

Formation of Peroxide on Aldehyde Cellulose and Its Ability to Initiate Graft Copolymerization

YOSHITAKA OGIWARA, TATSUO UMASAKA, and HITOSHI KUBOTA,
*Department of Polymer Chemistry, Faculty of Engineering, Gunma
University, Kiryu, Gunma 376, Japan*

Synopsis

Cellulose peroxide formed by the treatment of aldehyde cellulose with hydrogen peroxide (H_2O_2) was investigated with respect to formation and decomposition conditions and with respect to graft initiation. Periodic acid-oxidized cellulose was proved to produce the peroxide group on the substrate by subsequent treatment with H_2O_2 , whereas no peroxide was produced with unoxidized cellulose. Since the peroxide content of oxidized cellulose increased with increasing carbonyl content of the sample, the peroxide was presumed to be introduced at the site of the aldehyde group of the sample. The peroxide groups formed were proved to revert to aldehyde groups by decomposition upon heating with water to nearly the same level as the original. The structure of the peroxide group was believed therefore to be an α -hydroxy hydroperoxide type. The cellulose peroxide was found to initiate graft copolymerization of methyl methacrylate very easily in thermal initiation and photoinitiation systems.

INTRODUCTION

The authors¹ previously observed that peroxide groups are introduced into cellulose derivatives such as carboxymethyl cellulose (CMC), acrylic acid-grafted cellulose, and periodic acid-oxidized cellulose (aldehyde cellulose) by treatment with H_2O_2 in air. For CMC, carboxyl groups of the substrate were presumed to participate in the reaction to form a peroxide group of the peracid type. Further, the peroxides on CMC were found to initiate graft copolymerization of vinyl monomers by heat or light.² On the other hand, the structure of the peroxide group³ on aldehyde cellulose has not been clarified, although the aldehyde group of the sample seems to participate in its formation. In this study, the conditions needed to form peroxide groups on aldehyde cellulose and the structure of the groups were investigated together with their ability to initiate graft copolymerization.

EXPERIMENTAL

Materials

Commercial dissolving pulp from softwoods was treated with aqueous periodic acid solutions of various concentrations (solid-to-liquid ratio 1:100) at 45°C for 60 min, resulting in aldehyde cellulose. After the treatment the sample was washed with water, dried under reduced pressure, and used for further experiments. It is known that periodic acid oxidation leads to the introduction of aldehyde group on cellulose samples.⁴ The carbonyl content of aldehyde cellulose was determined according to the hydroxylamine method.⁵

TABLE I
Formation of Peroxide on Various Oxidized Celluloses

Oxidizing reagent	Oxidation conditions				Carbonyl, mmole/100 g cell.	Peroxide, ^a meq/100 g cell.
	Concn. of reagent mmole/l.	Temp., °C	Time, min	pH of bath		
HIO ₄	30	45	60	4	76.5	49.3
NaClO	50	60	120	12	13.1	0.5
NaClO	10	60	90	3	57.0	24.0
H ₂ O ₂	50	60	90	6	18.2	0.5
K ₂ Cr ₂ O ₇	9	25	300	3	23.9	16.0

^a Formation was carried out at 25°C for 120 min. Concentration of hydrogen peroxide, 2.14 mole/l. Ratio of bath, 100.

Formation of Peroxide on Aldehyde Cellulose

A flask containing 1.0 g aldehyde cellulose and 15 ml 35% aqueous solution of H₂O₂ was maintained at 25°C for a given time. Thereafter, the product was washed with 2 liters ice water to obtain a peroxide sample in the wet state. The peroxide content of the sample was determined iodometrically.⁶

Stability of Peroxide Group

A flask containing 0.50 g cellulose peroxide in the wet state was maintained at 0, 4, and 18°C for a given time. Thereafter, the content was filtered to separate the fibrous material from the aqueous medium, and the amounts of peroxide in each part were then determined.

