Studies of the Initiation Mechanism of Ferric Ion–Hydrogen Peroxide Systems in Graft Copolymerization on Cellulose

YOSHITAKA OGIWARA, YUKIE OGIWARA, and HITOSHI KUBOTA, *Faculty of Engineering, Gunma University, Kiryu, Japan*

Synopsis

The decomposition of hydrogen peroxide by ferric ion adsorbed on cellulose, the lowering of the degree of polymerization of cellulose, and the graft copolymerization in the systems containing methyl methacrylate were studied. As the amount of ferric ion adsorbed on cellulose and the concentration of hydrogen peroxide became higher, the amount of decomposition of hydrogen peroxide and the number of scissions of cellulose chains with higher rates at the initial stage of reaction were both observed to increase. It was recognized that the graft copolymerization was hardly initiated, while such initial reactions were proceeding. Assuming that the hydrogen peroxide decomposed with a higher rate was indifferent to the initiation reaction, a certain relationship was found between the amount of ferric ion adsorbed on cellulose and the initiation efficiency of hydrogen peroxide in graft copolymerization.

INTRODUCTION

It is well known that the graft copolymerization of vinyl monomers on cellulosic materials is initiated by many kinds of oxidizing agents. When hydrogen peroxide is used as an oxidizing agent, ferrous ion is generally used with it, in order to form a redox system and to produce hydroxyl radicals easily.[1-5] Ferric ion is also known to react with hydrogen peroxide and to produce hydroxyl radicals[6,7] and also to accelerate the decomposition of hydrogen peroxide remarkably.[8,9]

In our previous report[10] it was already shown that metal ions were adsorbed on cellulose firmly. In this report the decomposition of hydrogen peroxide by using cellulose on which various amounts of ferric ion were adsorbed, the lowering of degree of polymerization of cellulose during this procedure and, in relation to these, the graft copolymerization in the systems containing methyl methacrylate are investigated.

EXPERIMENTAL

Ferric Ion Adsorbed on Cellulose

Absorbent cotton (cotton) and bleached softwood sulfite pulp (SP1, SP2) were treated with various concentrations of ferric chloride aqueous solution

at 60°C for 60 min, washed with water, and treated with $0.1N$ HCl (ratio of liquid to material 150:1). After being washed with water to be neutral, the materials were used for further experiments. The adsorbed amount of ferric ion was determined by adding KI to the sample and titrating the isolated iodine with sodium thiosulfate. The maximum amount of adsorbed ferric ion was approximately equal to the molar number of total carbonyl groups in each cellulose sample.

Determination of the Hydrogen Peroxide Concentration

Cellulose (0.5 g) on which ferric ion was adsorbed reacted with 42.5 ml of hydrogen peroxide solution of various concentrations, and the variation of hydrogen peroxide concentration in aqueous solution was determined by iodometry.

Weight-Average Degree of Polymerization of Cellulose

Intrinsic viscosities were measured in cupriethylenediamine at 25°C, and the following equation[11] was used to obtain the weight-average degree of polymerization:

$$\bar{P}_w = 156 \times [\eta]$$

Graft Copolymerization

The polymerization reaction was carried out at 60°C for 60 min in a system consisting of 0.500 g of cellulose on which ferric ion was adsorbed, 2.5 ml of methylmethacrylate, 10 ml of hydrogen peroxide aqueous solution, and water, the total being made up to 42.5 ml with water and kept under nitrogen. A small amount of hydroquinone was added to stop the reaction. Homopolymer was extracted with acetone to obtain graft copolymer. Weight increase of graft polymer represented by percentage to cellulose was indicated as per cent grafting.

Weight-Average Molecular Weight of Grafts and Number of Grafted Chains

After being isolated by hydrolysis of cellulose with 72% H_2SO_4 the weight-average molecular weight of grafted poly(methyl methacrylate) was calculated from the intrinsic viscosity in acetone at 25°C by means of the following equation:[12]

$$[\eta] = 0.96 \times 10^{-4}M^{0.69}$$

The molar number of grafts per 100 g of cellulose was calculated from the molecular weight and per cent grafting and indicated as the number of grafted chains.

