Cellulose Peroxides with Structures of Peracid and α-Hydroxyhydroperoxide Types

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ABSTRACT

Cellulose peroxides derived from various cellulose derivatives with hydrogen peroxide were investigated. Fibrous carboxymethyl cellulose, periodic acid-oxidized cellulose, and methyl vinyl ketone-treated cellulose were employed as cellulose derivatives. Carboxyl and carbonyl groups in the cellulose derivatives were believed to react with hydrogen peroxide to form peroxides with structures of peracid and α-hydroxyhydroperoxide types, respectively. The decomposition of the cellulose peroxides and their abilities to initiate grafting reaction were examined.

INTRODUCTION

It has been reported that peroxide groups are introduced into cellulose and its derivatives by UV [1, 2] and γ-ray [3] irradiations under oxygen atmosphere, autoxidation [4] induced by means of radical initiator, and attack with ozone [5-7]. The authors observed that peroxide groups were easily introduced into cellulose material by the reaction between various cellulose derivatives and hydrogen peroxide (H_2O_2). Thus peroxide groups with structures of the peracid and α-hydroxyhydroperoxide types were estimated to be produced for

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fibrous carboxymethyl cellulose (CMC) [8] and cellulose derivatives
containing aldehyde [8, 9] and ketone [10] groups, respectively.

This paper deals with the comparison of characteristics among the
cellulose peroxides with peracid and α-hydroxyhydroperoxide types
with respect to the decomposition and the ability to initiate a grafting
reaction.

EXPERIMENTAL

Cellulose Derivatives

A commercial dissolving pulp from softwood (NDP) was treated
with monochloroacetic acid and sodium hydroxide to obtain CMC [11]
whose degree of substitution was 0.42. Aldehyde and carbonylated
celluloses were prepared by treating NDP with an aqueous solution
of periodic acid and with a methyl vinyl ketone in alkaline medium,
respectively. Aldehyde [12] and ketone [13] groups are known to be
introduced into the cellulose material by those treatments. The
hydroxylamine method [14] was applied to the determination of the
carbonyl content of the sample.

Formation and Decomposition of Cellulose Peroxides

A flask containing 0.50 g cellulose derivative, 10 mL aqueous H_2O_2
(35 or 60%), and 2 mL concentrated sulfuric acid was kept at 25°C
for 3 h. After the reaction the sample was washed with about 1 L
ice water. Cellulose peroxides with various peroxide contents were
prepared using cellulose derivatives with different carboxyl or car-
bonyl content. The peroxide content of the sample was determined
iodometrically [8].

The thermal decomposition was carried out at 40°C in a system
consisting of 0.50 g cellulose peroxide and 20 mL water. After the
reaction the content was filtered to separate the fibrous material
from the aqueous medium, and then the peroxide content in each
part was determined. The effects of ferrous salt and photoirradiation
on the decomposition of cellulose peroxide were examined by either
adding 20 mL of 1 mmol/L aqueous solution of ferrous ammonium sul-
fate or irradiating through a Pyrex glass tube to the system contain-
ing 0.50 g cellulose peroxide and 20 mL water with a Riko high-
pressure mercury lamp UVL-400P. The irradiation was carried out
at 40°C in a Riko rotary photochemical reactor RH400-10W around
which Pyrex tubes were set to rotate.

TABLE 1. Formation[a] of Cellulose Peroxides

| | | Peroxide (meq/100 g cellulose) | | | |
| | | 35% H_2O_2 | | 60% H_2O_2 | |
Cellulose sample	COOH or C=O (mmol/100 g cellulose)	Without H_2SO_4	With H_2SO_4	Without H_2SO_4	With H_2SO_4
CMC	246.2	4.5	22.9	-	61.1
Aldehyde cellulose	39.4	18.5	18.1	-	19.0
Carbonylated cellulose	21.0	10.2	17.8	-	21.2