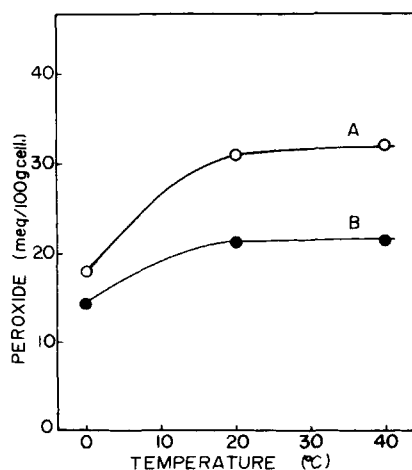


Fig. 1. Effect of reaction temperature on formation of cellulose peroxide. C=O Content (mmole/100 g cellulose): sample A, 59.4; sample B, 23.6. Concentration of hydrogen peroxide, 0.54 mole/l; time, 60 min.

Reduction of Peroxide Group

Cellulose peroxide was reduced by an aqueous solution of sodium iodide applying the conditions of iodometry. The product was then filtered, washed with water, and dried under reduced pressure to obtain a reduced sample.

Grafting

Thermal grafting was carried out in a system consisting of 0.50 g cellulose peroxide, 20 ml water, and 2 ml methyl methacrylate (MMA) under nitrogen atmosphere in a Pyrex glass tube at 60°C. Photografting was carried out at 30°C by irradiating the above system with a high-pressure mercury lamp.

The polymerization products were washed with water and extracted for 24 hr with acetone to remove homopolymer. The percent grafting and the graft efficiency were taken respectively as the percentage of weight increase of the original cellulose and the weight percent of grafted polymer relative to total conversion of monomer in the system.

RESULTS AND DISCUSSION

Formation of Peroxides on Oxidized Cellulose

Oxidized celluloses were found to form peroxide groups by treatment with H_2O_2 , whereas unoxidized celluloses did not. The formation of peroxide groups on various oxidized celluloses is shown in Table I. The peroxide formation was easiest for the periodic acid-oxidized cellulose, the carbonyl content of which was also the highest. Therefore, subsequent experiments were performed employing the periodic acid-oxidized cellulose, that is, aldehyde cellulose. Besides aldehyde cellulose, the sample oxidized with hypochlorous acid (acid medium) showed high levels of carbonyl and peroxide formation.

The effects of reaction temperature and time on the formation of peroxide on aldehyde cellulose were examined and are shown in Figures 1 and 2. It is clear that the reaction proceeds smoothly at room temperature and that some high temperatures are rather advantageous. On the other hand, the peroxide formation was found to reach a certain level after a reaction of about 30 min.

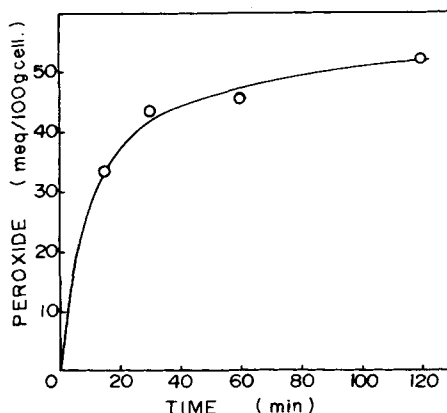


Fig. 2. Effect of reaction time on formation of cellulose peroxide. C=O content, 118.6 mmole/100 g cellulose; concentration of hydrogen peroxide, 11.4 moles/l; temperature, 25°C.

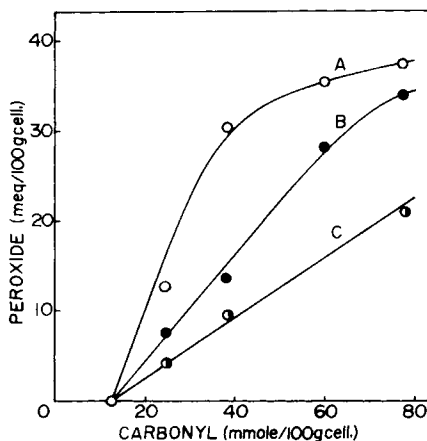


Fig. 3. Effect of carbonyl content of aldehyde cellulose on formation of cellulose peroxide. Concentration of hydrogen peroxide (mole/l): sample A, 11.40; sample B, 2.14; sample C, 0.54. Temperature, 25°C, time, 60 min.

