

Prior to grafting in organic solvents, water was removed from the pulp by sequential extraction with ethanol, acetone, and then pentane, and, finally, the solvent was removed by evaporation. Solvents used for grafting were brought to an apparent pH (measured by a pH meter) of about 2 by the addition of HCl.

The grafting procedure was otherwise the same as described for the aqueous medium.

RESULTS AND DISCUSSION

(a) Influence of PFA Viscosity

Our previous experiments indicated that PFA can be successfully grafted to cellulose in an aqueous slurry using a H_2O_2/Fe^{2+} oxidant, whereas FA produced very little graft. It was thus of interest to see whether viscosity and, consequently, the molecular weight of PFA also influenced grafting. Repetition of the grafting experiments using FA gave only 2.5% for the polymer loading and 0.5% for the grafting efficiency. The results of grafting experiments employing PFA of various viscosities indicated that polymer loading and grafting efficiency increased with viscosity and thus with molecular weight of PFA (Fig. 1).

Several explanations can be advanced for these results: (a) increasing PFA water solubility with decreasing molecular weight resulting in a decreasing activated PFA-to-cellulose ratio in the organic phase, (b) larger number of structural units per molecule available for activation and grafting in case of the higher molecular weight PFA, and (c) in-

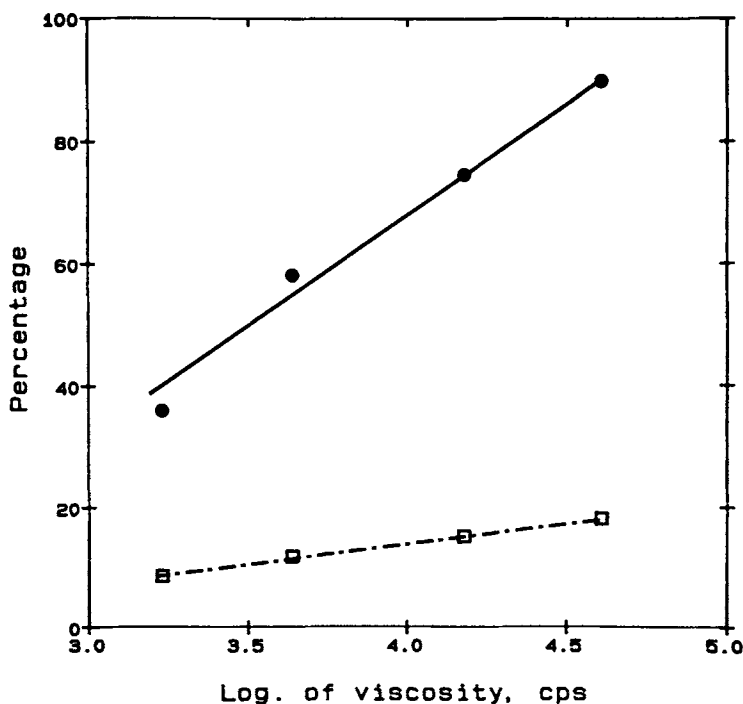
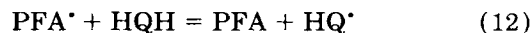
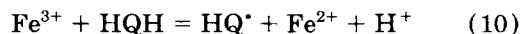
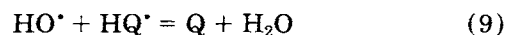
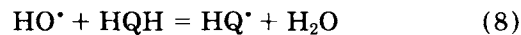
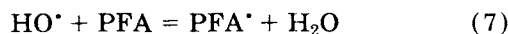
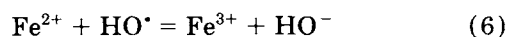
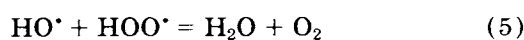
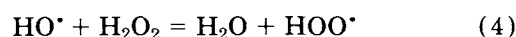
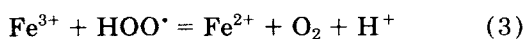
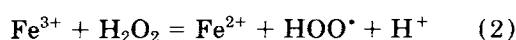
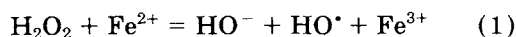


Figure 1 Effect of PFA viscosity on polymer loading (black circles) and grafting efficiency (squares) in PFA/cellulose grafting.

creasing weight/graft ratio with increasing PFA molecular weight.