[a]Cellulose samples were treated with hydrogen peroxide at 25°C for 3 h.
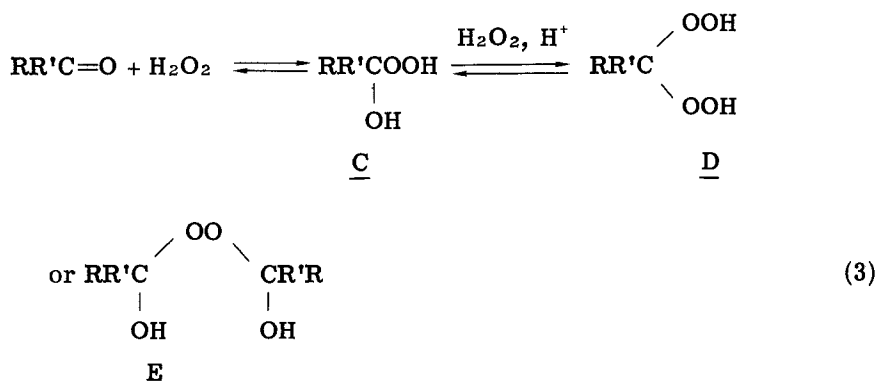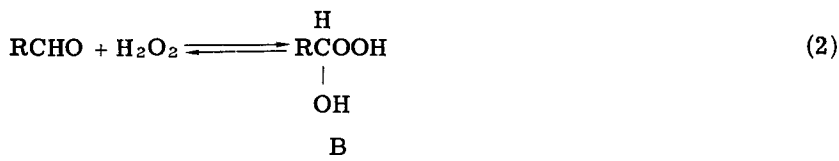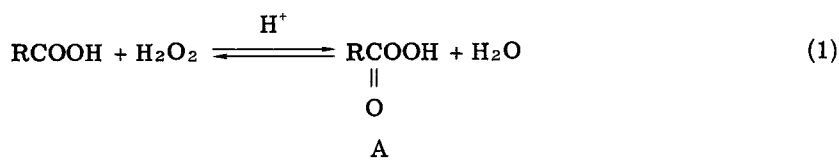
Grafting

Thermal grafting was carried out under nitrogen in a Pyrex glass tube containing 0.50 g cellulose peroxide, 20 mL water, and 2 mL methyl methacrylate at 60°C for 90 min. Photografting was carried out at 30°C for 40 min by irradiating the above system with the Riko high-pressure mercury lamp. The percent grafting and the graft efficiency were taken as the percentage of weight increase of the original sample and the weight percent of grafted polymer relative to total conversion of monomer in the system, respectively.

RESULTS AND DISCUSSION

Formation of peroxides on various cellulose derivatives induced by the reaction with H_2O_2 is presented in Table 1. Peroxidation of CMC was surely activated by the use of sulfuric acid, leading to an increased formation of peroxide. The amount increased further with the use of 60% H_2O_2, and the maximum value reached about one-fourth of the carboxyl content of the sample. The value in the case of carbonylated cellulose, 60% H_2O_2, and the sulfuric acid system recorded a level almost as high as the carbonyl content of the sample. On the other hand, the concentration of H_2O_2 and sulfuric acid did not affect the peroxidizing reaction of aldehyde cellulose.

The reactions shown in Eqs. (1) to (3) are known in the case of peroxidation of carboxylic acids and carbonyl compounds of low molecular weight [15, 16]:

$$RCOOH + H_2O_2 \; \underset{}{\overset{H^+}{\rightleftharpoons}} \; \underset{\underset{\underset{A}{O}}{\|}}{RCOOH} + H_2O \tag{1}$$

$$RCHO + H_2O_2 \; \underset{}{\overset{H}{\rightleftharpoons}} \; \underset{\underset{B}{OH}}{\overset{|}{RCOOH}} \tag{2}$$

$$RR'C{=}O + H_2O_2 \; \rightleftharpoons \; \underset{\underset{C}{OH}}{\overset{|}{RR'COOH}} \; \underset{}{\overset{H_2O_2,\ H^+}{\rightleftharpoons}} \; \underset{D}{RR'C\overset{\diagup OOH}{\diagdown OOH}} \tag{3}$$

$$\text{or} \; \underset{\underset{E}{OH}}{\overset{|}{RR'C}} \overset{\diagup OO \diagdown}{} \underset{OH}{\overset{|}{CR'R}}$$

