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Effect of Lignin in Graft Copolymerization of Methyl Methacrylate on Cellulose by Ceric Ion

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Synopsis

The effect of lignin contained in cellulosic materials in graft copolymerization of methyl methacrylate on such materials using ceric ion as initiator was studied. It was found that the percent grafting and the average molecular weight of grafts became lower in samples having a larger lignin content but the number of grafts formed increased proportionally up to lignin content of about 2.5%. Ceric ion reacted at a faster rate with lignin than with cellulose in wood pulp, and the results indicating that the active sites formed on lignin by oxidation with ceric ion accelerate the formation of grafts and increase the number of grafts were obtained. But on the other hand, the active sites participated in the termination reaction of the growing graft polymer radicals to cause lowering of the average molecular weight of grafts.

INTRODUCTION

It is generally believed that the activity of cellulose in graft copolymerization on cellulosic materials using ceric ion as initiator is due to functional groups such as hydroxyl, aldehyde, and carbonyl groups.[1–7] On the other hand, wood pulp is a complicated high polymer from the composition point of view as it contains, besides cellulose, some hemicellulose and lignin, and of these, lignin has a very high reactivity toward oxidizing agents. In view of this, it can be assumed that the reaction between lignin in the pulp and ceric ion has a large effect in graft copolymerization on wood pulp using ceric ion as initiator. In the present study the graft copolymerization of methyl methacrylate on various pulps of different lignin content was examined, and efforts were made to obtain information on the effect of lignin in graft copolymerization.

EXPERIMENTAL

Samples and Reagents

Commercial unbleached semichemical pulp from softwoods was bleached with acidic aqueous solutions (pH 3.5) of sodium chlorite of various concentrations. Various cellulose samples containing 0.2–20% lignin were prepared and these samples were used in the wet condition. Methyl methacrylate was treated by the conventional method and then refined

by distillation under reduced pressure. As the ceric ion, special-grade ceric ammonium nitrate reagent was used. As soluble lignin, thiolignin obtained from the waste of kraft pulping process of hardwoods was used.

Graft Copolymerization

Graft copolymerization was carried out by adding to 0.50 g (oven-dried weight) of cellulose sample, distilled water, 2.5 ml methyl methacrylate, and 15 ml 0.1*N* nitric acid, made up to 42.5 ml, and polymerizing at 45°C for 60 min under nitrogen using ceric ion of various concentrations. Polymerization was terminated with hydroquinone, the homopolymer was separated by acetone extraction to obtain the graft copolymer, and the percentage increase in weight on the basis of the cellulose sample was indicated as per cent grafting.

Determination Method

The reduction behavior of ceric ion was examined with the 42.5-ml system from which monomer was removed under the above-mentioned condition at varying time intervals. After reacting for the specified time, a fixed quantity of aqueous ferrous sulfate solution was added to the system and the residual ceric ion was obtained by titrating the excess ferrous sulfate with an aqueous ceric sulfate solution using *o*-phenanthrolin as indicator. Lignin in the cellulose sample was determined as the residue after treating with 72% sulfuric acid in accordance with the Tappi standard method T221m-51. The average molecular weight of grafts and the number of grafts were obtained by the methods described in the previous papers.[5,8]

RESULTS AND DISCUSSION

Effect of Lignin on Per cent Grafting

Figure 1 shows the relation between the per cent grafting and ceric ion concentration for various cellulose samples having different lignin content, in which a maximum per cent grafting is indicated at the ceric ion concentration intrinsic to each sample. This maximum per cent grafting is higher in samples with lower lignin content. It was observed that, for the various samples, graft copolymerization starts only when ceric ion above a certain concentration is used, and the value of this concentration was larger in samples having higher lignin content. Graft copolymerization of a sample prepared by treating the cellulose sample containing 2.5% lignin with a 10 mmole/liter concentration of ceric ion at 45°C for 30 min indicated a higher per cent grafting than that of the original sample. Also, a remarkable effect of lignin on the per cent grafting was observed, as shown in Figure 2, and the per cent grafting indicated a sharp decrease with increase in the lignin content at various ceric ion concentrations. It was thus made clear that the dependence of the per cent grafting on lignin content in the pulp is great.