RESULTS AND DISCUSSION

It was confirmed that the ferric ion adsorbed on cellulose was hardly eluted into aqueous solution, in contact with hydrogen peroxide aqueous
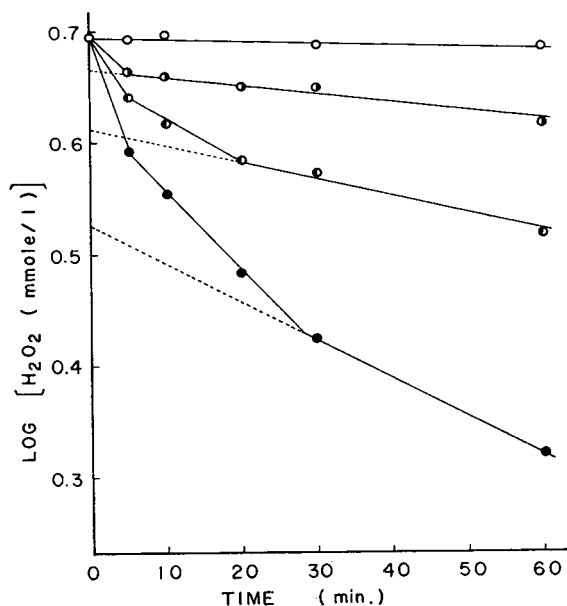
Fig. 1. Changes of concentration of hydrogen peroxide with time (SP1). Reaction temperature, 60°C; $[H_2O_2]$ = 5.0 mmole/l. Adsorbed Fe^{3+} (mmols per 100 g of cellulose): (O) 0; (◑) 7.20; (◒) 15.4; (●) 25.4.

solution. The original amount of ferric ion in SP1 is less than 1 ppm, and the amount of decomposition of hydrogen peroxide by that is extremely small, as shown in Figure 1. Therefore, most of the decomposition reaction of hydrogen peroxide is supposed to occur in the vicinity of cellulose on which ferric ion is adsorbed.

Rate of Decomposition of Hydrogen Peroxide with Cellulose on which Ferric Ion is Adsorbed

The concentration changes of hydrogen peroxide aqueous solution (5 mmol/l) by the reaction with SP1 on which various amounts of ferric ion are adsorbed are shown in Figure 1. At the initial stage of reaction a region is observed in which the rate of decomposition is high, and A is obtained from the intercept of the ordinate by extrapolating the following straight line; it increases as the amount of ferric ion adsorbed on the sample becomes larger (A is the amount of hydrogen peroxide decomposed in the initial stage of the reaction).

The relations between A and the adsorbed amount of ferric ion are shown in Figure 2 for cotton, SP1 and SP2, respectively. Almost no difference among the values of A is observed in various cellulose samples, and a good linear relation is obtained between A and the amount of ferric ion adsorbed.
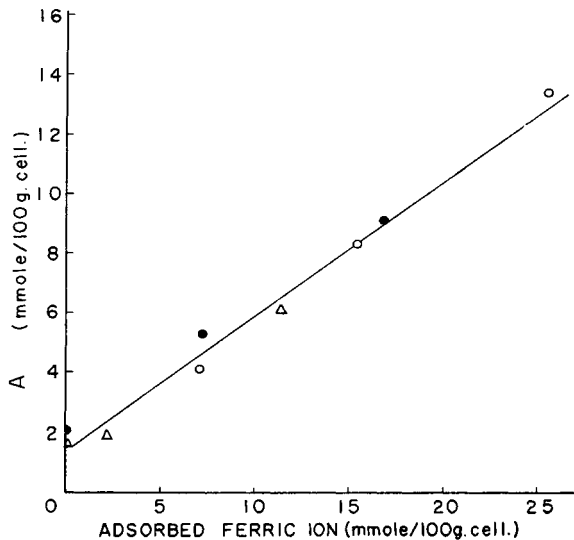
Fig. 2. Relationship of A (amount of hydrogen peroxide decomposed at initial stage with a higher rate, Fig. 1): to amount of adsorbed ferric ion, with [H$_2$O$_2$] = 5.0 mmol/l: (O) SP1; (●) SP2; (△) cotton.
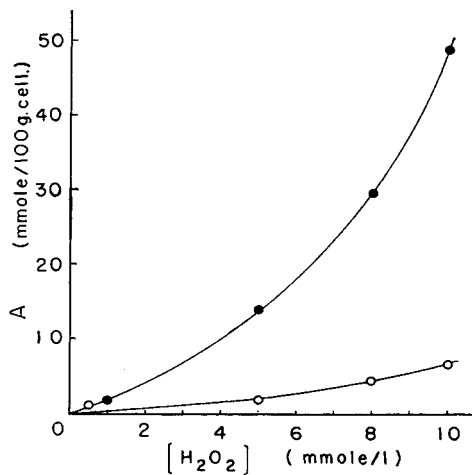

Fig. 3. Relationship of A to concentration of hydrogen peroxide (SP1). Reaction temperature, 60°C. Adsorbed Fe^{3+} (mmols per 100 g of cellulose): (O) 2.70; (●) 25.4.