These reactions seem to be true in the peroxidations of various cellulose derivatives with H_2O_2 [8-10]. A carboxyl group in the CMC sample may react with H_2O_2 to yield a peroxide of the peracid type according to Eq. (1). The peroxidation of aldehyde cellulose may proceed according to Eq. (2) to give B of the α-hydroxyhydroperoxide type, and the formation is not influenced by acid. As shown in Eq. (3), a ketone group of the carbonylated cellulose may react with H_2O_2 to form C, which perhaps converts to D or E in the presence of excess H_2O_2 and acid [15]. Thus the peroxides on carbonylated cellulose are believed to include peroxide groups of the D or E type besides the C type.

Table 2 presents the stability of cellulose peroxides in a sample drying process. CMC peroxides were observed to be very unstable, and almost all the peroxide groups of the sample were lost during the drying process. On the other hand, peroxides of aldehyde and carbonylated celluloses were more stable during drying. About 40 and 90% peroxides of the sample were retained in aldehyde and carbonylated celluloses, respectively, after drying for 24 h at 25°C.

The thermal decompositions of cellulose peroxides in aqueous

TABLE 2. Stability of Cellulose Peroxides in Sample Drying Process[a]

| | Peroxide (meq/100 g cellulose) | |
	Before drying	After drying
Cellulose peroxide		
CMC	41.0	0
Aldehyde cellulose	31.9	12.8
Carbonylated cellulose	27.4	24.7

[a]Cellulose peroxides were dried under reduced pressure for 24 h at 25°C.

FIG. 1. Thermal decompositions of cellulose peroxides at 40°C in aqueous medium. Initial amounts of peroxides on CMC (○), aldehyde cellulose (◐), and carbonylated cellulose (●) were 50.0, 20.8, and 28.5 meq/100 g of cellulose, respectively. T, S, and L represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively.
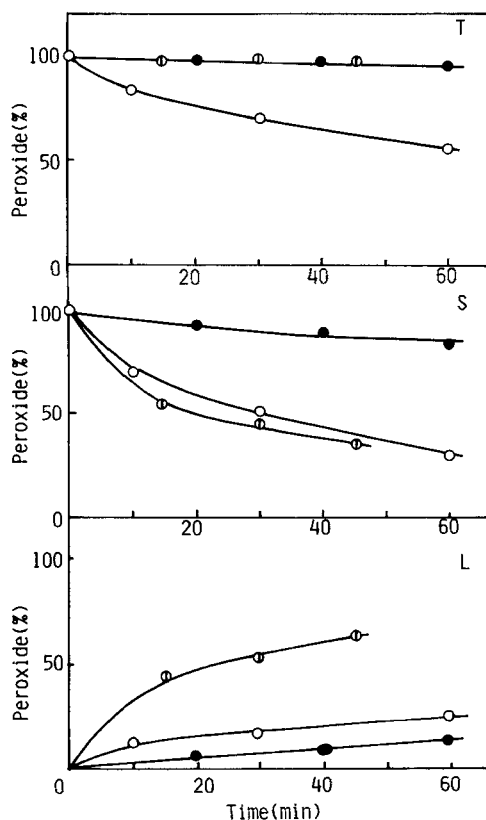
FIG. 2. Effect of ferrous salt on thermal decomposition of cellu-
lose peroxides at 40°C in aqueous medium. Initial amounts of per-
oxides on CMC (○), aldehyde cellulose (⊕), and carbonylated cellu-
lose (●) were 40.1, 44.0, and 27.4 meq/100 g of cellulose, respec-
tively. T, S, and L represent amounts of peroxide in total system, in
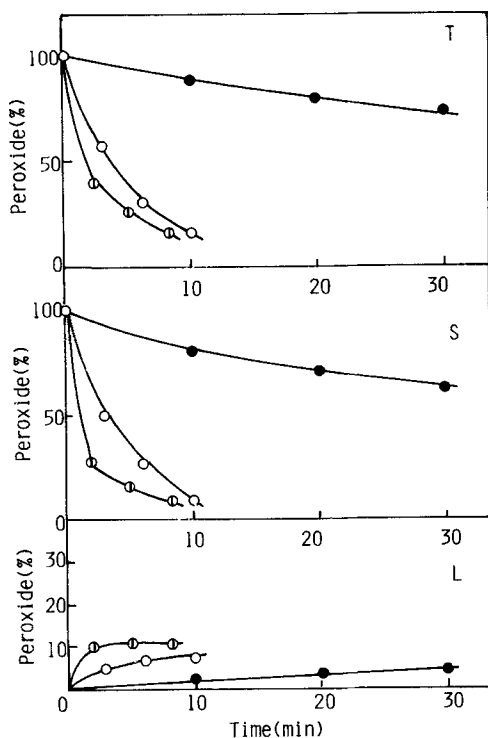fibrous material, and in aqueous medium, respectively.