The relationship between the amount of peroxide and the carbonyl content, that is, the degree of oxidation of the substrate, is shown in Figure 3. The amount of peroxide increased with increasing carbonyl content of the sample and also with the concentration of H_2O_2 in the system. The amount of peroxide introduced into the substrate reached a level of about 30% of mole equivalent of the carbonyl content. The carbonyl group of the sample seems to be an essential factor in introducing the peroxide groups into the substrate by means of H_2O_2 . The peroxide prepared by this method should therefore have a structure based on interaction between the aldehyde group and H_2O_2 .

Stability of Peroxide on Aldehyde Cellulose

Table II shows the stability of peroxide on aldehyde cellulose in the presence of water at various temperatures. The peroxide groups on the fiber were sensitive to temperature, being very stable at 0°C, and decreasing in amount sharply by standing at room temperature for 48 hr. Contrary to the decrease in peroxide on the fibrous part due to the decomposition, H_2O_2 was found to be generated in the water part, the amount of which corresponded nearly to that of lost peroxide on the fiber part. There was no large difference between the initial amount

TABLE II
Stability of Peroxide on Aldehyde Cellulose

Temperature, °C	Time, hr	Peroxide, meq/100 g cellulose		
		Sample part	Water part	Total system
0	0	24.5	0	24.5
0	24	23.3	1.7	25.0
0	48	22.4	2.8	25.2
4	0	24.5	0	24.5
4	24	17.5	7.4	24.9
4	48	13.2	11.8	25.0
18	0	24.5	0	24.5
18	24	7.8	17.2	22.0
18	48	3.4	21.4	24.8

TABLE III
Peroxide and Carbonyl Contents of Various Samples Before and After Chemical Reduction or Thermal Decomposition

Treatment	Peroxide, meq/100 g cell.		Carbonyl, mmole/100 g cell.		Peroxide ^a on treated sample, meq/100 g cell.
	Before	After	Before	After	
Reduction by KI	28.3	0	78.4	71.9	28.3
Thermal decomposition 80°C, 30 min	36.2	0	67.1	63.3	28.5
Drying under reduced pressure, 17°C, one day	32.6	12.4	79.9	74.3	34.0

^a Peroxidation of treated sample was carried out at 25°C for 60 min using cellulose sample after treatment described in the table.

From the above considerations it is believed that the cellulose peroxide formed by the reaction of aldehyde cellulose with H_2O_2 has mainly the α -hydroxy hydroperoxide structure.

Decomposition of Peroxide on Aldehyde Cellulose

Figure 4 shows the thermal decomposition of peroxide on aldehyde cellulose in water at 40°C. The amount of peroxide on the fibrous part decreased with reaction time, while generation of H_2O_2 was observed in the water part. Therefore, the loss of total amount of peroxide in the system by decomposition was very small as shown by the curve A in the figure.

Figure 5 shows effects of ferrous salt and UV light ($\lambda > 300$ nm) on the decomposition of peroxide. The ferrous salt and the light were found to accelerate the decomposition markedly. Based on the above results, the fundamental processes of the decomposition of cellulose peroxide could be presented by eqs. (6) to (10). The amount of total peroxide in the system was very small upon thermal decomposition, so that it is suggested that the generation of H_2O_2 based on eq. (7) might be the main reaction in this system. However, both ferrous salt

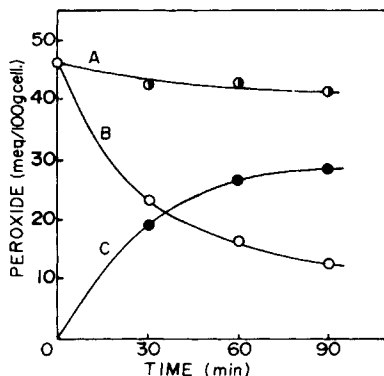


Fig. 4. Thermal decomposition of cellulose peroxide in aqueous media at 40°C. A, B, and C represent amounts of peroxide in total system (A), on cellulose part (B), and in water part (C), respectively.