The effect of hydrogen peroxide concentration on A is shown in Figure 3 for SP1. It is observed that as its concentration becomes higher and the amount of ferric ion adsorbed larger, the value of A increases.

Although the ability of cellulose itself to decompose hydrogen peroxide was extremely small, cellulose samples on which ferric ion was adsorbed obviously accelerated the decomposition of hydrogen peroxide, and it was observed that A, the amount decomposed at the initial stage with a higher
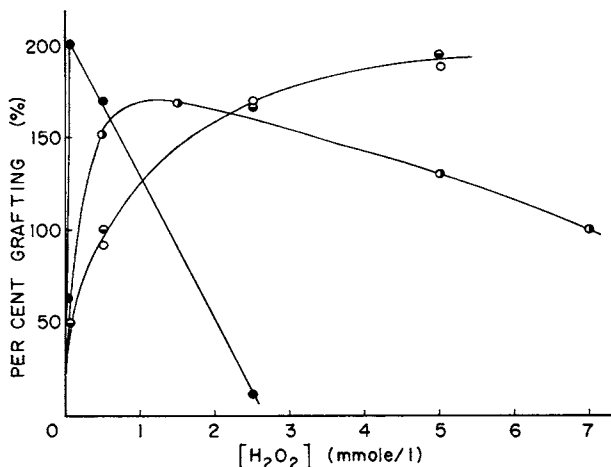
Fig. 4. Effect of amount of adsorbed ferric ion and concentration of hydrogen peroxide on the per cent grafting (SP1). Polymerization temperature, 60°C; polymerization time, 60 min. Adsorbed Fe^{3+} (m/mols per 100 g of cellulose): (O) 1.90; (◖) 3.30; (◑) 9.30; (●) 21.0.

rate, increased as the amount of ferric ion adsorbed became larger and the initial concentration of hydrogen peroxide became higher.

Effect of Amount of Ferric Ion Adsorbed and Concentration of Hydrogen Peroxide on Graft Copolymerization

Hydrogen peroxide in various concentrations and a given amount of methyl methacrylate reacted with SP1 on which various amounts of ferric ion were adsorbed, at 60°C for 60 min. The per cent grafting obtained is shown in Figure 4.

Depending on the amount of ferric ion adsorbed, the maximum value of per cent grafting was attained at different concentrations of hydrogen peroxide. The sample on which a larger amount of ferric ion is adsorbed has a lower hydrogen peroxide concentration at the maximum per cent grafting. The number of grafted chains of copolymer takes its maximum at almost the same concentration of hydrogen peroxide as that at which the maximum per cent grafting occurs, as shown in Figure 5, and it was about 0.04 mmols per 100 g of cellulose, regardless of the amount of ferric ion adsorbed.

Figure 6 shows the relation between per cent grafting and polymerization time, in which the initial concentration of hydrogen peroxide was kept at 5 mmol/l. It was observed that the initiation of graft copolymerization was rather retarded, as the amount of ferric ion adsorbed on the cellulose sample increased.

The amount of hydrogen peroxide decomposed per unit time increased as the concentration of hydrogen peroxide and the amount of ferric ion adsorbed became higher. Nevertheless, the graft copolymerization was observed to be rather retarded. This phenomenon is thought to be very
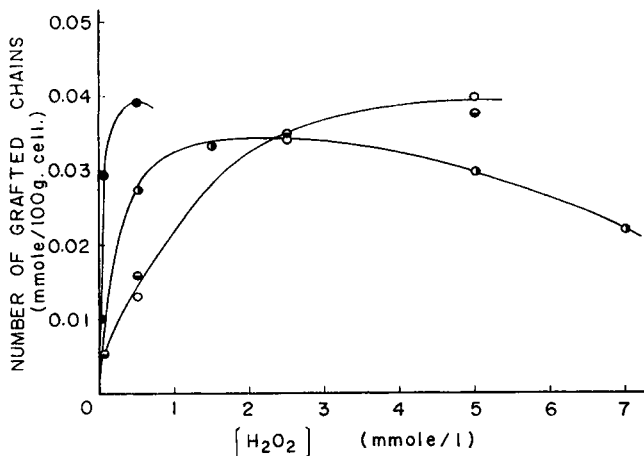
Fig. 5. Relationship of number of grafted chains to concentration of hydrogen peroxide (SP1). Polymerization temperature, 60°C.; polymerization time, 60 min. Adsorbed Fe^{3+} (mmols per 100 g of cellulose): (O) 1.90; (◐) 3.30; (◑) 9.30; (●) 21.0.
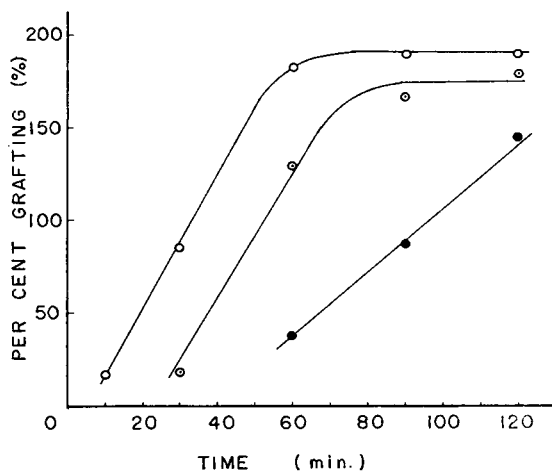