medium are shown in Fig. 1. The peroxide content of the sample was
gradually decreased by setting the cellulose peroxides in the aqueous
medium at 40°C. As the reaction proceeded, the generation of H_2O_2
was observed in the aqueous medium. The phenomenon can be explained
with the assumption that H_2O_2 is liberated from the cellulose peroxides
in aqueous medium according to the reverse reactions of Eqs. (1) to (3).
The reverse reaction appeared to be easiest for the peroxide of B type
among cellulose peroxides. As for the loss of total peroxide of the
system by decomposition, a very small amount was recorded as shown
in Fig. 1-T. Thus the decomposition according to Eq. (4) seems to be
hard to initiate. However, the decomposition of A according to Eqs.
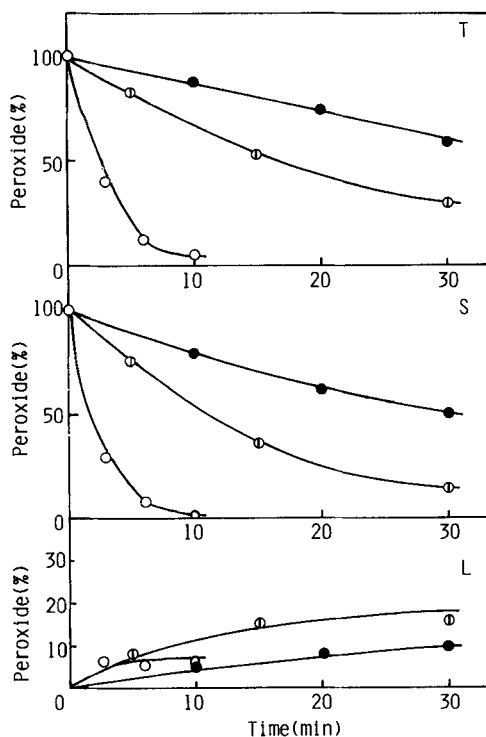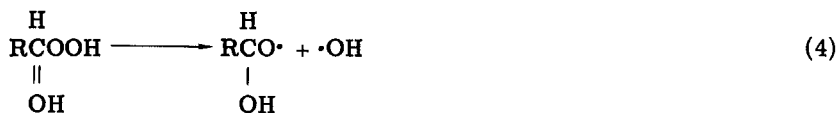(5) and (6) may be rather easier, resulting in a loss of an appreciable

