

## Comparison of $\text{Fe}^{2+}$ - $\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}$ - $\text{H}_2\text{O}_2$ Initiation Systems in Graft Copolymerization of Cellulosic Materials

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### Synopsis

Studies were carried out on decomposition of hydrogen peroxide by ferrous and ferric ions adsorbed on cellulosic materials (SP, SCP), scission of the cellulose chain and formation of grafts by graft copolymerization. As a result, it was found that the activity of ferrous ion is always higher than that of ferric ion, but there exists a common relation between the amount of decomposition of hydrogen peroxide and the number of grafts for all cellulose samples and kinds of metallic ions, and it was inferred that essentially, copolymerization takes place by the same mechanism irrespective of the kind of metallic ions. Consequently, it can be considered that the difference in degree of activity between ferrous ion and ferric ion is due to the difference in the decomposition mechanism of hydrogen peroxide by these metallic ions and it is assumed that the high activity of ferrous ion in graft copolymerization is due to the high hydrogen peroxide decomposition effect.

### INTRODUCTION

The authors reported in the preceding paper<sup>1</sup> that ferric ion adsorbed on cellulosic materials accelerates decomposition of hydrogen peroxide and this decomposition reaction is composed of two parts, one participates in the violent scission of cellulose chain at the initial period in which graft copolymerization is not initiated, and the other participates in the initiation of graft copolymerization in which the scission of cellulose chain occurs mildly. It is known that ferrous ion-hydrogen peroxide system has high action initiating graft copolymerization and numerous studies have been reported.<sup>2-7</sup>

The object of this study is to obtain information on the graft copolymerization mechanism by comparing ferrous ion and ferric ion initiation systems, both of which accelerate decomposition of hydrogen peroxide, but which essentially differ in the ionic charge and the manner of binding with cellulose.<sup>8</sup>

## EXPERIMENTAL

### Cellulose Samples on Which Metallic Ions are Adsorbed

Commercial bleached sulfite pulp from softwoods (SP) and bleached semi-chemical pulp from hardwoods (SCP) were treated for 60 min at 45°C with a 5 mmole/l aqueous ferrous sulfate solution or for 30 min at 60°C with a 1 mmole/l aqueous solution of ferric chloride, washed with water and used as cellulose samples on which metallic ions were adsorbed. The adsorbed amount of ferrous ion was obtained by titrating with ceric sulfate solution using *o*-phenanthroline as indicator, while the adsorbed amount of ferric ion was obtained by titrating iodine liberated by adding potassium iodide with 0.1 *N* sodium thiosulfate solution.

### Change in Concentration of Hydrogen Peroxide

The cellulose sample of 0.50 g (bone-dry weight) on which metallic ion was adsorbed and reacted with 42.5 ml of 4–5 mmole/l aqueous solution of hydrogen peroxide at 60°C. The sample filtered after a specified time and the hydrogen peroxide concentration in the filtrate was determined by iodometry.

### Graft Copolymerization

Ten milliliters of aqueous solution of hydrogen peroxide of the specified concentration was added to a 200 ml polymerization tube containing 0.50 g, the cellulose sample on which metallic ion was adsorbed, 2.5 ml of methyl methacrylate and 30 ml of distilled water and maintained at 60°C in nitrogen atmosphere. Graft copolymer was obtained by separating the homopolymer by extraction with acetone and the weight increase of graft polymer represented by percentage to cellulose was indicated as percent grafting. The weight average molecular weight of grafts, the number of grafts and the weight average degree of polymerization of the cellulose samples were obtained in accordance with the preceding paper.<sup>1</sup>

## RESULTS AND DISCUSSION

### Decomposition of Hydrogen Peroxide by Cellulose Sample on Which Metallic Ions are Adsorbed

Table I shows the amount of metallic ion adsorbed on the cellulose samples, from which it can be seen that the adsorbed amount of ferric ion is larger than that of ferrous ion and the adsorbability of SCP for metallic ion is better than that of SP.

