

Graft Copolymerization of Methyl Methacrylate on Stone Ground Wood Using the $\text{H}_2\text{O}_2\text{—Fe}^{2+}$ Method

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SYNOPSIS

Graft copolymerization of methyl methacrylate on stone ground wood (SGW) of masson pine was investigated. The effect of lignin on grafting was carefully examined. The phenolic hydroxyl groups of lignin were found to accelerate the decomposition of hydrogen peroxide and graft copolymerization of lignocellulose when minor ferrous ions were added to the system. Nevertheless, the α -hydroxyl groups of lignin had no great influence on grafting. Also, the graft copolymerization could be initiated with low ferrous ions to the hydrogen peroxide molar ratio, and, additionally, the lignin was observed to be more suitable for grafting than was the hollocellulose.

INTRODUCTION

Graft copolymerization on pure cellulose has been studied extensively in the past 20 years.^{1,2} However, research on graft copolymerization of lignocellulose has been done relatively little. Abou-Zeid et al.³ found that lignin could accelerate grafting at the initial stage of reaction when $\text{H}_2\text{O}_2\text{—Fe}^{2+}$ was used as initiator. Fanta et al.⁴ reported that no or little graft copolymerization occurred when Ce^{4+} was used as initiator; nevertheless, the graft copolymerization proceeded well when $\text{H}_2\text{O}_2\text{—Fe}^{2+}$ was used as initiator. However, there has been no further information reported about the effect of lignin on grafting.

Lignocellulose is a natural composite material that contains cellulose, hemicellulose, and lignin. Lignin is usually very sensitive to polymerization. Though the composition of lignocellulose and the structure of lignin are rather complicated, the sensitive component for polymerization might be the phenolic hydroxyl and α -hydroxyl groups of lignin. The phenolic hydroxyl groups of lignin could be

shrouded by methylation with diazomethane (CH_2N_2) and α -hydroxyl groups could also be shrouded by methylation with methanolic hydrochloric acid. If these components (functional groups of lignin) have an influence on grafting, the grafting copolymerization will be different after the functional groups of lignin were shrouded. Based on this assumption, the effect of lignin on grafting was investigated. The competition between lignin and hollocellulose for grafting was studied. Some parameters affecting grafting were also examined.

EXPERIMENTAL

Materials

Stone ground wood (SGW) of masson pine was used as the lignocellulose material and was extracted with a benzyl/alcohol (2 : 1) mixture and hot water. Methyl methacrylate was purified by the conventional method. All other chemicals were of AR grade.

Methylation of Phenolic Hydroxyl Groups of Lignin

SGW was treated with diazomethane (CH_2N_2) according to the procedure described by Gierer and Wallin.⁵

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Methylation of α -Hydroxyl Groups of Lignin

SGW was treated with methanolic hydrochloric acid (HCl—CH₃OH) according to the method described by Marton and Adler.⁶

Determination of Phenolic Hydroxyl and α -Hydroxyl Groups of Lignin

The phenolic hydroxyl and α -hydroxyl groups of the milled wood lignin⁷ prepared from various samples were determined according to the selective aminolysis method.⁸

Adsorption of Ferrous Ions

SGW (0.5 g) was impregnated in a freshly prepared aqueous ammonium sulfate solution for 15 min at 30°C using a material-to-liquor ratio of 1 : 5, then washed thoroughly with distilled water. The adsorbed amount of ferrous ions was determined according to the GB standard (by absorptiometry).

Determination of Hydrogen Peroxide

The SGW adsorbed with ferrous ions reacted with 25 mL of hydrogen peroxide solution at 70°C for a desired period of time, and the variation concentration of hydrogen peroxide was determined by idometry.

Graft Copolymerization

The SGW adsorbed ferrous ions were transferred into a three-necked flask equipped with a mechanical stirrer, and then the desired amount of distilled water and monomer were added using a material-to-liquor ratio of 1 : 50 and kept under nitrogen. The polymerization was started by adding hydrogen peroxide solution and terminated by adding a small amount of hydroquinone. The homopolymer was separated by acetone extraction.