FIG. 3. Effect of photoirradiation on thermal decomposition of cellulose peroxides at 40°C in aqueous medium. Initial amounts of peroxides on CMC (○), aldehyde cellulose (⦶), and carbonylated cellulose (●) were 43.0, 48.5, and 27.4 meq/100 g of cellulose, respectively. T, S, and L represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively.

amount of peroxide as the total system. The peroxides on carbonylated cellulose were shown to be more stable thermally than the peroxides on aldehyde cellulose and CMC.

$$
\begin{array}{c}
\text{H} \\
\text{RCOOH} \\
\parallel \\
\text{OH}
\end{array}
\longrightarrow
\begin{array}{c}
\text{H} \\
\text{RCO} \cdot + \cdot \text{OH} \\
\mid \\
\text{OH}
\end{array}
\qquad (4)
$$

$$
\begin{array}{c}
\text{RCOOH} \\
\parallel \\
\text{O}
\end{array}
\longrightarrow
\begin{array}{c}
\text{RCO} \cdot + \cdot \text{OH} \\
\parallel \\
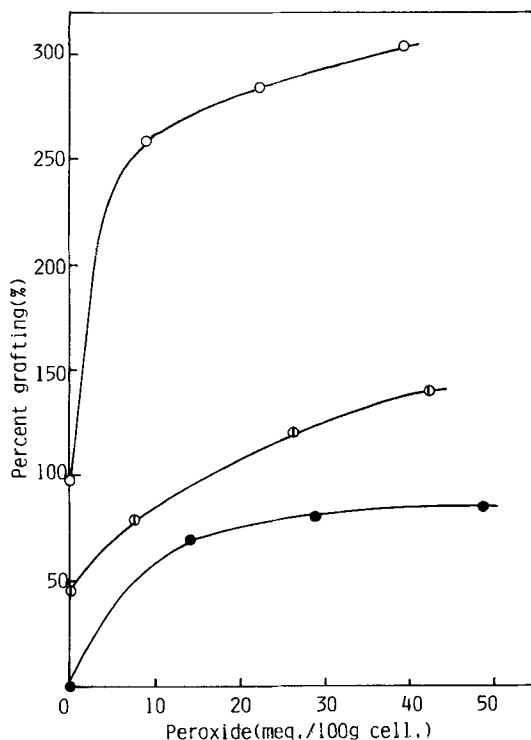\text{O}
\end{array}
\qquad (5)
$$

FIG. 4. Thermal graftings of methyl methacrylate induced by per-
oxides on CMC (o), aldehyde cellulose (Φ), and carbonylated cellu-
lose (●) at 60°C for 90 min.

$$RCO \cdot \longrightarrow R \cdot + CO_2 \qquad\qquad (6)$$
$$\underset{O}{\overset{\|}{}}$$

The effects of ferrous salt and irradiation with light of $\lambda > 300$ nm
on the thermal decomposition of cellulose peroxides are shown in
Figs. 2 and 3, respectively. The decomposition of cellulose peroxides
was markedly accelerated by ferrous salt and/or irradiation with
light. That is, both the amounts of peroxide on the cellulose material
and H_2O_2 generated in the aqueous medium were observed to decrease
by the actions of ferrous salt and/or light, leading to an increased
loss of peroxides as the total system. Thus it is conceivable that
ferrous salt works on the decomposition process of peroxides through
a redox mechanism and the photoirradiation promotes the reaction of
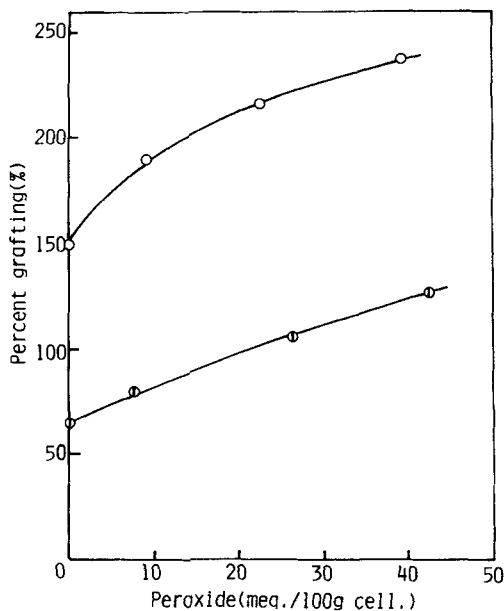Eqs. (4) to (6).