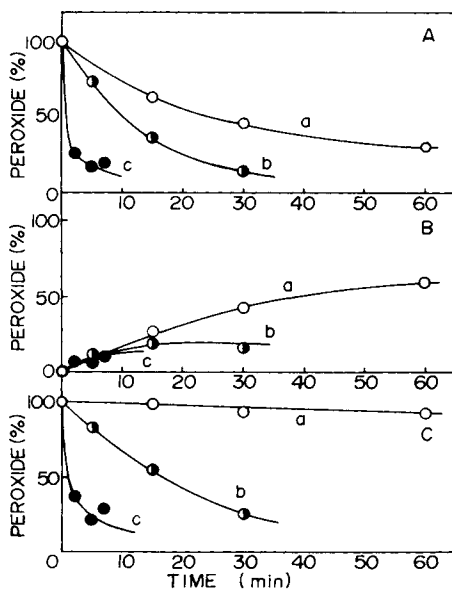
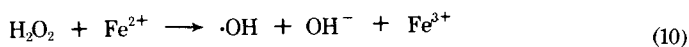
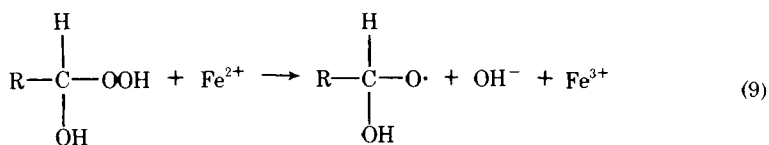
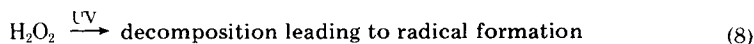
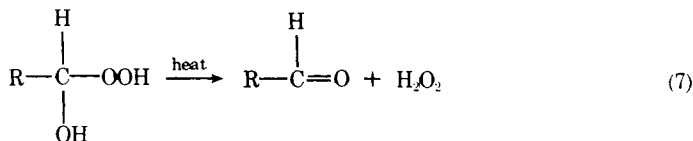
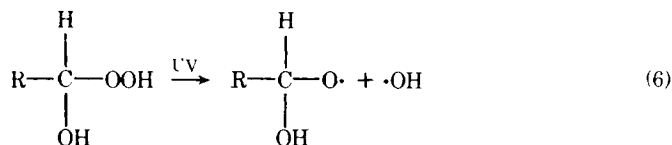


Fig. 5. Decomposition of cellulose peroxide at 40°C due to heat (a), UV light (b), and ferrous ion (c). A, B, and C represent amounts of peroxide in cellulose part, in water part, and in total system, respectively. [Fe²⁺], 1.0 mmole/l.; UV, λ > 300 nm; medium, water.

and UV seem to affect the decomposition of H₂O₂ as well as that of peroxide, promoting the decrease of total peroxide in the system. Among the following reactions, ferrous salt is believed to contribute to the redox type reaction, eqs. (9) and (10), while UV promotes the reaction of eqs. (6) and (8):



where R = cellulose residue.

Grafting Induced by Cellulose Peroxide

Figure 6 shows the thermal grafting of MMA induced by cellulose peroxide. The ability of aldehyde cellulose itself to initiate thermal grafting was comparatively low. It is clear from the figure that the percent grafting increases with increasing peroxide content of the sample. Thus, the initiation of grafting seems to be related to the peroxide group of the substrate. It was reported that peroxides introduced on cellulose and its derivatives by γ -ray irradiation,^{9,10} ozonization,¹¹ and autoxidation¹² employing azobisisobutyronitrile can contribute to the initiation of grafting of vinyl monomers.

The results of photografting are shown in Figure 7. Aldehyde cellulose itself has been observed to have the ability to initiate photografting because of the high activity of carbonyl group toward light.¹³ However, the activity of cellulose peroxide was found to be higher than that of aldehyde cellulose alone, and the percent grafting was shown to increase with increase in peroxide content. The graft efficiencies of the thermal initiation and the photoinitiation systems were in the range of 80% to 85% and 60% to 65%, respectively.