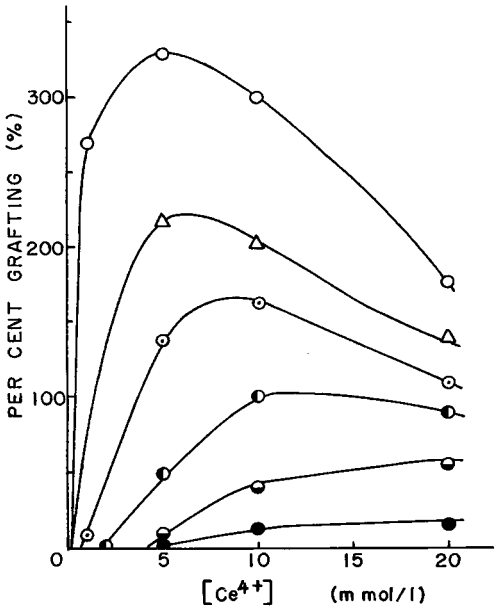

Fig. 1. Relation between per cent grafting and ceric ion concentration: polymerization temperature, 45°C; polymerization time, 60 min. Lignin content (%): (O) 0.19; (⊙) 0.77; (◐) 2.50; (◒) 6.10; (●) 21.5; (△) sample pretreated with ceric ion.

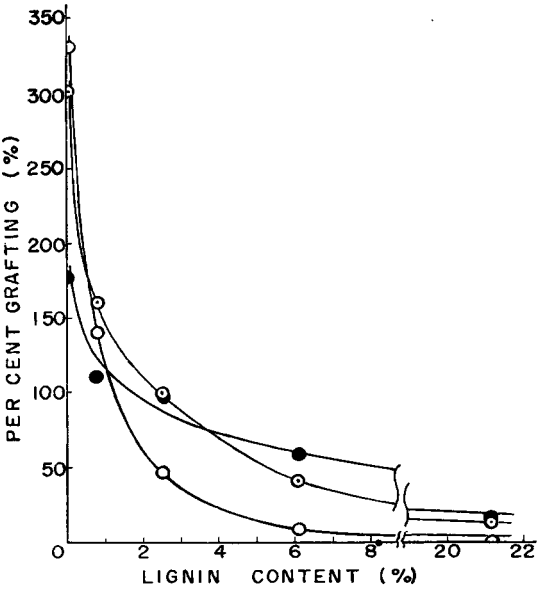

Fig. 2. Effect of lignin content on per cent grafting: polymerization temperature, 45°C; polymerization time, 60 min. Ceric ion concentration (mmole/liter): (O) 5.0; (⊙) 10.0; (●) 20.0.

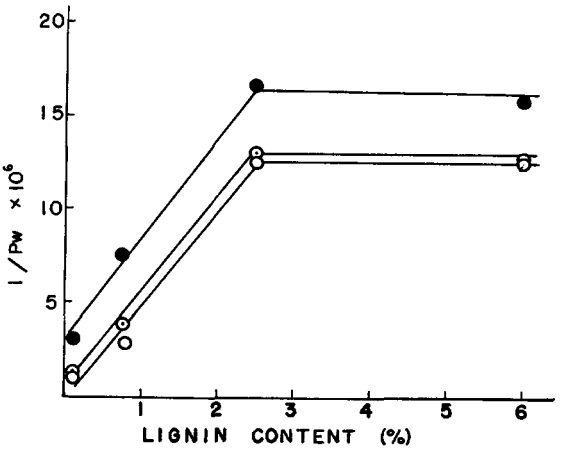

Fig. 3. Relation between reciprocal of average molecular weight of grafts and lignin content: ceric ion concentration (mmole/liter): (○) 5.0; (⊙) 10.0; (●) 20.0.

Effect of Lignin on Average Molecular Weight of Grafts

The average molecular weight of grafts has a general tendency to become lower in samples with higher ceric ion concentration and higher lignin content.

