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Fe²⁺-H₂O₂ Initiated Grafting of Lignocellulose with Methyl Methacrylate and Its Mechanism

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Fe²⁺-H₂O₂ INITIATED GRAFTING OF LIGNOCELLULOSE WITH METHYL METHACRYLATE AND ITS MECHANISM

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Key Words: Grafting; Fe²⁺-H₂O₂ redox; Grafting mechanism of lignin; Lignocellulose; Bagasse pith

ABSTRACT

Graft copolymerization of MMA onto bagasse pith, a lignocellulose material, using Fe²⁺-H₂O₂ as an initiator was investigated. To examine the behaviors of lignin and holocellulose in graft copolymerization, the grafted poly(methyl methacrylate) chains on lignin and holocellulose were separated by delignification with acid chlorite and hydrolysis of holocellulose with 72% sulfuric acid, and their molecular weights were measured. The roles of phenolic hydroxyl, alcoholic hydroxyl, and carbonyl groups are discussed by investigating the effect of pretreatments of lignocellulose on grafting, and a grafting mechanism is proposed.

INTRODUCTION

To make better utilization of wood, plant waste, and other lignocellulose materials, graft copolymerization has been widely investigated for the modification of these natural polymers. Various initiators, such as Ce⁴⁺ [1, 2], xanthate-Fe²⁺-H₂O₂ [3], Fe²⁺-H₂O₂ [4–6], NaHSO₃-soda lime glass [7, 8], and KMnO₄ [9],

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and an irradiation technique [10] have been used in the modification of bamboo, unbleached pulp, bagasse and jute fiber, etc. Many studies on the graft copolymerization of lignocellulose have been reported, but knowledge of the grafting mechanism is limited due to the complex chemical structure of lignin.

Bagasse is an important resource for papermaking in China, but bagasse pith must be removed before cooking because of its morphological defect. Therefore, most bagasse pith is burned as a fuel or thrown away as a waste. Bagasse pith may be converted into a product useful for something more than a fuel by proper modification. The irradiation technique [10] and NaSO_3 -soda lime glass [8] have been used to initiate the graft copolymerization of bagasse with vinyl monomers, and the properties of the resulting composites, including compression strength, density, and deformation, were measured [8].

In the graft copolymerization of lignocellulose, the grafting mechanism of holocellulose can be considered to be similar to that of pure cellulose, and it has been widely investigated [11–13], although lignin doesn't behave as simply as holocellulose due to its complex structure. Besides the alcoholic hydroxyl groups which cellulose contains, phenolic hydroxyl, carbonyl groups, and aromatic nuclei must be involved in the formation of grafting sites. In this report a grafting mechanism which explains the roles of phenolic hydroxyl, alcoholic hydroxyl, and carbonyl groups of lignin in grafting is proposed.

EXPERIMENTAL

Purification of Bagasse Pith

Bagasse pith was pulverized and the 40–60 mesh part was extracted with a benzene-ethanol mixture (2:1 v/v) for 6 hours in a Soxhlet apparatus and then with hot de-ionized water three times in a beaker. The klason lignin content was 24.2% and the ash content about 1%.

Methylation of Bagasse Pith with Diazomethane

Diazomethane, prepared from 10 g nitrosomethylurea, was dissolved in 250 mL of 1,4-dioxane, and 10 g of purified bagasse pith was added. The mixture was kept at 0°C for 4 days, and then the same amount of diazomethane, dissolved in 20 mL diethyl ether, was added again. After storage at 0°C for another 4 days, the reaction mixture was filtered and the residue was washed with de-ionized water. During washing, 0.1% aqueous acetic acid was used to decompose the residual diazomethane.

