Cellulose Peroxides Derived From Carbonylated Cellulose and Hydrogen Peroxide

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Synopsis

Cellulose peroxides derived from hydrogen peroxide and cellulose derivative into which a ketone group is introduced by reaction with methyl vinyl ketone were investigated. The amount of peroxide formed on the cellulose substrate increased linearly with increasing carbonyl content of the sample, and sulfuric acid activated the formation of peroxide. The cellulose peroxide was gradually decomposed at 60°C in aqueous medium, and the decomposition was accelerated by addition of ferrous salt or irradiation with light of $\lambda > 300$ nm. Grafting was initiated by adding methyl methacrylate to the thermal decomposition system under nitrogen. The formation, stability, thermal decomposition, and structure of the cellulose peroxide were discussed in comparison with one derived from aldehyde cellulose and hydrogen peroxide.

INTRODUCTION

The authors observed previously that peroxide groups are easily introduced into the substrate of cellulose[1-3] and poly(vinyl alcohol)[4] derivatives containing carboxyl and aldehyde groups by treatment with hydrogen peroxide (H_2O_2) and that the resultant peroxide groups have an ability to initiate thermal- and photografting. The carboxyl and aldehyde groups on the polymeric substrate were inferred to react with H_2O_2 to form peroxides of peracid and α-hydroxyhydroperoxide types, respectively.

In this paper cellulose peroxides derived from H_2O_2 and cellulose derivative containing ketone group were examined in terms of the formation, thermal decomposition, stability, and structure while comparing with cellulose peroxides produced by aldehyde cellulose and H_2O_2.

EXPERIMENTAL

Cellulose Samples

Commercial dissolving pulp from softwoods was used as the untreated cellulose sample. The untreated sample was treated with methyl vinyl ketone in alkaline medium to prepare carbonylated cellulose sample.[5] By this treatment ke-

$$\text{Cell OH} + \text{CH}_2\text{CHCCH}_3 \xrightarrow{\text{NaOH}} \text{Cell OCH}_2\text{CH}_2\text{CCH}_3 \quad (1)$$

tone groups were introduced into cellulose substrate as shown in eq. (1). Aldehyde cellulose was prepared using periodic acid according to the same procedure as reported previously.[3] The carbonyl content of the cellulose samples was determined according to the hydroxylamine method.[6]

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Formation of Cellulose Peroxides

Cellulose sample, 0.50 g, 10 ml aqueous H_2O_2 (35%), and 2 ml concentrated sulfuric acid were placed in a flask adjusted at 25°C for 3 hr. The sample after reaction was washed with about 1 liter ice water followed by immediate determination of peroxide. The peroxide content of the sample was determined iodometrically.[3] Peroxides formed on the carbonylated cellulose with and without sulfuric acid were termed as peroxides I and II, respectively.

Decomposition of Cellulose Peroxides

Thermal decomposition was carried out in a system consisting of 0.50 g cellulose peroxide and 20 ml water at 60°C. After the reaction, the content was filtered to separate the fibrous material from the aqueous medium, and then the amount of peroxide in each part was determined. The effect of ferrous salt (ferrous ammonium sulfate) on the thermal decomposition of cellulose peroxide was examined using 20 ml of 1 mmol/l. aqueous solution of ferrous salt. In the case of photodecomposition, a Pyrex glass tube containing 0.50 g cellulose peroxide and 20 ml water was exposed to a Riko high-pressure mercury lamp UVL-400P. The irradiations were carried out at 60°C in a Riko rotary photochemical reactor RH400-10W around which Pyrex tubes were set to rotate.