The decomposition behavior of hydrogen peroxide by SP and SCP on which metallic ions are adsorbed is shown in Figure 1. When the metallic ions are compared, the decomposition rate of ferrous ion is faster than ferric ion in spite of the fact that its adsorbed amount is smaller. In the comparison between the cellulose samples, as a direct comparison is not

TABLE I  
Amount of Metallic Ions Adsorbed on Cellulose Samples

| Metallic ion     | SP   | SCP  |
|------------------|--|--|
|                  | Amount of adsorbed metallic ion, mmole per 100 g of cell | Amount of adsorbed metallic ion, mmole per 100 g of cell |
| Fe <sup>2+</sup> | 0.67   | 1.36   |
| Fe <sup>3+</sup> | 2.08   | 5.27   |

Treatment conditions are as follows: cellulose samples are treated with 5 mmole/l of aqueous ferrous sulfate solution for 60 min at 45°C or 1 mmole/l of aqueous ferric chloride solution for 30 min at 60°C.

possible because the amount of adsorbed metallic ion differs, the amount of decomposed hydrogen peroxide per a unit amount of adsorbed metallic ion in a reaction time of 60 min was compared, by which the decomposition

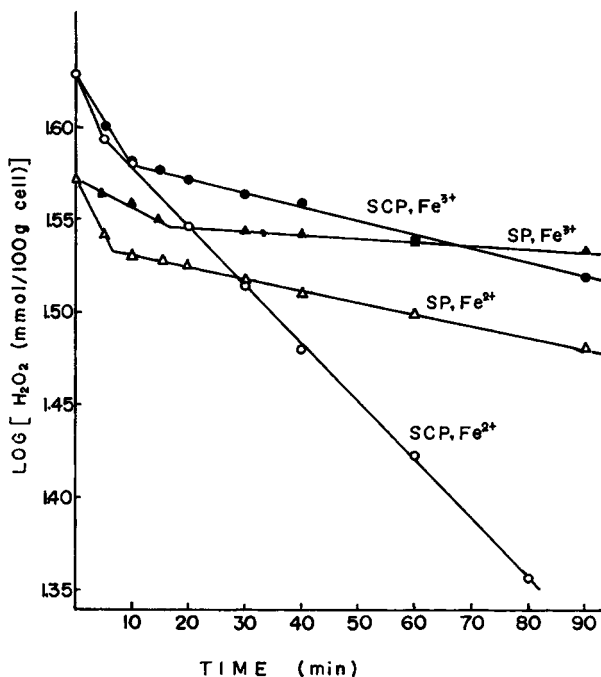


Fig. 1. Changes of hydrogen peroxide concentration with time in SP and SCP on which metallic ions are adsorbed. Concentration of hydrogen peroxide used (mmole/l) SP, 4.4; SCP, 5.0. Reaction temperature; 60°C.

rate of SCP was slightly faster than that of SP. It was observed in the decomposition of hydrogen peroxide in each system that there were two stages of a fast initial decomposition and a slightly slower decomposition which follows this.

The number of scission in the cellulose chain by hydrogen peroxide was obtained in the same manner as in the preceding paper<sup>1</sup> and the change with time is shown in Figure 2. The rate of the scission reaction differs in accordance with the combination of cellulose samples and metallic ions,

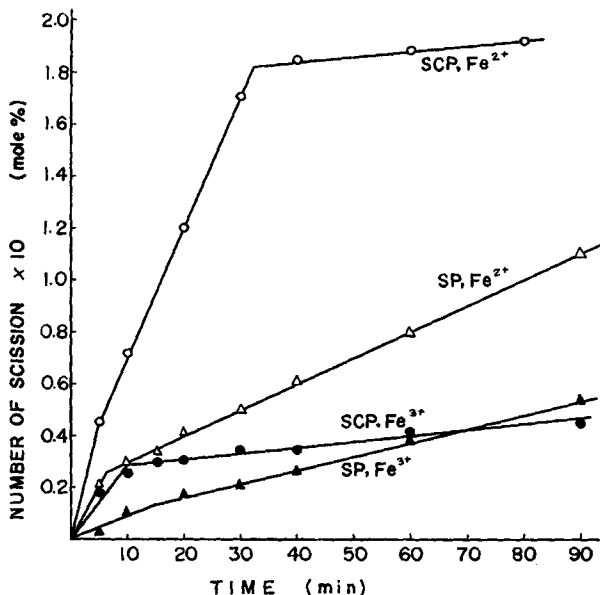


Fig. 2. Changes of number of scission of cellulose chain with time.