(b) Influence of Polyhydroxy Phenols

PFA-to-cellulose grafting with $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ most likely involves participation of HO^\bullet radicals¹ (reactions 1-7, below). As is well known, hydroquinone and related antioxidant compounds are efficient free-radical trapping reagents and have been found to retard or inhibit the free-radical graft polymerization of vinyl monomers.⁵ Thus, they could be expected to inhibit the oxidative grafting of PFA by removal of HO^\bullet (reactions 8 and 9):



HQH = hydroquinone; Q = quinone.

On the other hand, hydroquinone compounds can also react with Fe^{3+} , reducing it to Fe^{2+} , essential for the formation of HO^\bullet (reactions 10 and 11) and thereby also suppressing undesirable reactions 2 and 3. Thus, Morin et al.⁶ found that addition of hydroquinone as well as of other reducing compounds accelerated $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ grafting of acrylonitrile to cellulose.

The effect of the addition of hydroquinone on the PFA polymer loading of cellulose is demonstrated in Figure 2. The positive influence of hydroquinone (reactions 10 and 11) clearly dominates, particularly at lower hydroquinone concentrations. The slower rise of polymer loading at higher hydroquinone concentrations could be connected either with an increased participation of undesirable reactions 8 and

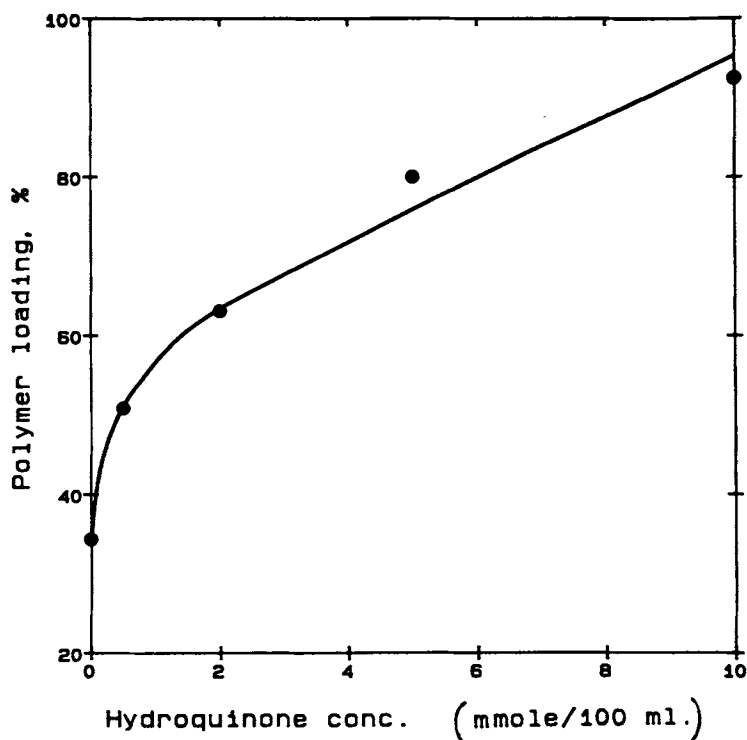


Figure 2 Effect of the addition of hydroquinone on polymer loading in PFA/cellulose grafting.

9 or with the inactivation by hydroquinone of the active free-radical sites formed on PFA or cellulose (reaction 12).⁶

Omitting PFA from the reaction mixture and using hydroquinone concentration of 5 mmol/100 mL resulted in a polymer loading of only 1.2%, indicating that hydroquinone itself played a negligible role as a grafting partner (grafting chemical).

(c) Effect of the Lignin Content of Cellulose

Since lignin is a phenolic polymer, the lignin contained in cellulosic products such as wood pulp might be expected to affect positively⁷ or negatively^{8,9} the grafting reaction via the mechanisms just described. However, experiments with thermomechanical pulp containing 5.4–30.0% of lignin (Table I) demonstrated that the lignin content of the pulp had no measurable influence on polymer loading or grafting efficiency. This is not surprising since lignin is insoluble in the aqueous phase of the reaction mixture, which is where the reactions 1–6 and 8–11 promoting or inhibiting grafting occur.