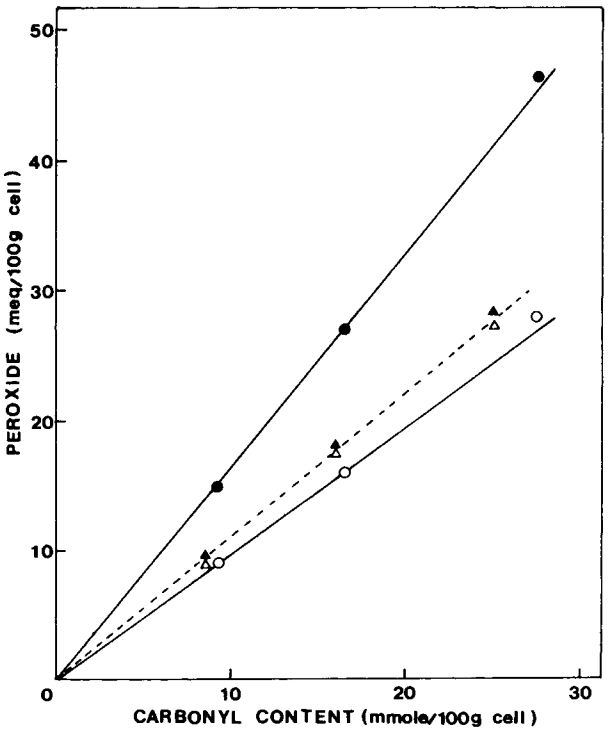


Fig. 1. Formation of peroxides on carbonylated cellulose (—) and aldehyde cellulose (- - -) in the presence (●,▲) or absence (○,△) of sulfuric acid.

TABLE I
Comparison of Peroxide Content Before And After Drying[a]

Cellulose peroxide	Peroxide, meq/100 g cell. Before drying	After drying
Peroxide I	35.5	33.9
Peroxide II	17.7	14.0
Aldehyde cellulose	35.4	13.1

[a] Cellulose peroxides were dried under reduced pressure at 25°C for 20 hr.

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 60 min. Polymer products were washed with water and extracted with acetone to remove homopolymers. The percent grafting and the graft efficiency were calculated as described in a previous paper.[2]

RESULTS AND DISCUSSION

Peroxide groups were introduced into cellulose substrate by treatment of carbonylated cellulose with H_2O_2, and the amount of peroxide increased linearly with increasing the amount of ketone groups in the sample, as shown in Figure 1. In the cellulose sample into which ketone groups were not introduced, no peroxides were formed on the substrate by the same treatment with H_2O_2. Consequently, it seems that the ketone group of the sample contributes effectively to the formation of peroxide. The formation of peroxide was accelerated by the use of sulfuric acid, as shown in Figure 1. The amount of peroxide I formed in the system using acid was higher than that of peroxide II obtained in the system without acid. A dotted line in the figure represents the peroxides formed on aldehyde cellulose. In this case, the formation of peroxides was not influenced by the sulfuric acid in the reaction system. Thus, the function of acid in the reaction forming peroxides was believed to differ in each cellulose sample having a different kind of carbonyl group.

The peroxides on carbonylated cellulose were fairly stable toward sample drying. As shown in Table I, about 95 and 80% of the initial amount of peroxides were retained for peroxides I and II, respectively, after drying for 20 hr at 25°C. On the other hand, the value fell to about 40% for aldehyde cellulose after drying.

Figure 2 shows the thermal decomposition of peroxides on carbonylated cellulose in aqueous medium. The peroxides contained in the fibrous material (S) were gradually decreased by keeping the peroxide-containing sample at 60°C in the aqueous medium, while an increasing formation of H_2O_2 was observed in the aqueous medium (L). The loss of peroxide in the total system (T) owing to thermal decomposition was small. The consumption of peroxide in the fibrous material and the generation of H_2O_2 in the aqueous medium were both lower for peroxide I than for peroxide II, which indicates that peroxide I is more stable thermally. The decomposition of peroxides on the substrate was promoted largely through the use of ferrous salt or light of $\lambda > 300$ nm to the system of

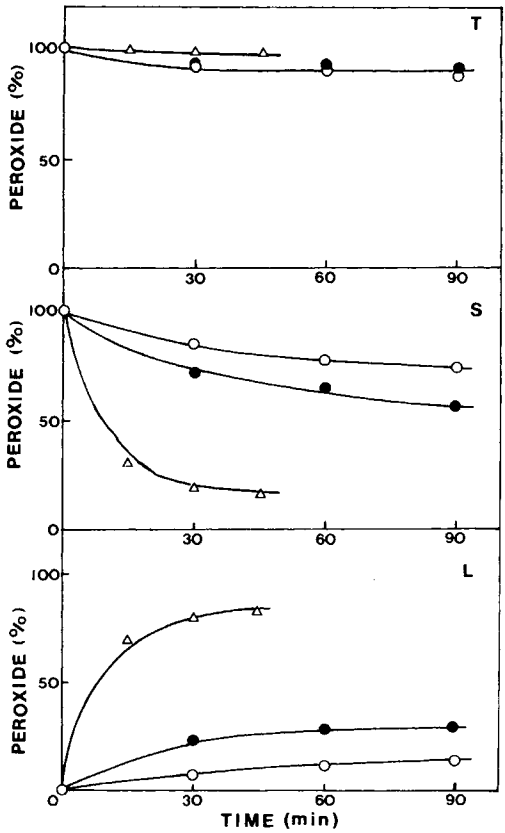


Fig. 2. Thermal decomposition of peroxides on carbonylated cellulose and aldehyde cellulose at 60°C. T, S, and L represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively. Initial amounts of peroxide I (○), peroxide II (●), and aldehyde cellulose peroxide (△) are 28.5, 28.1, and 20.8 meq/100 g cell, respectively.