Treatment of Bagasse Pith with Fe^{2+} - H_2O_2

Ten grams of the purified bagasse pith was soaked in 500 mL of freshly prepared 0.0003 M aqueous $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ at 25°C for 30 minutes and then filtered and reacted with 500 mL of 0.004 M H_2O_2 under a nitrogen atmosphere at 70°C for 100 minutes. The reaction mixture was treated by the same method as described in preceding methylation section. The loss was about 1.0%, and this treatment has no measurable effect on the lignin content.

Reduction of Carbonyl Groups with Sodium Borohydride

In a three-neck flask, the purified bagasse pith (10 g) was reacted with 2.5 g sodium borohydride in 250 mL absolute ethanol under a nitrogen atmosphere at room temperature for 24 hours. The same method as described in the methylation section was used in purification of the reaction product.

Graft Copolymerization and Separation of Grafted PMMA Chains

Bagasse pith [dried weight (W_0), 0.500 g] was soaked in 25 mL of freshly prepared aqueous $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ solution at 50°C for 30 minutes and then filtered and thoroughly washed with de-ionized water. The residue was transferred into a 50-mL three-neck flask using de-ionized water. After the contents were bubbled with nitrogen gas for 20 minutes, 0.80 mL monomer and the other reagents were added. A total of 25 mL of de-ionized water was used as the reaction medium. After reaction under a nitrogen atmosphere with gentle stirring, the reaction mixture was poured into a sintered glass crucible and the residue was washed and dried in vacuum to a constant weight (W_1). The dried residue was then extracted with acetone in a Soxhlet apparatus for 24 hours to remove homopolymer, and then it was dried in vacuum to a constant weight (W_2).

The procedures used in the separation of grafted PMMA chains from lignin and holocellulose are illustrated in Fig. 1. The graft copolymer was transferred into a 50-mL Erlenmeyer flask, containing 30 mL de-ionized water, in a water bath at 75°C , and then 0.1 mL acetic acid and 2.0 mL 15% (g/mL) aqueous sodium chlorite were added per hour. After treatment for 6–7 hours, the contents were poured into a sintered glass crucible. The residue was washed, dried in vacuum to a constant weight (W_3) and then extracted with acetone in a Soxhlet apparatus for 24 hours. The poly(methyl methacrylate) in the concentrated extraction solution was

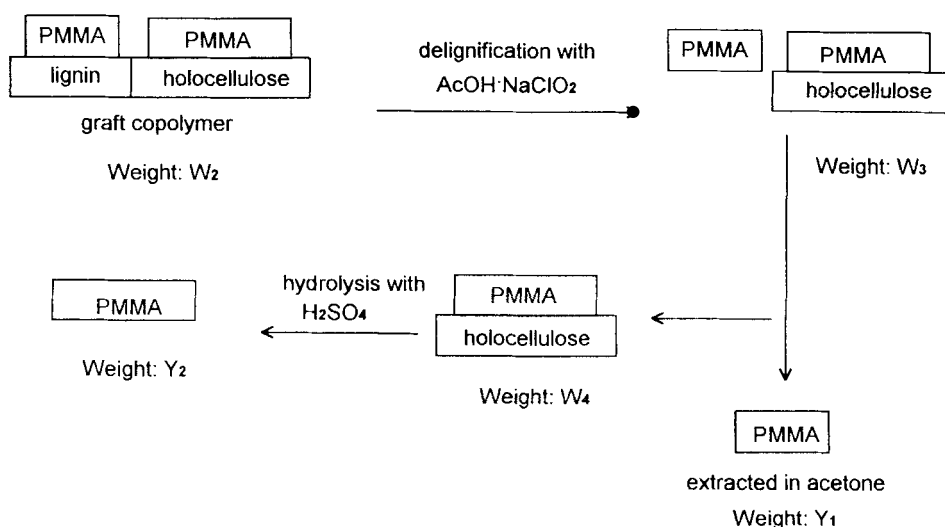


FIG. 1. Separation of graft copolymer.

precipitated with 200 mL of 0.005 M aqueous sulfuric acid, and the precipitate, which can be considered to be grafted PMMA chains on lignin, was collected and dried in vacuum to a constant weight (Y_1).