(d) Effect of Acids and Composition of the Atmosphere

It was previously established¹ that the optimum conditions for grafting required a pH of about 2.0. Investigation of the influence of various acids on grafting indicated that acetic, formic, hydrochloric, nitric, perchloric, and sulfuric acids yielded comparable polymer loadings (31.2–37.6%) and grafting efficiencies (7.0–8.7%). Use of phosphoric acid, on the other hand, reduced polymer loading to 6.4% and grafting efficiency to 1.3%, most likely due to the chelation of Fe²⁺ (or Fe³⁺) catalyst.

It is well known that oxygen can act as a free radical scavenger. Since PFA grafting is likely to

involve formation of free-radical sites on PFA or on cellulose, it was of interest to see whether the composition of the atmosphere above the reaction mixture would influence grafting. The experiments were done by sparging various gases including oxygen, air, nitrogen, hydrogen, and helium through the aqueous mixture during the reaction. In all cases, resultant polymer loadings ranged from 33.7 to 37.3%, and grafting efficiencies, from 7.7 to 8.5%; i.e., atmospheric composition had little or no effect on grafting.

(e) Effect of the Nature of Solvents and Oxidants

The insolubility of cellulose in water and all common organic solvents makes grafting to cellulose a heterogeneous reaction and introduces several additional controlling parameters, including (1) characteristics of the solvent used, especially solubility of the grafting partner in that solvent; (2) adsorption of the grafting partner to cellulose; and (3) amount of cellulosic surface available for grafting. Since PFA has widely different solubilities in different solvents, we investigated the influence of various solvent media on PFA/cellulose grafting.

The results (Table II) indicate that only a reaction in an aqueous medium gives a high polymer loading. Although it has been demonstrated that the interaction of grafting partners with an organic solvent (electrostatic forces, dipole–dipole interactions, hydrogen bonding) have a pronounced effect on free radical copolymerization,⁹ the absence of PFA grafting to cellulose in organic solvents is most likely due to two factors: (1) higher solubility of PFA in organic solvents, decreasing the contact between PFA and cellulose, and (2) removal of HO· radicals by reactions with the organic solvent molecules, rather than with the grafting partners. Such free-radical removal by solvent reactions is, of course, impossible with water.

In all previous experiments, grafting was done using H₂O₂/Fe²⁺ as an oxidative activation agent. It was thus of interest to examine the suitability of other oxidation agents, particularly those known to be effective in grafting reactions in general.^{12,13}

The results (Table III) indicate that the peroxidic compounds H₂O₂/Fe²⁺ and potassium persulfate are about equally effective, whereas H₂O₂ catalyzed with thiourea or thiourea dioxide failed to initiate grafting. Nonperoxidic compounds, such as potassium dichromate and ceric sulfate, performed well, with the ceric ion surpassing H₂O₂/Fe²⁺ in polymer loading and grafting efficiency. A similar finding has been reported by other investigators in grafting experi-

Table I Effect of Lignin Content of Thermomechanical Pulp on Graft Copolymerization PFA/Cellulose

Lignin Content (%)	Polymer Loading (%)	Grafting Efficiency (%)
0.0	34.3	7.9
5.4	32.2	6.5
9.9	30.8	6.2
16.4	32.7	6.6
19.9	32.7	6.6
26.4	31.4	6.3
30.0	31.4	6.3

Table II Solvent Influence on PFA/Cellulose Grafting

Solvent	Solubility Parameter ¹⁰ (cal/cm ³) ^{1/2}	Dielectric Constant ¹¹ (20°)	Boiling Point (°C) (1 atm)	Swelling of Cellulose ^a	Solubility of PFA at the Reaction Temp ^a	Polymer Loading
<u>Strongly hydrogen-bonded</u>						
Acetic acid	10.1	6.15	116.8	Moderate	Soluble	0.2
Butanol	11.4	17.8	117–118	Moderate	Slightly soluble	0
Ethylene glycol	14.6	37.0	196–198	Good	Insoluble	0
Formamide	19.2	109.0	210	Excellent	Slightly soluble	0
Water	23.4	78.5	100	Good	Insoluble	34.3
<u>Moderately hydrogen-bonded</u>						
Dioxane	10.0	2.2	101	Moderate	Soluble	0
DMF	12.1	36.7	153	Good	Soluble	0
DMSO	12.0	47.0	189	Excellent	Soluble	0
<u>Poorly hydrogen-bonded</u>						
Acetonitrile	11.9	39.0	81–82	Poor	Soluble	0