The monomer conversion, graft yield, and graft efficiency were calculated as follows:

Monomer conversion (%)

$$= \frac{\text{wt. of total synthetic polymer}}{\text{wt. of monomer added}} \times 100$$

Graft yield (%)

$$= \frac{\text{wt. of graft copolymer} - \text{wt. of substrate}}{\text{wt. of substrate}} \times 100$$

Graft efficiency (%)

$$= \frac{\text{wt. of total synthetic polymer} - \text{wt. of homopolymer}}{\text{wt. of total synthetic polymer}} \times 100$$

Determination of Grafted Polymer on Lignin and on Hollocellulose

The graft copolymer of lignocellulose was treated with a delignification agent (NaClO₂) and then extracted with acetone. The graft copolymer of hollocellulose was also obtained in this way. The percentage of the grafted polymer on lignin was thus calculated as follows:

Percentage of the grafted polymer on lignin (%)

$$= \frac{\text{wt. of grafted polymer on lignin}}{\text{wt. of total grafted polymer}} \times 100$$

RESULTS AND DISCUSSION

Effect of Phenolic Hydroxyl and α -Hydroxyl Groups of Lignin on Grafting

Table I shows that the phenolic hydroxyl groups of lignin were considerably reduced by the methylation with CH₂N₂ and the α -hydroxyl groups were reduced by the methylation with HCl—CH₃OH. The ferrite in the substrate, which might be a factor influencing grafting, was also greatly reduced after methylation in both cases. To counteract this factor, a control that was prepared by treating SGW with hydrochloric acid in dioxan to reduce ferrite in SGW was used (Table I).

Figure 1 shows that the rate of graft copolymerization did not change much after SGW was methylated with HCl—CH₃OH compared with that of the control. Nevertheless, the graft copolymerization slowed down greatly after SGW was methylated with CH₂N₂, showing that the phenolic hydroxyl groups of lignin had a favorable influence on grafting and the α -hydroxyl groups had no obvious influence on grafting.

Effect of Phenolic Hydroxyl and α -Hydroxyl Groups of Lignin on Decomposition of Hydrogen Peroxide

The rate of graft copolymerization is often related to the rate of the decomposition of the initiator. The

Table I Contents of Phenolic Hydroxyl Groups and α -Hydroxyl Groups of Lignin and Ferrite in Substrate

Treating Method	Methylated with Diazomethane	Methylated with Methanolic Hydrochloric Acid	After Desorption of Ferrite (Control)
Phenolic hydroxyl groups ($1/C_9$)	0.12	0.34	0.32
α -Hydroxyl groups ($1/C_9$)	0.62	0.28	0.85
Ferrite (mol/g) 10^6	1.90	0.42	1.80

effect of phenolic hydroxyl and α -hydroxyl groups of lignin on the decomposition of hydrogen peroxide was, thus, examined (Fig. 2). The hydrogen peroxide is shown to have decomposed very rapidly when the SGW was methylated with HCl—CH₃OH, which was similar to the case of the unmethylated (control). However, when the SGW was methylated with CH₂N₂, the decomposition of the hydrogen peroxide was extremely slow, indicating that the phenolic hydroxyl groups of lignin accelerate the decomposition of hydrogen peroxide.

We think that the phenolic hydroxyl groups of lignin, reducible when compared with hydrogen per-

oxide, might react directly or indirectly with hydrogen peroxide. Table II further shows that the hydrogen peroxide decomposed extremely slowly if the ferrous ions were not present in the system. The decomposition of hydrogen peroxide was very slow when the SGW was methylated with CH₂N₂ even if ferrous ions were presented in the system. Contrarily, the hydrogen peroxide decomposed rapidly when the SGW was not treated with CH₂N₂ if the ferrous ions were presented. We could infer that the phenolic hydroxyl groups of lignin could accelerate the decomposition of hydrogen peroxide only if some ferrous ions were presented in the system. A mech-