After the above extraction the residue was dried to constant weight (W_4), the holocellulose-PMMA graft copolymer was transferred into a 50-mL Erlenmeyer flask, and then 15 mL of 72% sulfuric acid was added. The flask was kept in a water bath at 20°C for 2 hours, followed by dilution of sulfuric acid with de-ionized water to 3% in a 1000-mL Erlenmeyer flask. The contents were heated and boiled for 4 hours. The insoluble part was collected in a sintered glass crucible, washed, dried, and extracted with acetone in a Soxhlet apparatus for 7 hours. Almost no residue remained after extraction. The poly(methyl methacrylate) in the extraction solution was collected by the same method as mentioned above, and then it was dried in vacuum to constant weight (Y_2).

The viscosities of the grafted PMMA chains were measured in acetone at 25.00 ± 0.05°C, and the following Mark-Houwink equation, which was calibrated by number-average molecular weight [14], was adopted to calculate the molecular weights:

$$[\eta] = 2.45 \times 10^{-5} M^{0.80}$$

Homopolymer yield, percentage conversion of monomer, grafting efficiency, and percentage grafting were calculated using the following equations.

$$\text{Homopolymer yield (\%)} = \frac{W_1 - W_2}{\text{weight of monomer (0.755 g)}} \times 100$$

$$\text{Percentage grafting of bagasse pith (\%)} = \frac{\text{weight of grafted PMMA } (W_2 - W_0)}{\text{weight of bagasse pith } (W_0)} \times 100$$

$$\text{Percentage conversion of monomer (\%)} = \frac{W_1 - W_0}{\text{weight of monomer (0.755 g)}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

$$\text{Percentage grafting of lignin (\%)} = \frac{\text{weight of grafted PMMA on lignin } (Y_1)}{\text{weight of lignin } (W_2 - W_3)} \times 100$$

$$\begin{aligned} &\text{Percentage grafting of holocellulose (\%)} \\ &= \frac{\text{weight of grafted PMMA on holocellulose } (Y_2)}{\text{weight of holocellulose } (W_4 - Y_2)} \times 100 \end{aligned}$$

Determination of Phenolic and Alcoholic Hydroxyl Groups in Lignin

The milled bagasse pith lignin was prepared according to Björkman method [15]. The contents of phenolic and alcoholic hydroxyl groups were determined according to the literature [16].

RESULTS AND DISCUSSION

Graft Copolymerization

In the separation of graft copolymer, the delignification with acid chlorite [17], one of methods used in the preparation of holocellulose, was adopted, and the resulting holocellulose was designated chlorite holocellulose. Whereas a longer reaction time is necessary due to the retardation of delignification by grafted PMMA, some hemicellulose is readily decomposed under drastic condition. Therefore, the extent of delignification was controlled by adjusting the reaction time depending on the percentage grafting. The calculated lignin and holocellulose contents are listed in Table 3. On the other hand, the treatment of homopolymer by the separation procedure indicated that PMMA loss is below 3.0 mg, and the molecular weights decrease by 5 and 3% in the delignification by acid chlorite and in the hydrolysis by sulfuric acid, respectively.

The changes of percentage grafting and molecular weights of grafted PMMA chains during grafting are shown in Table 1. As the reaction proceeds, monomers are grafted onto lignin and holocellulose gradually, and lignin shows a faster increase in percentage grafting than does holocellulose. The difference in the percentage grafting of lignin and holocellulose must be related to their characteristic chemical structures, which will be discussed in the Grafting Mechanism section. The data in Table 1 also show that the molecular weights of grafted PMMA chains on both lignin and holocellulose become larger as grafting proceeds, indicating that chain termination is slowed down considerably due to the insolubility of grafted PMMA chains in the reaction medium.