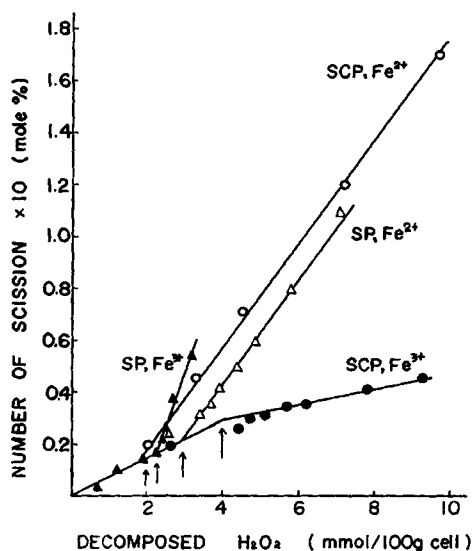


Fig. 3. Relation between the number of scission of cellulose chain and the amount of decomposed hydrogen peroxide.

but a fast scission reaction and a slow reaction which follows this were observed in all systems. It was found that in the scission reaction also, the rate by ferrous ion was faster than that by ferric ion in case of both SP and SCP. Thus, it was made clear that a common, characteristic initial reaction exists in the decomposition behavior of hydrogen peroxide and in the scission reaction of the cellulose chain and furthermore, both reactions are almost the same with respect to time, from which it is believed that there is a close relationship of some sort between these.

Figure 3 shows the relation between the number of scission in the cellulose chain and the amount of decomposed hydrogen peroxide. A characteristic relation is indicated in each system but all relations are composed of two straight lines and the number of scission increases with increase in the amount of decomposed hydrogen peroxide. Furthermore, with respect to the initial part of the reaction, a common, straight line is indicated for all systems and the limiting value of the common portion is indicated by an arrow in the figure. It can be inferred that probably a reaction of the same kind has taken place in the range of this common portion for all cellulose samples and metallic ions.

#### Graft Copolymerization on Cellulose Samples on Which Metallic Ions are Adsorbed

As shown in Figures 1 and 2, hydrogen peroxide is decomposed by cellulose sample on which metallic ion is adsorbed, by which decrease in the molecular weight of the cellulose resulted. Graft copolymerization in case methyl methacrylate was added to these systems was investigated. Figure

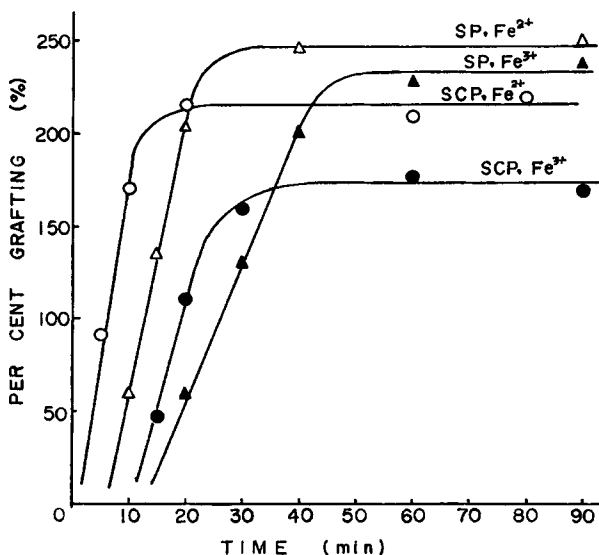


Fig. 4. Changes of percent grafting with time. Concentration of hydrogen peroxide used (mmole/l) SP, 4.4; SCP, 5.0. Polymerization temperature; 60°C.