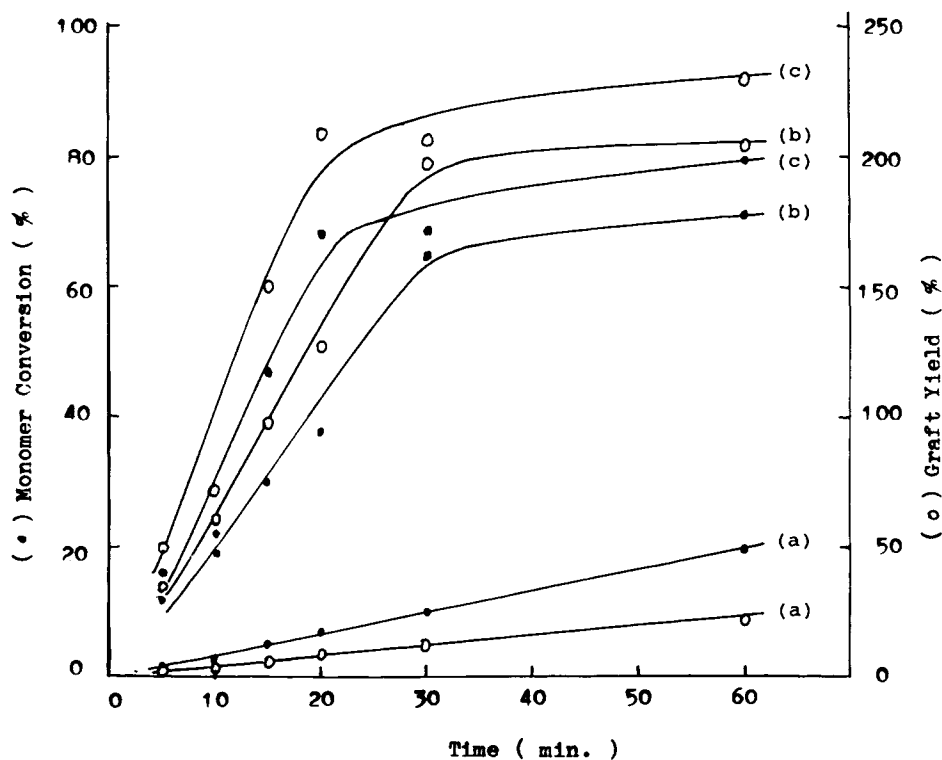
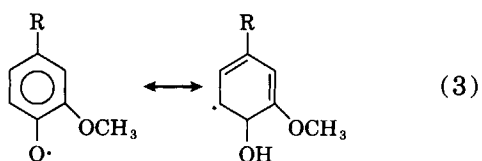
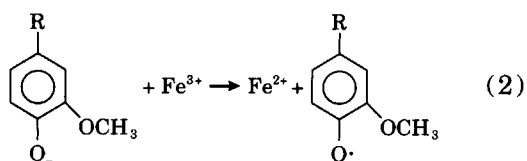
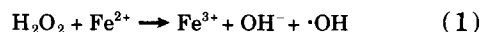


Figure 1 Effect of phenolic hydroxyl and α -hydroxyl groups of lignin on grafting. $[H_2O_2] = 3.5$ mmol/L; temp $70^\circ C$; Fe^{2+}/H_2O_2 molar ratio 0.036. Substrate: (a) methylated with diazomethane; (b) methylated with methanolic hydrochloric acid; (c) control.

anism of graft copolymerization of lignocellulose in this system is proposed as follows:



The hydrogen peroxide molecules react with ferrous ions primarily to produce ferric ions and hydroxyl radicals (1). Then, the hydroxyl radicals might attack lignocellulose to produce macroradicals or to initiate homopolymerization. The freshly produced ferric ions might react with phenolic hydroxyl groups of lignin to produce phenolic radicals and ferrous ions. The produced ferrous ions could again

participate in the decomposition of hydrogen peroxide.

Effect of Hydrogen Peroxide Concentration on Grafting

The effect of hydrogen peroxide concentration on grafting was shown in Figure 3. The monomer conversion and graft yield increased with the increase of hydrogen peroxide concentration up to 3.5 mmol/L and remained unchanged if the hydrogen peroxide concentration increased further. The graft efficiency was almost unaltered when the hydrogen peroxide concentration was varied.

Effect of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ Molar Ratio on Grafting

The graft yield increased with the increase of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio up to 0.085, and beyond that, the graft yield decreased slightly (Fig. 4). The variation of monomer conversion over the molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ had the same trend as did the graft yield. Graft efficiency decreased slightly with the in-