Fig. 6. Relationship of per cent grafting to polymerization time (SP1). Polymerization temperature, 60°C; $[H_2O_2]$ = 5.0 mmol/l. Adsorbed Fe^{3+} (mmols per 100 g of cellulose): (O) 4.10; (◉) 9.00; (●) 16.8.

important in discussing the initiation mechanism of graft copolymerization with ferric ion–hydrogen peroxide systems.

Relation between Scission of Cellulose Chain and Graft Copolymerization

It is indicated that in the graft copolymerization of cellulosic materials ferrous ion–hydrogen peroxide[1,2,4,13] or ferric ion–caro's acid[14] as initiators, the trunk polymer is damaged and its molecular weight lowered. This is attributed to the scission of chains as a result of oxidation by oxidizing

agents.   Therefore, the relation between the scission reaction of cellulose chain and the decomposition reaction of hydrogen peroxide was examined in detail.   Assuming the weight-average degree of polymerization of cellulose to be twice the number-average degree of polymerization, according to
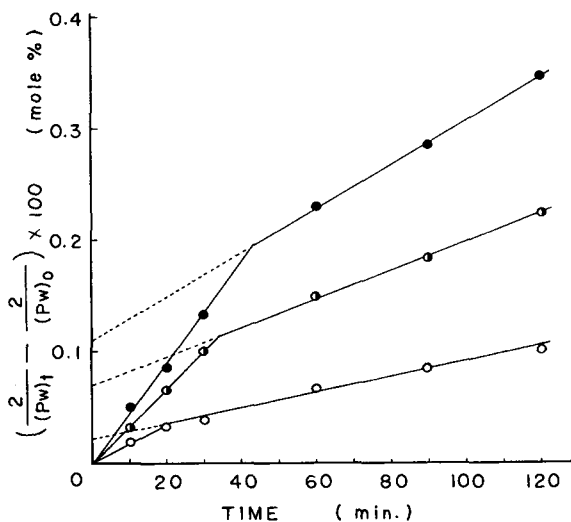

Fig. 7. Changes of number of scissions of cellulose chains with time (SP1).   Adsorbed Fe^{3+}, 15.5 mmols per 100 g of cellulose; reaction temperature, 60°C. $(\bar{P}_w)_0$ = weight-average degree of polymerization at time 0; $(\bar{P}_w)_t$ = weight-average degree of polymerization at time t. H_2O_2 concentration (mmol/l):   (O) 1.0;   (◑) 5.0;   (●) 10.0.
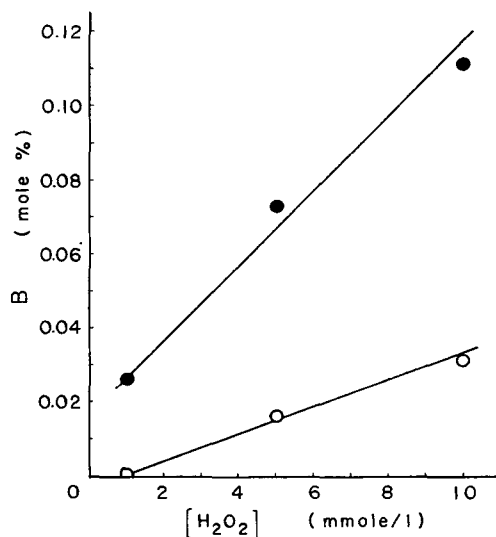