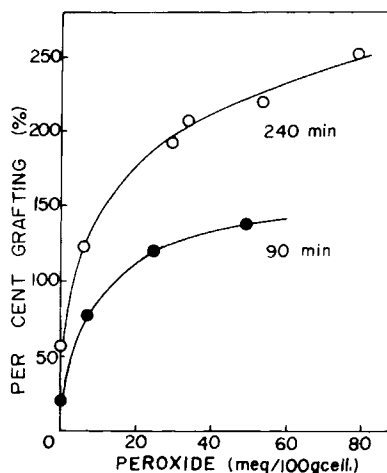


Fig. 6. Thermal grafting on cellulose peroxide upon warming at 60°C. Concentration of cellulose peroxide, 54.1 meq/100 g cellulose.

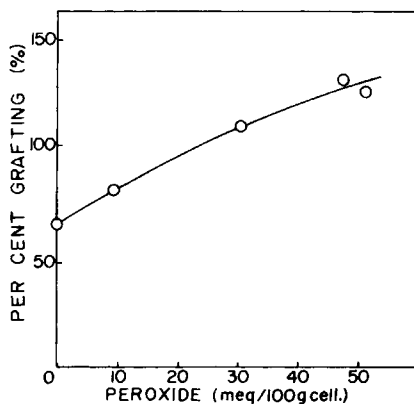


Fig. 7. Grafting on cellulose peroxide using UV light ($\lambda > 300$ nm). Grafting conditions 30°C, 45 min.

TABLE IV
Thermal Grafting^a of MMA on Aldehyde Cellulose in the Presence of H₂O₂

Concentration of H ₂ O ₂ , mmole/l	Total conversion of MMA, %	Percent grafting, %	Graft efficiency, %
0.3	69.1	245.6	95.0
3.0	68.7	240.6	95.7
15.0	66.9	236.4	94.3

^a Temperature, 60°C; time, 90 min.

As shown above, H₂O₂ may be dissociated from cellulose peroxide under conditions of grafting reaction. The separated H₂O₂ is also believed to participate in the initiation of graft copolymerization. If the cellulose aldehyde substrate is attacked directly by H₂O₂, some cellulosic radicals may be formed which are capable of grafting.^{14,15} Table IV shows the thermal grafting of aldehyde cellulose in the presence of H₂O₂, the amount of which was adjusted nearly to the mole corresponding to the peroxide content of the cellulose peroxide. As seen in the table, H₂O₂ was found to initiate actively the grafting on the aldehyde cellulose. On the other hand, H₂O₂ is known to accelerate the photografting of MMA on cellulose.¹⁵

Accordingly, the thermal grafting and photografting induced by cellulose peroxide are inferred to be based on two mechanisms. One is the initiation due to radicals induced by the decomposition of peroxide group on the substrate, and the other is the initiation by cellulose radicals derived from the reaction of generated H₂O₂ with the cellulose substrate.

References

1. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **22**, 3363 (1978).
2. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **23**, 241 (1979).
3. P. Cremonesi and L. D'Angiuro, *Cell. Chem. Technol.*, **4**, 373 (1970).
4. S. A. Rydholm, *Pulping Processes*, Wiley, New York, 1965, p. 131.
5. U. Ströle, *Makromol. Chem.*, **20**, 19 (1956).
6. Y. Ogata, Ed., *Chemistry of Organic Peroxides*, Nankodo, Tokyo, 1971, p. 332.
7. P. Cremonesi and L. D'Angiuro, *Cell. Chem. Technol.*, **2**, 145 (1968).
8. D. Swern, Ed., *Organic Peroxides*, Vol. I, Wiley, New York, 1970, p. 24.
9. K. Matsuzaki, S. Nakamura, and S. Shindo, *J. Appl. Polym. Sci.*, **16**, 1339 (1972).
10. A. Chapiro, *J. Polym. Sci. C*, **No. 50**, 181 (1975).
11. L. Neimo, H. Sihtola, O. Harva, and A. Sicola, *Pap. Puu*, **49**, 509 (1967).
12. E. Gleason and V. Stannett, *J. Polym. Sci.*, **44**, 183 (1930).
13. K. Hayase, H. Kubota, and Ogiwara, presented at 34th Japan Chemistry Conference, Tokyo, 1976.
14. Y. Ogiwara, Y. Ogiwara, and H. Kubota., *J. Appl. Polym. Sci.*, **12**, 2575 (1968).
15. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **14**, 2879 (1970).

Received November 4, 1977

Revised January 5, 1978