Figure 3 shows the relation between the reciprocal of the average molecular weight of grafts and lignin content. An approximately linear relation exists between both in a range of lignin content up to 2.5%. A tendency of a sharp decrease in the average molecular weight of grafts is indicated with increase in the lignin content, but almost no lowering in the average molecular weight of grafts was observed when the lignin content increased above this range. It is believed that this phenomenon can be explained by a similar mechanism[5] which was studied previously with respect to the relation between average molecular weight of grafts and total carbonyl contents in the cellulose sample, i.e., the group which reacts easily with oxidizing agents. That is, it can be inferred that the radicals which are formed on the lignin by oxidation with ceric ion probably contribute to the termination reaction of graft polymer radicals.

Effect of Lignin on Number of Grafts

The number of moles of grafts per 100 g of cellulose obtained from the per cent grafting and average molecular weight of grafts was taken as the number of grafts, and the relation between this and the ceric ion concentration is shown in Figure 4. A linear relation is obtained between the number of grafts and the logarithm of ceric ion concentration. The ceric ion concentration at the intersection of the extension of this line and the abscissa shows good agreement with the minimum concentration required to start graft copolymerization shown previously in Figure 1. This indi-

cates that the ceric ion concentration necessary for forming grafts is characteristic of each sample. It was observed that this concentration was larger the higher the lignin content. That is, it is inferred that reduction

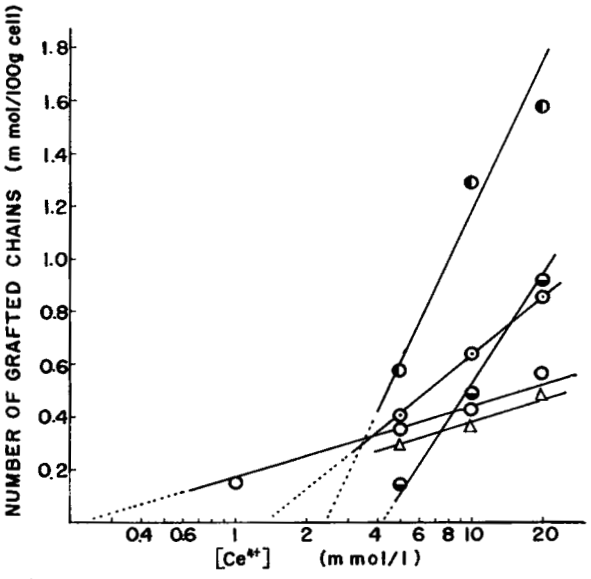

Fig. 4. Relation between number of grafts and ceric ion concentration: lignin content (%): (○) 0.19; (⊙) 0.77; (◐) 2.50; (◒) 6.10; (△) sample pretreated with ceric ion.

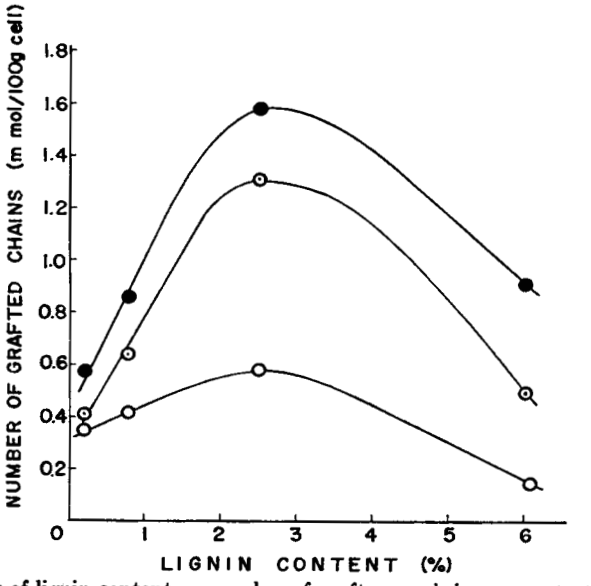

Fig. 5. Effect of lignin content on number of grafts: ceric ion concentration (mmole/-liter): (○) 5.0; (⊙) 10.0; (●) 20.0.

of ceric ion which does not participate directly in the formation reaction of grafts is present in samples containing lignin. However, such ceric ion concentration was low in samples which had been pretreated with ceric ion; and also, the graft formation effect was inferior as the number of grafts was about $^1/_2$ to $^1/_4$ that of untreated samples and gave results similar to samples with lower lignin content. The relation between number of grafts and