FIG. 5. Photograftings of methyl methacrylate induced by per-
oxides on CMC (○) and aldehyde cellulose (⊕) at 30°C for 40 min.

Thermal graftings of methyl methacrylate induced by cellulose
peroxides are shown in Fig. 4. Each peroxide exhibited an ability
to initiate grafting, and the percent grafting increased with an in-
crease in the peroxide content of the substrate. The graft efficiency
was in the range of 70 to 90% for each peroxide. The cellulose per-
oxides were also active toward photografting as shown in Fig. 5.
The peroxide of $\overline{A}$ is considered to decompose in aqueous medium
to form CMC radicals capable of initiating grafting according to
Eqs. (5) and (6). On the other hand, the peroxide of α-hydroxyhydro-
peroxide type on aldehyde cellulose has the property of releasing
H_2O_2 thermally from the substrate in aqueous medium. The re-
sultant H_2O_2, which can be activated by heat [9] and light [17],
might attack the cellulose material itself, resulting in the initiation
of grafting. Accordingly, with the peroxides on aldehyde cellulose,
cellulose radicals induced by Eq. (4) and/or the regenerated H_2O_2
are inferred to contribute to the initiation of grafting. The same
mechanisms as mentioned above are available for grafting initiated
by the peroxides on carbonylated cellulose. However, the ability of
the peroxides on carbonylated cellulose to initiate thermal grafting
was somewhat lower than those on aldehyde cellulose and CMC. This

can be ascribed to the considerably stable character of the peroxides on carbonylated cellulose toward thermal decomposition.

REFERENCES

[1] T. N. Kleinert, Holzforschung, 18, 24 (1964).
[2] C. Kujirai, Sen-i-Gakkaishi, 21, 631 (1965).
[3] K. Matsuzaki, S. Nakamura, and S. Shindo, J. Appl. Polym. Sci., 16, 1339 (1972).
[4] E. Gleason and V. Stannett, J. Polym. Sci., 44, 183 (1960).
[5] V. A. Kargin and U. Usmanov, Vysokomol. Soedin., 1, 149 (1959).
[6] A. A. Katai and C. Schuerch, J. Polym. Sci. A-1, 4, 2683 (1966).
[7] L. Neimo, H. Sihtola, O. Harva, and A. Sivola, Pap. Puu, 49, 509 (1967).
[8] H. Kubota and Y. Ogiwara, J. Appl. Polym. Sci., 22, 3363 (1978).
[9] Y. Ogiwara, T. Umasaka, and H. Kubota, Ibid., 23, 837 (1979).
[10] H. Kubota and Y. Ogiwara, Ibid., 25, 683 (1980).
[11] R. L. Whistler (ed.), Methods in Carbohydrate Chemistry, Vol. III, Academic, New York, 1963, p. 322.
[12] E. Ott, M. Spurlin, and M. W. Grafflin (eds.), Cellulose and Cellulose Derivatives, Part I, Interscience, New York, 1954, p. 148.
[13] M. Tsunooka, M. Tanaka, and J. Murata, Kobunshi Kagaku, 22, 107 (1965).
[14] U. Ströle, Makromol. Chem., 20, 19 (1956).
[15] Y. Ogata (ed.), Chemistry of Organic Peroxides, Nankodo, Tokyo, 1971, pp. 54, 104.
[16] D. Swern (ed.), Organic Peroxides, Vol. I, Wiley, New York, 1970, pp. 24, 313.
[17] H. Kubota and Y. Ogiwara, J. Appl. Polym. Sci., 14, 2879 (1970).