thermal treatment, as shown in Figure 3. The effect of photoirradiation was especially remarkable, and almost all the peroxides were decomposed after irradiation of 60 min.

As shown in the experiment, peroxides on aldehyde cellulose were more unstable thermally than peroxides I and II; however, the loss of peroxide owing to heat in the total system was rather small for each sample. It was confirmed in the previous studies[1,3] that the formation of peroxides on aldehyde cellulose can be given as eq. (2) and that H_2O_2 is generated from the peroxide of the α-hydroxyhydroperoxide type in aqueous medium according to the reverse reaction of eq. (2):

$$\text{RCHO} + \text{H}_2\text{O}_2 \rightleftharpoons \begin{array}{c} \text{H} \\ | \\ \text{RCOOH} \\ | \\ \text{O} \\ \text{H} \end{array} \qquad (2)$$

where RCHO denotes aldehyde cellulose.

It is known that various types of peroxides[7,8] can be formed by the reaction

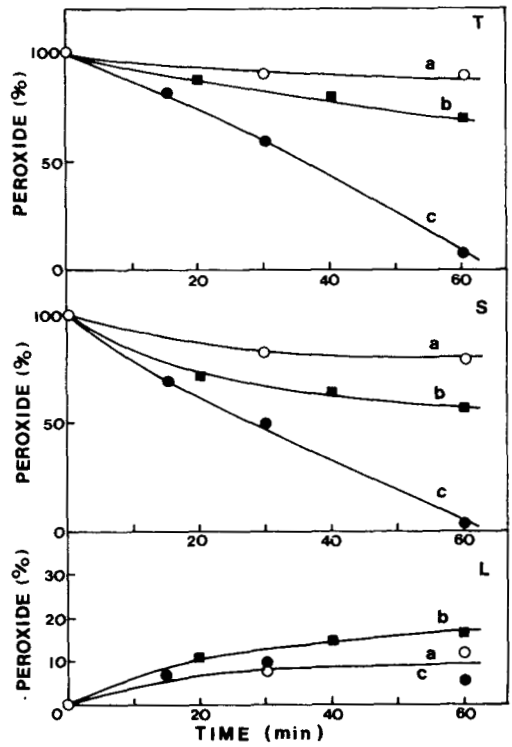


Fig. 3. Decomposition of peroxide I at 60°C owing to heat (a), ferrous ion (b), and light (c). T, S, and L represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively. Initial amount of peroxide I is 28.5 meq/100 g cell.

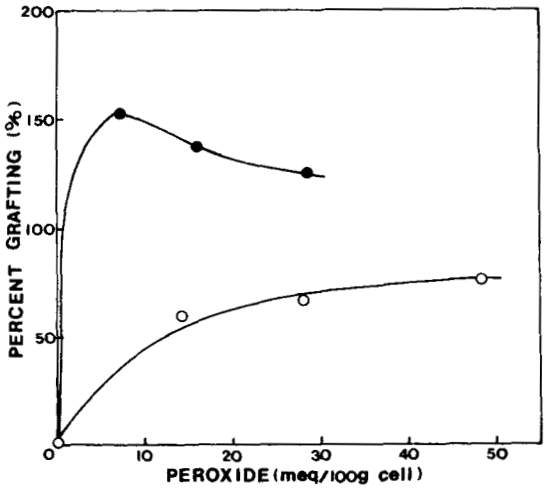


Fig. 4. Thermal grafting of methyl methacrylate by peroxide I (○) and peroxide II (●) at 60°C for 60 min.

between carbonyl compound of low molecular weight and H_2O_2, as shown in eq. (3). First, the carbonyl group reacts with H_2O_2 to form A of the α-hydroxyhydroperoxide type, which may next convert to B or C in the presence of excess H_2O_2 and acid. B and C are capable of participating in the further forma-