For the effective initiation of grafting by the Fe^{2+} - H_2O_2 redox, the adsorption of ferrous ions onto bagasse pith is necessary. This can be understood from the data shown in Table 2. In 0.01 M H_2SO_4 , the desorption of ferrous ions by sulfuric acid results in a rather lower percentage grafting and a higher homopolymer yield as compared with the grafting near neutrality. The favorable homopolymerization in 0.01 M H_2SO_4 impedes the diffusion of monomers to the propagating grafting

TABLE 1. Effect of Reaction Time on Grafting^a

	Reaction time (min)			
	5.0	10.0	15.0	45.0
Homopolymer yield (%)	2.6	5.2	9.2	14.5
Conversion of monomer (%)	19.3	32.6	48.9	67.6
Grafting efficiency (%)	86.8	83.9	82.2	78.5
Percentage grafting of lignin (%)	23.0	42.5	71.8	98.6
Percentage grafting of holocellulose (%)	27.6	42.7	53.2	72.0
$M\eta^b$ of PMMA on lignin (10^5)	1.03	1.34	2.01	2.34
$M\eta^b$ of PMMA on holocellulose (10^5)	0.89	1.39	1.73	2.02

^aReaction conditions: adsorbed ferrous ion, 473 ppm; H_2O_2 concentration, 5.0 mM; MMA, 0.80 mL; 70°C; without addition of H_2SO_4 and NaOH.

^bViscosity-average molecular weight.

TABLE 2. Graft Copolymerization in Different Reaction Media^a

	Initial reaction medium		
	10 mM H ₂ SO ₄	H ₂ O	10 mM NaOH
Homopolymer yield (%)	58.2	14.5	2.5
Conversion of monomer (%)	80.7	67.6	17.9
Grafting efficiency (%)	28.3	78.5	86.1
Percentage grafting of lignin (%)	25.9	98.6	30.1
Percentage grafting of holocellulose (%)	36.5	72.0	24.4
<i>M_n</i> of PMMA on lignin (10 ⁵)	1.25	2.34	8.65
<i>M_n</i> of PMMA on holocellulose (10 ⁵)	1.59	2.02	6.34

^aReaction conditions: adsorbed ferrous ion, 473 ppm; H₂O₂ concentration, 5.0 mM; MMA, 0.80 mL; 70°C; 45 minutes.

polymer radicals, as indicated by the lower molecular weights of grafted PMMA chains. On the other hand, compared with grafting near neutrality, the lower percentage grafting and homopolymer yield in 0.01 M NaOH indicate ineffective initiation due to the conversion of ferrous ions into ferrous hydroxide, and the higher molecular weights of PMMA chains are ascribable to the less active sites formed in initiation.

The data in Table 3 show the effect of H₂O₂ concentration on grafting. It is clear that 0.001 M H₂O₂ is sufficient for effective grafting and that excess hydrogen peroxide leads to a higher homopolymer yield. An increase of H₂O₂ concentration from 0.001 to 0.005 M is favorable for grafting onto lignin and holocellulose, and any further increase in H₂O₂ concentration has no measurable effect on grafting

TABLE 3. Effect of H₂O₂ Concentration on Grafting^a

	H ₂ O ₂ concentration (mM)			
	1.0	5.0	10.0	40.0
Homopolymer yield (%)	12.4	14.5	28.6	30.2
Conversion of monomer (%)	55.3	67.6	78.7	78.8
Grafting efficiency (%)	78.3	78.5	63.6	61.7
Percentage grafting of lignin (%)	69.0	98.6	95.3	98.6
Percentage grafting of holocellulose (%)	61.3	72.0	66.6	59.7
<i>M_n</i> of PMMA on lignin (10 ⁵)	3.69	2.34	1.63	1.26
<i>M_n</i> of PMMA on holocellulose (10 ⁵)	3.05	2.02	1.50	1.25
Calculated lignin in separation (mg)	113	108	118	121
Calculated holocellulose in separation (mg)	383	387	369	367

^aReaction conditions: adsorbed ferrous ion, 473 ppm; MMA, 0.80 mL; 70°C; 45 minutes; without addition of H₂SO₄ and NaOH.