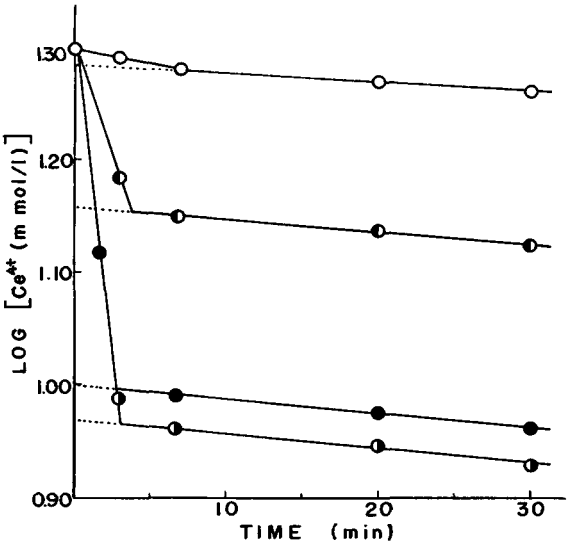

Fig. 6. Reactivity of lignin toward ceric ion: concentration of soluble lignin added to the system with cellulose sample containing 0.1% lignin (%): (○) 0; (◐) 3.0; (◑) 6.0; (●) 6.0 (without cellulose sample); reaction temperature, 45°C; ceric ion concentration used, 20 mmole/liter.

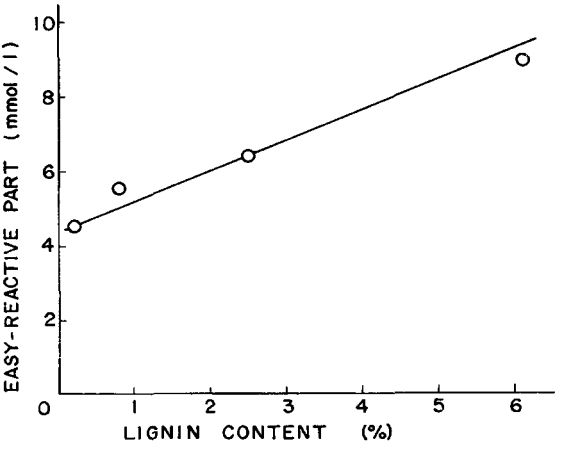

Fig. 7. Relation between reactive portion of cellulose samples and lignin content: reaction temperature, 45°C; ceric ion concentration used, 10 mmole/liter.

lignin content is shown in Figure 5, in which a tendency of a large number of grafts being formed with increase in the lignin content of cellulose sample within a certain range of content is indicated. When the lignin content exceeds a certain limit, however, the formation of grafts is obstructed. It is believed that lignin has a rather complex effect on formation of grafts because of the high reactivity of lignin.

Reactivity of Lignin Toward Ceric Ion

The reduction behavior of ceric ion when various quantities of soluble lignin are added to a system in which bleached sulfite pulp from softwoods containing 0.1% lignin is present is shown in Figure 6. The reduction rate of ceric ion is very low when only pulp is present and the quantity of ceric ion which is reduced at a high rate at the initial stage of the reaction, i.e., the reactive portion,[9] was about 0.60 mmole/liter. The reduction rate of ceric ion when 3.0% and 6.0% of soluble lignin are added to such a system becomes very fast. Reduction quantities at the initial stage with a higher rate were 5.5 and 10.6 mmole/liter respectively, and increased almost proportionally with the lignin quantity. Consequently, it was confirmed that ceric ion reacts at a higher rate with lignin than with cellulose. Similar studies were carried out on various cellulose samples used in graft copolymerization having different lignin content. The reactive portion was obtained and the relation between this and lignin content is shown in Figure 7. As is clear from the figure, the reactive portion is larger in samples with a higher lignin content, and it was observed that lignin in pulp plays an important role in reactivity toward ceric ion. The effect of lignin in the formation reaction of grafts which was observed in Figures 4 and 5 is believed to be due to such reactivity of lignin toward ceric ion.

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