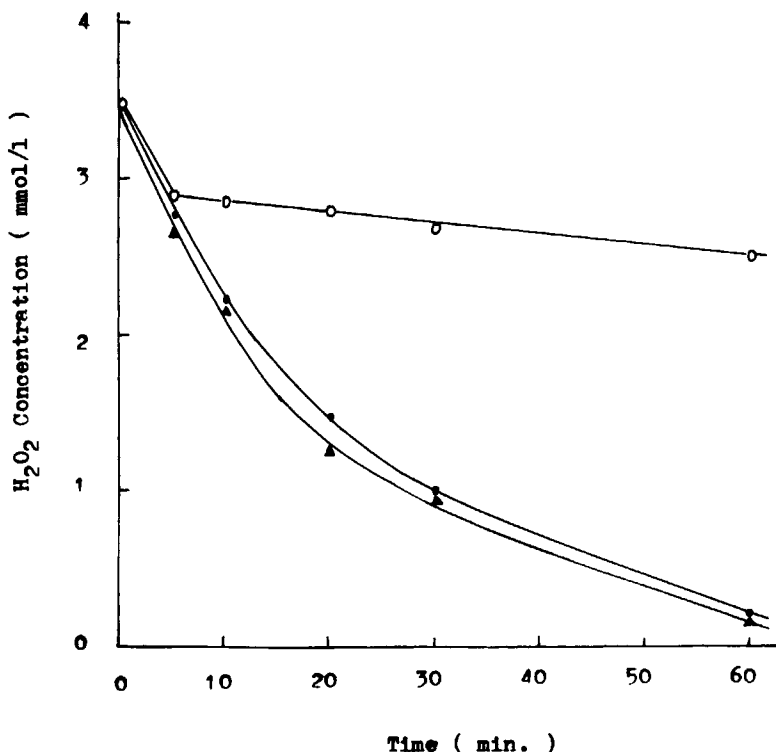


Figure 2 Effect of phenolic hydroxyl and α -hydroxyl groups of lignin on the decomposition of hydrogen peroxide. $[\text{H}_2\text{O}_2] = 3.5$ mmol/L; temp 70°C ; $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ molar ratio 0.036. Substrate; (○) methylated with diazomethane; (▲) methylated with methanolic hydrochloric acid; (●) control.

Table II Decomposition of Hydrogen Peroxide

Treating Method	Methylated with Diazomethane		Methylated with Methanolic Hydrochloric Acid		After Desorption of Ferrite (Control)	
Fe ²⁺ /H ₂ O ₂ molar ratio	0	0.036	0	0.036	0	0.036
Final concentration of H ₂ O ₂ (mmol/L)	2.71	2.49	2.87	0.17	3.02	0.21

Reaction time 60 min; initial concentration of H₂O₂ 3.5 mmol/L.

crease of the Fe²⁺/H₂O₂ molar ratio. The graft copolymerization could be initiated successfully with a low Fe²⁺/H₂O₂ molar ratio (about 0.085). By referring to the mechanism proposed above, we suggest that the ferrous ions in the system might be used repeatedly in a way that the freshly produced ferric ions might react with phenolic hydroxyl groups of lignin to reproduce ferrous ions. Thus, only a low Fe²⁺/H₂O₂ molar ratio was required to initiate the graft copolymerization. It, in turn, supports the mechanism proposed above.

Effect of Temperature on Grafting

The temperature on grafting is shown in Figure 5. The optimum temperature for graft copolymerization was about 70–80°C.

Percentage of Grafted Polymer on Lignin

Figure 6 shows that the percentage of the grafted polymer on lignin increased with the lapse of reaction time. In other words, the percentage of the