TABLE 4. Relationship between Adsorbed Ferrous Content and Grafting^a

	Adsorbed ferrous content (ppm)				
	0	194	473	766	862
Homopolymer yield (%)	4.6	8.3	14.5	31.9	35.4
Conversion of monomer (%)	38.7	60.5	67.6	81.4	82.3
Grafting efficiency (%)	88.2	86.2	78.5	60.6	57.0
Percentage grafting of lignin (%)	62.6	96.4	98.6	100.7	82.5
Percentage grafting of holocellulose (%)	46.5	69.9	72.0	65.2	65.0
M_n of PMMA on lignin (10^5)	8.61	2.91	2.34	1.82	1.29
M_n of PMMA on holocellulose (10^5)	5.72	2.29	2.02	1.69	1.40

^aReaction conditions: H_2O_2 concentration, 5.0 mM; MMA, 0.80 mL; 70°C; 45 minutes; without addition of H_2SO_4 and NaOH.

onto lignin but a negative effect on grafting onto holocellulose. Unlike percentage grafting, the molecular weights of grafted PMMA chains are greatly affected by H_2O_2 concentration. Apparently shorter grafted PMMA chains are formed in higher H_2O_2 concentrations because more active sites are generated. A similar effect of adsorbed ferrous content on grafting was also observed, as shown in Table 4.

The data in Table 4 also show an interesting phenomenon in that iron (132 ppm), which was absorbed from soil during the growth of sugarcane, can also catalyze the decomposition of hydrogen peroxide and so initiate grafting without adsorbed ferrous ions. The existing states of these Fe ions are not as definite as ferrous ions, but they have a great influence on grafting, as demonstrated in Fig. 2. Extrapolation of the curve in Fig. 2 implies that some Fe ions seem unable to react with hydrogen peroxide to initiate grafting, probably because they are surrounded tightly by lignin and holocellulose.

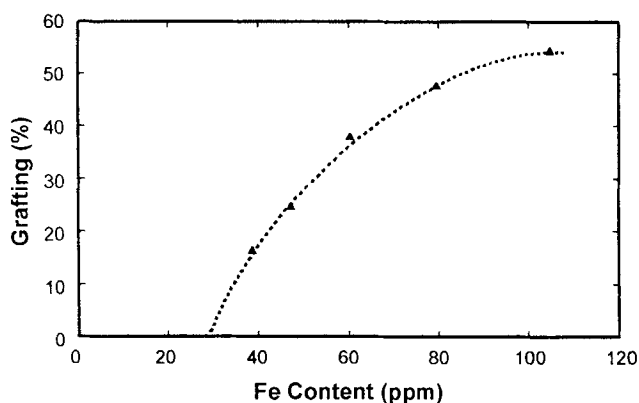
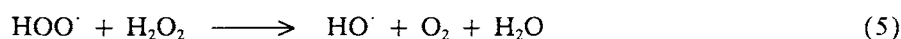


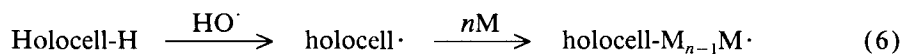
FIG. 2. Relationship between graft ratio and original Fe content of bagasse pith. Fe content was controlled by the pretreatment of bagasse pith with dilute sulfuric acid. Graft copolymerization was carried out at 70°C for 45 minutes using 1.0 mM H_2O_2 as the initiator.