^a Swelling of cellulose and solubility of PFA were recorded at 90°C, except for acetonitrile, where grafting was performed at 70°C and swelling of cellulose and solubility of PFA were recorded at that temperature.

ments with vinyl monomers¹³ and was explained by chelation of the ceric ion by cellulose, initiating oxidative degradation and the formation of free-radical sites. Since the radicals were almost exclusively produced on cellulose, grafting was favored over homopolymerization of vinyl monomers. Although it seems likely that in our case ceric ion chelation by cellulose is also in some way responsible for the increase in polymer loading, the exact mechanism

might not be so simple, since it has been demonstrated¹ that activation of PFA rather than of cellulose is likely the predominant mechanism in grafting.

The satisfactory performance of potassium dichromate is of some interest in that during the reaction the pH increased from 2.0 to 5.8, a value at which H₂O₂/Fe²⁺ performed poorly.¹ The possibility of conducting grafting reactions at a higher pH

Table III Effect of Oxidant System on PFA/Cellulose Grafting

Oxidant	Oxidant Concentration (mmol/100 mL)	Initial pH	Final pH	Polymer Loading	Grafting Efficiency
H ₂ O ₂ /Fe ²⁺	8.8; 2.5 × 10 ⁻³	2.0	2.0	34.3	7.9
H ₂ O ₂ /thiourea dioxide	8.8; 0.1	7.4	3.3	0.2	0.0
H ₂ O ₂ /thiourea	8.8; 0.1	2.0	2.1	0.6	0.1
K ₂ S ₂ O ₈	5	2.0	1.8	36.5	7.3
	1	2.0	1.9	0	0
Ce(SO ₄) ₂ · 4H ₂ O	5	2.0	2.0	42.0	8.5
	1	2.0	2.0	1.6	0.3
K ₂ Cr ₂ O ₇	5	2.0	5.8	36.0	7.8
NH ₄ VO ₃	5	2.0	6.1	2.8	0.6
KMnO ₄	1	2.0	8.2	2.4	0.5
KNO ₃	5	2.0	2.2	0.2	0.0
	15	2.0	2.0	0.8	0.2
Mn ³⁺ acetylacetonate	1	2.0	6.4	0	0
Azobisisobutyronitrile ^a	5	5.0	6.0	0	0

^a Grafting was carried out in a mixture of 75% water and 25% propanol by volume at 85°C for 1.5 h.

Table IV Effect of Rate of Oxidant Addition on PFA/Cellulose Grafting

Time for Addition (min)	Polymer Loading (%)	Grafting Efficiency (%)
0	34.3	7.9
15	39.4	7.9
30	40.6	8.2
45	39.8	8.0

might be desirable, since acidic degradation of the cellulose would be minimized.

(f) Effect of the Rate of Oxidant Addition

In all previous experiments, the entire amount of oxidant was added at the beginning of the reaction. We decided to see whether grafting could be improved by adding the oxidant gradually.

The results (Table IV) indicate that gradual rather than instantaneous addition of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ improved grafting somewhat but the effect was not significant. Beyond the initial improvement at 15 min, no further increase in polymer loading was found.

CONCLUSIONS

Increasing the viscosity, and, consequently, the molecular weight, of PFA increases the grafting of PFA onto cellulose with aqueous $\text{H}_2\text{O}_2/\text{Fe}^{2+}$. Water-soluble polyhydroxy phenols, such as hydroquinone, most likely increase grafting by reducing the formed Fe^{3+} to the catalytically active Fe^{2+} ; water insoluble lignin has no effect. Among other oxidants, potassium persulfate, potassium dichromate, and ceric sulfate are also effective. Substitution of organic solvents for water results in no grafting. Phosphoric acid decreases grafting by chelating metal-ion catalysts. All in all, it appears that the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ grafting reaction of PFA bears analogy to the free-

radical grafting of acrylics to cellulose only so far as the formation of free hydroxy radicals and their initial interaction with organic substrates is concerned; the mechanism of PFA attachment to cellulose is likely to be appreciably different.

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