4 shows the percent grafting with time. When the same cellulose sample is used, initiation of graft copolymerization by ferric ion is faster than in case ferrous ion is used and furthermore, a higher percent grafting is obtained. Also, with respect to the kind of cellulose sample, the initiation of graft

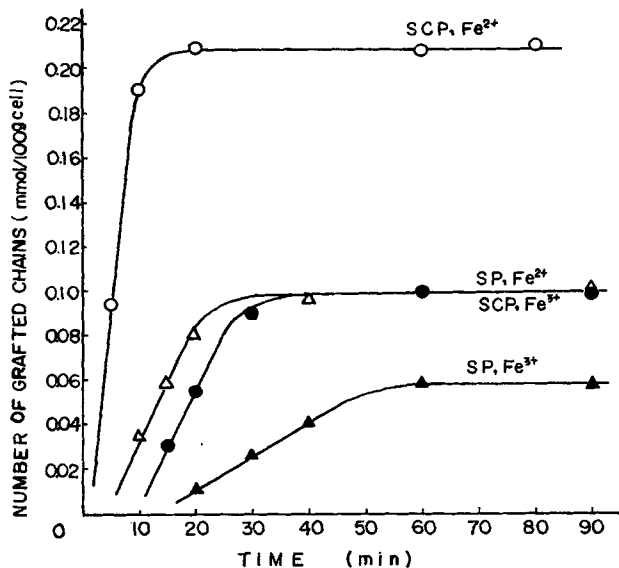


Fig. 5. Changes of number of grafted chains with time.

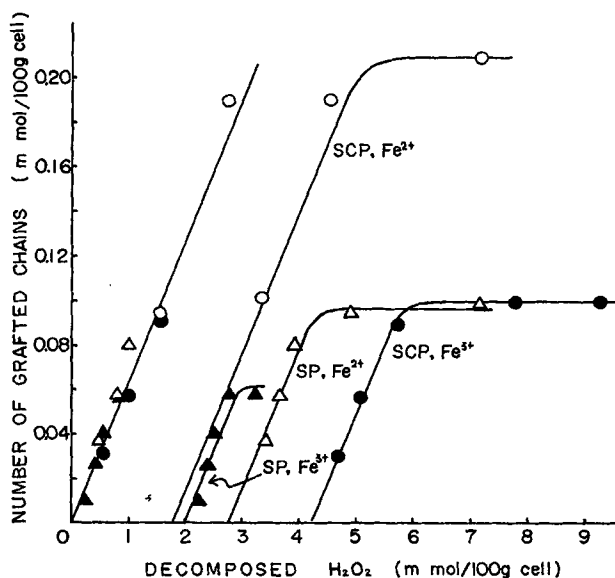


Fig. 6. Relation between the number of grafted chains and the amount of decomposed hydrogen peroxide.

copolymerization is slower in case of SP than SCP but a high percent grafting was indicated.

Grafted poly (methyl methacrylate) was separated from the copolymer by the 72% sulfuric acid method<sup>9</sup> and the weight average molecular weight was determined. It was found that a system in which SCP and ferrous ion was used indicated a tendency of the average molecular weight of grafts being lower than in case of SP and ferric ion and it was several million in both systems. The changes of the number of grafts calculated from the percent grafting and the average molecular weight of grafts with polymerization time are shown in Figure 5. It was found that a combination of SCP and ferrous ion indicated the fastest initiation of formation of grafts and the largest number of grafts and the formation was completed within about 40 min even in the system in which the initiation was the slowest. A polymerization induction period was present at the beginning in all polymerization reactions and this period was longer in case of SP than SCP, and in case of ferric ion than ferrous ion. That is, there is a decomposition of hydrogen peroxide with a fast rate at the initial period of the reaction and in spite of the fact that a violent scission reaction of the cellulose chain is taking place there, a phenomenon in which there is no initiation of graft formation is present.

The relation between the number of grafts and the amount of decomposed hydrogen peroxide is shown in Figure 6, from which the presence of hydrogen peroxide decomposition in which formation of grafts does not participate can be observed. If it is assumed that this amount of decomposed hydrogen peroxide which does not have any relation with the initiation of graft copolymerization is the same as the amount of decomposed hydrogen peroxide which corresponds to the arrow in Figure 3, it will be possible to obtain a common relation between the number of grafts and the amount of decomposed hydrogen peroxide in all systems. It can be inferred from this that a reaction of graft formation by the same mechanism which is unrelated with the kind of metallic ion and cellulose sample is present in a metallic ion-hydrogen peroxide initiation system. Consequently, though ferrous ion always indicated a higher activity than ferric ion in the decomposition of hydrogen peroxide, scission of cellulose chain and formation of grafts in graft copolymerization, it is inferred that such differences are due to the difference in the hydrogen peroxide decomposition mechanism of these metallic ions.

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