Grafting Mechanism

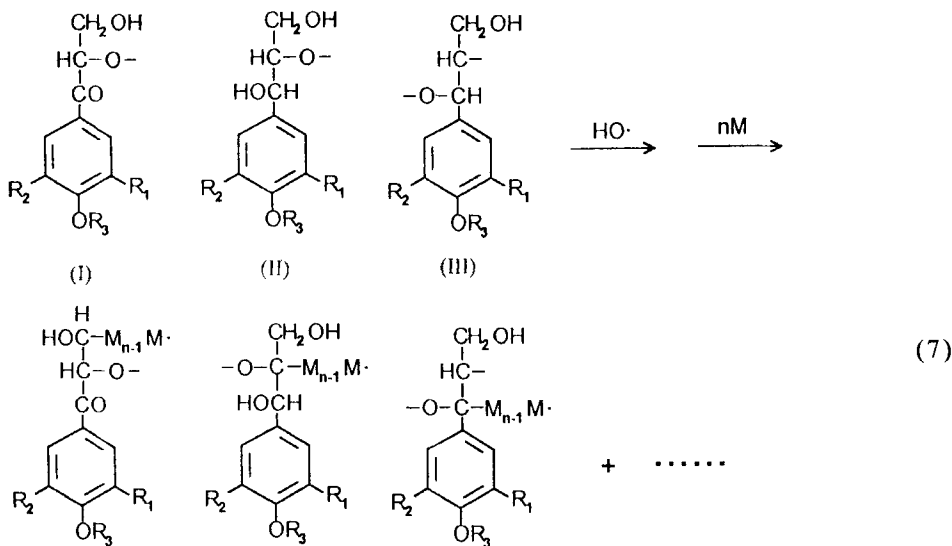
The decomposition and chain reactions of hydrogen peroxide in the presence of ferrous ion are known to be as follows:



The hydroxyl radical formed in the above reactions can abstract a hydrogen atom from holocellulose to form a grafting site [12, 13]:



Unlike holocellulose, lignin is a phenolic polymer composed of phenylpropane units. Hydroxyl radicals can also abstract hydrogen atoms from aliphatic side chains of the phenylpropane unit, and active sites for grafting are generated. Thus, some grafting pathways onto aliphatic side chains of lignin can be represented as



R_1, R_2 = hydrogen or methoxy

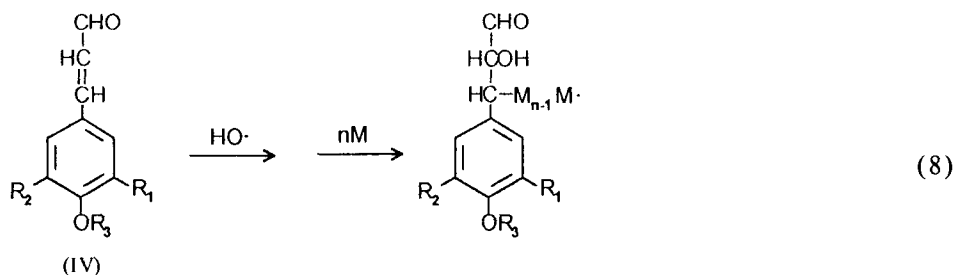
R_3 = hydrogen, alkyl or aryl

M = monomer

Whereas it is impossible to estimate which is the main grafting site among α -, β -, and γ -carbons of aliphatic side chains due to the complex structures of lignin, it has been pointed out that the abstraction of hydrogen atom by hydroxyl radical from the O—H is less significant than from the C—H bond of alcohols [18], and ethers show higher reactivity compared with alcohols [19].

The data in Table 5 show the effect of chemical structure of lignin on grafting. When bagasse pith is treated with sodium borohydride under the same grafting condition, the percentage grafting of lignin increases slightly, whereas the molecular weight of grafted PMMA chains decreases by about 14% (No. 3 and 4). This result may be ascribed to the more active sites formed during grafting. The reduction of α -carbonyl group leads to an increase in Structure (II), as indicated by an increase in alcoholic hydroxyl groups per phenylpropane unit from 0.87 to 1.04. Such a change is apparently favorable for the formation of a radical on the α -carbon atom.