Fig. 8. Relationship of B (number of scissions at the stage of faster scission reaction, Fig. 7) to concentration of hydrogen peroxide (SP1).   Adsorbed Fe^{3+} (mmols per 100 g of cellulose):   (O) 2.70;   (●) 15.5.
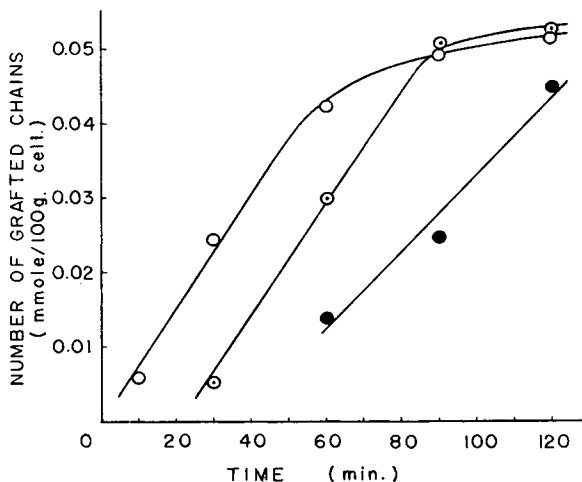
Fig. 9. Changes of number of grafted chains with time (SP1). Polymerization temperature, 60°C; [H_2O_2] = 5.0 mmol/l. Adsorbed Fe^{3+} (mmols per 100 g of cellulose): (O) 4.10; (⊙) 9.00; (●) 16.8.

Sharples,[15] the number of chain scissions was calculated according to Haword's equation,[16] and its change with the reaction time is plotted in Figure 7. Clearly, at the initial stage of reaction the scission reaction is observed to be fast.

From the intercept of the ordinate obtained by the extrapolation of a straight line the number of scissions, B, at the stage of faster scission reaction was given. The value of B increased with the increase of both the concentration of hydrogen peroxide and the amount of ferric ion adsorbed on cellulose, as shown in Figure 8.

The relation between the number of grafted chains and the polymerization time is shown in Figure 9 for the graft copolymerization, with 5 mmol/l of hydrogen peroxide. The larger the amount of ferric ion adsorbed on cellulose, the longer the induction period of the initiation of graft copolymerization; this shows the same tendency as the per cent grafting. The beginning of the initiation of graft copolymerization is almost equal to the time at the inflection point of the broken line in Figures 1 and 7 for each sample. Therefore, it is supposed that the values of A and B must be seriously related to the graft copolymerization. That is to say, it was observed that the larger the amount of ferric ion adsorbed on cellulose, and the higher the concentration of hydrogen peroxide, the longer the period in which scission reactions mainly occurred and the graft copolymerization hardly took place at all.

Taking into account these considerations, it is difficult to suppose that the copolymers assume a block structure,[14] from only the reason that the remarkable scission of cellulose chain occurred in the process of graft copolymerization initiated by the oxidizing agents.

Initiation Efficiency of Graft Copolymerization

The rate of decomposition of hydrogen peroxide mainly contributes to the scission of cellulose chains and relates very little to the formation of grafts. Therefore, the relation between C, which results from the subtraction of A from the amount of decomposition of hydrogen peroxide after 60 min of reaction, and the number of grafted chains of copolymer after the same duration of polymerization is shown in Figure 10. (C is the net amount of hydrogen peroxide pertaining to graft formation).
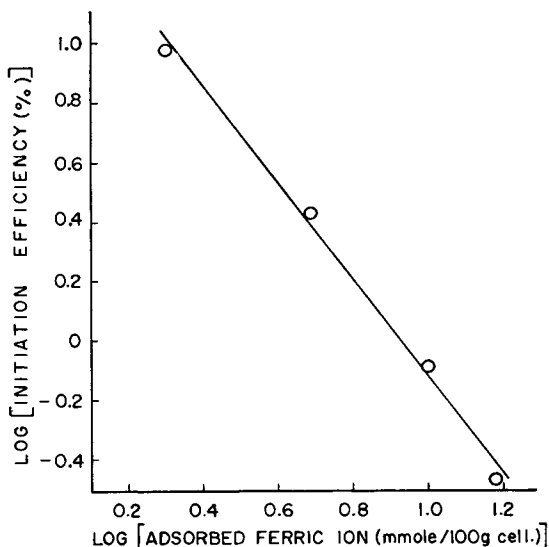

Fig. 10. Initiation efficiency (per cent ratio of number of grafted chains formed to C which is the amount of hydrogen peroxide decomposed initially (A), subtracted from the amount decomposed after 60 min of reaction), versus amount of adsorbed ferric ion (SP1).

In this figure an almost linear relation is observed between the logarithm of the per cent ratio of the number of grafted chains formed to C and that of the amount of ferric ion adsorbed on cellulose. As the amount of ferric ion adsorbed increased, an apparent decrease of the initiation efficiency of hydrogen peroxide in graft copolymerization was observed.

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