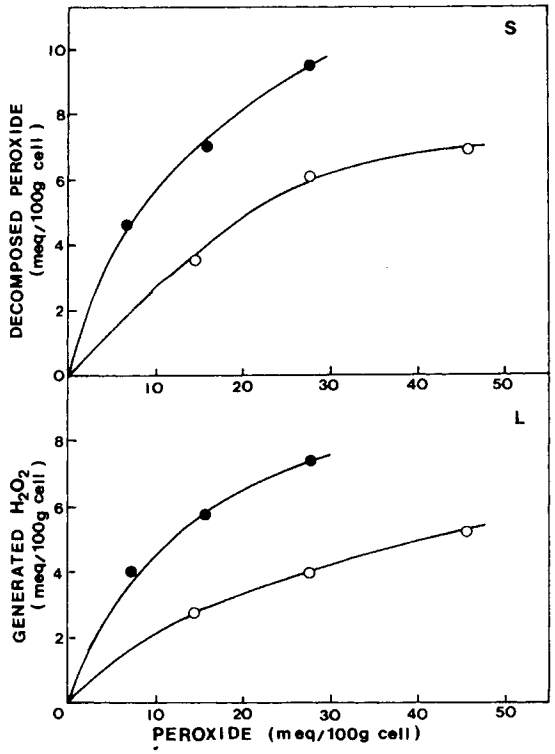
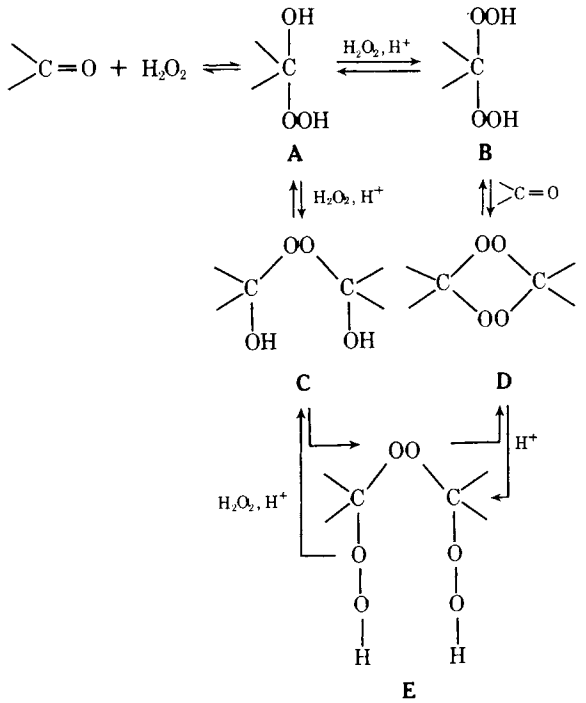


Fig. 5. Thermal decompositions of peroxide I (○) and peroxide II (●) at 60°C for 60 min. S and L represent decomposition of peroxide on the substrate and generation of H_2O_2 in aqueous medium, respectively.



(3)

tion of D- or E-type peroxide, so that acid is required for the formation of B or C, though the formation of A is independent of the presence of acid. Considering the peroxide formation in carbonyl compound of low molecular weight, it may be suggested that peroxide II consists mainly of the A-type peroxide group, while peroxide I may contain peroxide group of the B or C type besides the A type.

The ability of peroxides I and II to initiate thermal grafting was examined, and the results are presented in Figure 4. Both peroxidized samples initiated grafting of methyl methacrylate under conditions of 60°C for 60 min, while carbonylated cellulose itself did not with the same conditions. Peroxide II showed a higher percent grafting than peroxide I did, but the percent grafting of the former decreased slightly as the amount of peroxide group on the sample increased. The graft efficiency was in the range of 70–90% in common with peroxides I and II, which decreased with increase in the amount of peroxide group.

Figure 5 presents the thermal decomposition of peroxides I and II in the system of grafting in the absence of monomer. It was observed again that the levels of decomposition of peroxides on the substrate and generation of H_2O_2 in the aqueous medium are higher for peroxide II than those for peroxide I. These phenomena are considered to be true in the grafting system. Accordingly, the higher activity of peroxide II toward grafting may be ascribed to its easier adaptability of thermal decomposition mentioned above. The mechanisms of graft initiation of cellulose peroxide might be considered to follow the two ways mentioned before:[3] one is through radicals induced by the decomposition of peroxide group on the substrate, and the other is through radicals by the reaction of generated H_2O_2 with the cellulose material.

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