Besides the main Structures (I), (II), and (III), lignin of bagasse pith also contains a small amount of olefinic Structure (IV). The addition of a hydroxyl radical onto a β -carbon atom generates an active site on an α -carbon atom on which grafting can occur.



Recently, the reactions of hydroxyl radicals with carbohydrate and lignin have been investigated because of their important roles in oxygen, hydrogen peroxide, and ozone bleaching. Using model compounds, Gierer and coworkers [20] found that hydroxyl radicals attack the lignin structure about 5–6 times faster than the carbohydrate structure. Thus, the higher percentage grafting of lignin may be related to such a fast reaction of hydroxyl radicals with lignin. The preferential addition of hydroxyl radicals to aromatic nuclei as compared to their abstraction of hydrogen atoms from aliphatic carbon atoms was also pointed out [20]. The addition of hydroxyl radical to aromatic nucleus, giving a hydroxycyclohexadienyl radical, was considered to be the initial step in hydroxylation of the aromatic nucleus [21]. Thus, the reactions of hydroxyl radicals with aromatic nuclei and the subsequent chain propagations may be considered to be

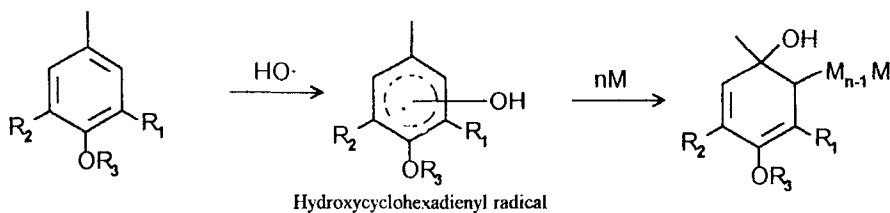
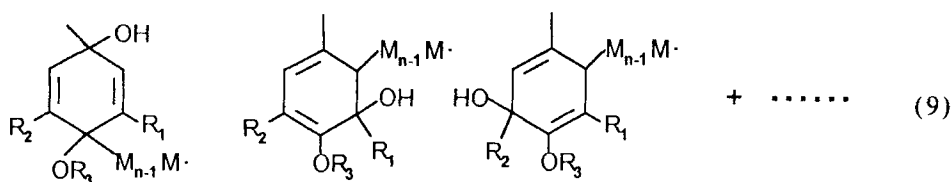


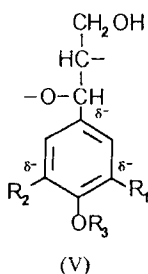
TABLE 5. Effect of Pretreatments on Graft Copolymerization^a

No.	Pretreatment	Fe content (ppm)	Percentage grafting of holocellulose	M η of PMMA on holocellulose (10^5)	Percentage grafting of lignin	M η of PMMA on lignin (10^5)	Hydroxyl group per phenylpropane unit	
							Phenolic	Alcoholic
1	Untreated	148	67.4	3.58	74.4	4.18	0.36	0.87
2	CH ₂ N ₂	150	44.1	5.34	101.4	4.70	0.12	0.98
3	Untreated	400	63.8	1.91	68.0	1.69	0.36	0.87
4	NaBH ₄	392	67.4	1.64	72.8	1.46	0.34	1.04
5	Fe ²⁺ -H ₂ O ₂	399	74.8	2.30	95.9	2.30	0.31	1.12

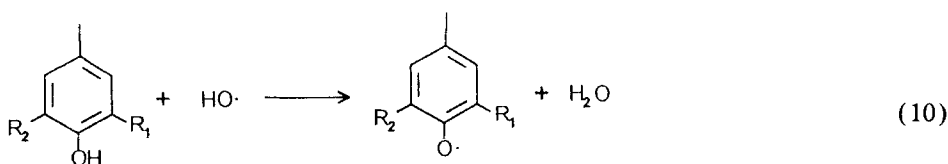
^aReaction conditions: MMA, 0.80 mL; H₂O₂ concentration, 5.0 mM; 70°C; 45 minutes.