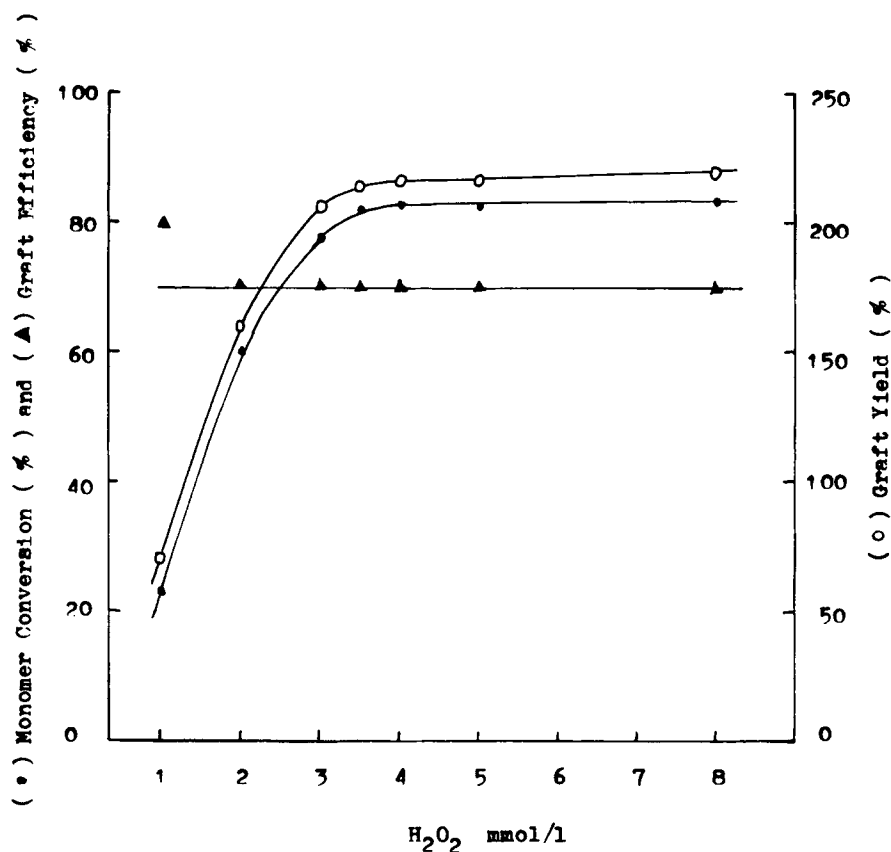


Figure 3 Effect of H₂O₂ concentration on grafting. Adsorbed Fe²⁺ 1.95×10^{-5} mol/g; temp 70°C; time 60 min.

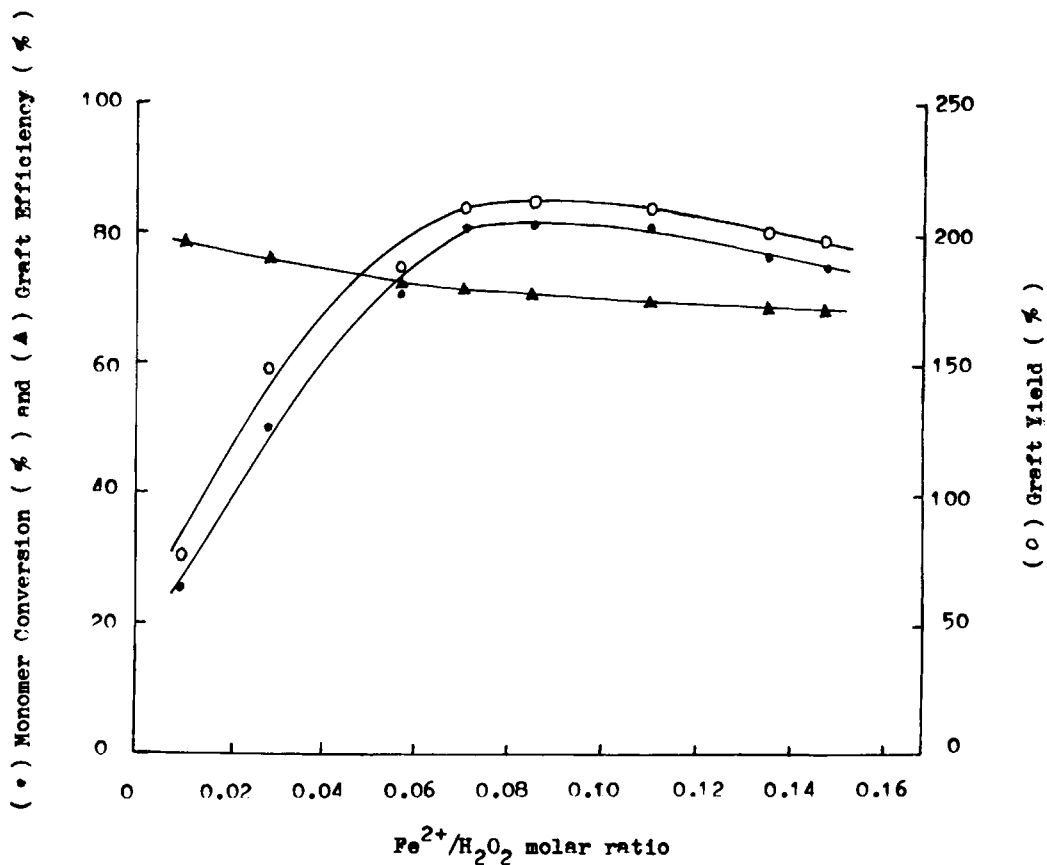


Figure 4 Effect of Fe²⁺/H₂O₂ molar ratio on grafting. H₂O₂ = 3.5 mmol/L; temp 70°C; time 60 min.