The sites in aromatic nuclei for preferential attack by electrophilic hydroxyl radicals are considered to be ortho- and para-positions relative to free or etherified phenolic hydroxyl groups, designated δ - in Structure V [21].



On the other hand, hydroxyl radical can also abstract a hydrogen atom from the phenolic hydroxyl group, giving a phenoxyl radical, i.e.,



The resonance structures of phenoxyl radicals are usually considered to be the active sites that initiate grafting [4, 23]. However, it is noteworthy that, as shown by the data in Table 5, when the phenolic nucleus decreases from 36 to 12% as a result of methylation with diazomethane, the percentage grafting of lignin and the molecular weight of grafted PMMA chains on lignin increase by 36 and 12%, respectively (No. 1 and 2 of Table 5). The larger increase in percentage grafting as compared to the increase in the molecular weight of grafted PMMA chains means more grafting sites are formed. This result implies that the resonance structures of phenolic radicals are not as significant as those of hydroxycyclohexadienyl radicals for grafting onto lignin, and the formation of hydroxycyclohexadienyl radicals on methylated sample may be enhanced due to the suppression of Reaction (10).

Unlike the effect on grafting onto lignin, methylation with diazomethane leads to an evident decrease in the grafting sites of holocellulose. For the Fe^{2+} - H_2O_2 initiator, it has been pointed out that the reduction of ferric ion to ferrous ion by phenolic hydroxyl groups of lignin accelerates the decomposition of hydrogen peroxide [4]. Thus, as a result of methylation with diazomethane, the concentration of

hydroxyl radicals must become lower during the grafting, as indicated by a decrease in the grafting sites on holocellulose.

It is known that phenoxyl radicals can be further oxidized into quinoid structures by hydroxyl radicals [22, 24]. Thus, the shorter grafted PMMA chains formed in grafting onto nonmethylated sample are ascribable to the inhibiting effect of such quinoid structures (No. 1 and 2 of Table 5). The pretreatment of bagasse pith with $\text{Fe}^{2+}-\text{H}_2\text{O}_2$ leads to a decrease in the number of phenolic hydroxyl group from 0.36 to 0.31, indicating that some phenolic structures were destroyed (No. 3 and 5 of Table 5). As a result of such pretreatment, the percentage grafting and the molecular weight of grafted PMMA chains evidently increase. This result indicates that some inhibiting structures related to phenolic structures have been eliminated during the pretreatment with $\text{Fe}^{2+}-\text{H}_2\text{O}_2$.

The precise elucidation of the grafting mechanism onto lignin is difficult because various radicals can be formed through some complex reactions [22, 24].

CONCLUSIONS

The $\text{Fe}^{2+}-\text{H}_2\text{O}_2$ redox is an efficient initiator for the grafting of methyl methacrylate onto bagasse pith in neutral medium. The Fe ions which exist in the original bagasse pith can also react with hydrogen peroxide to initiate grafting. During grafting, a gradual increase in the molecular weights of grafted PMMA chains with reaction time was observed because chain termination slowed down. Although lignin is a phenolic polymer, it shows a higher percentage of grafting than does holocellulose. This higher percentage grafting is consistent with the preferential addition of hydroxyl radicals to the aromatic nuclei of lignin over their abstraction of hydrogens from holocellulose.

The grafting sites seem to increase when more hydrogen atoms are available for attack by hydroxyl radicals in aliphatic side chains as a result of the reduction of α -carbonyl groups with sodium borohydride. It was also found that as a result of methylation of phenolic hydroxyl groups with diazomethane, more grafting sites are formed on lignin although the decomposition of hydrogen peroxides slows down. Thus, it is concluded that for grafting onto the aromatic nuclei of lignin, the resonance structures of the phenoxyl radicals are not as significant as those of the hydroxycyclohexadienyl radicals formed through the addition of hydroxyl radicals to aromatic nuclei.

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