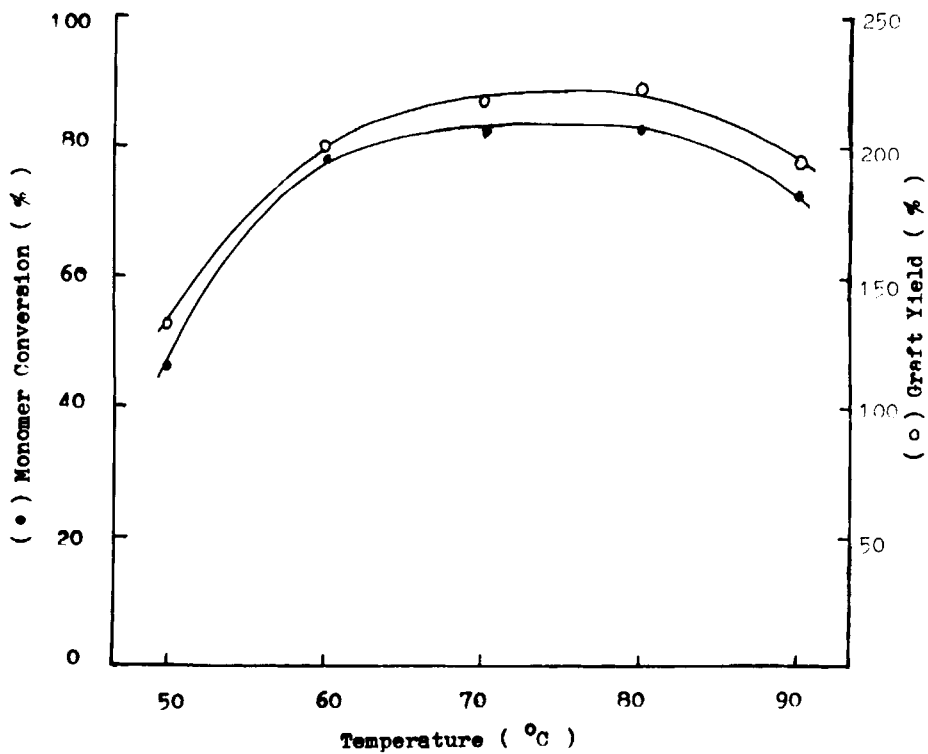


Figure 5 Effect of temperature on grafting. H₂O₂ = 3.5 mmol/L; Fe²⁺/H₂O₂ molar ratio 0.11; reaction time 60 min.

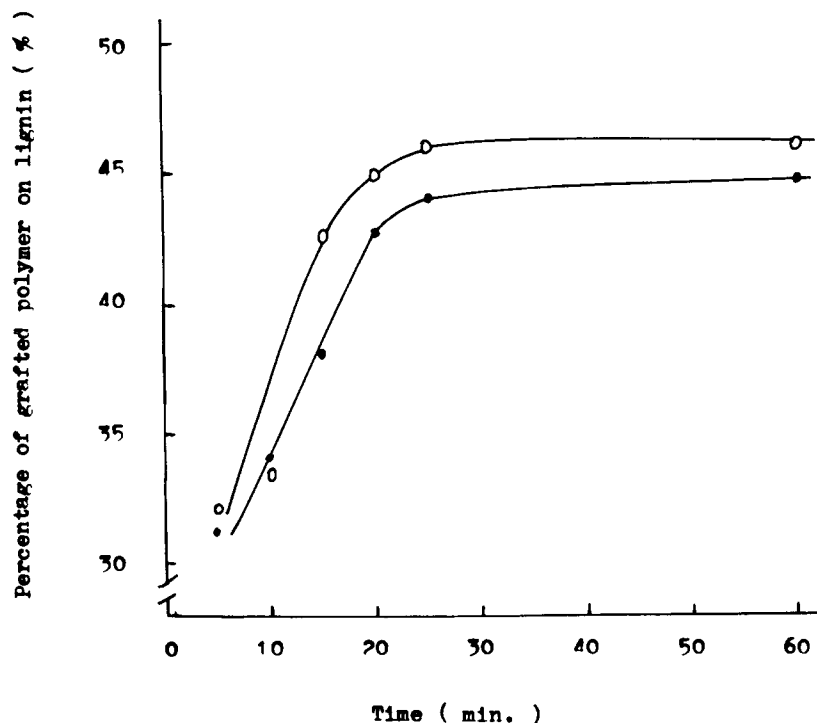


Figure 6 Relationship between percentage of grafted polymers on lignin and reaction time. Substrate: (○) methylated with diazomethane; (●) control.

grafted polymer on hollocellulose decreased as the reaction time increased. This implies that lignin is more suitable for grafting than is hollocellulose.

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