

Formation of Peroxides on Cellulose Derivatives

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Synopsis

Formation of peroxides on cellulose derivatives such as fibrous carboxymethyl cellulose, acrylic acid-grafted cellulose, and aldehyde cellulose with the use of hydrogen peroxide was investigated. Formation of peroxides was observed for each cellulose derivative with the reaction at 25°C and the amount of formation was related closely to the carboxyl or carbonyl contents in the samples. The peroxides were fairly stable in wet samples at low temperatures, but almost all peroxides were decomposed at 60°C. When the cellulose peroxides were warmed with water, hydrogen peroxide separated from the cellulose peroxides into an aqueous medium. The structure of the peroxides formed on the cellulose derivatives is discussed on the basis of the experimental results.

INTRODUCTION

It is known that peroxy groups are introduced into cellulose and its derivatives by UV¹⁻³ and γ -ray⁴ irradiation under oxygen atmosphere. The authors⁵ observed that a certain amount of hydrogen peroxide (H₂O₂) was formed in the system where cellulose in water was irradiated with UV light ($\lambda > 220$ nm) under air atmosphere. It was postulated that an intermediate is formed during the reaction, which decomposed to produce H₂O₂ in the system. The intermediate was believed to be a cellulose peroxide type with a structure of α -hydroxy hydroperoxide. Matsuzaki et al.⁴ reported that acetyl cellulose has the ability to form peroxy group upon γ -ray irradiation, while cellulose itself has not under the same conditions.

On the other hand, Gleason and Stannett⁶ succeeded in introducing hydroperoxide groups into benzyl and ethyl celluloses, which were dissolved in cumen and benzene containing α, α' -azobisisobutyronitrile and warmed at 60°C with air bubbling into the solutions. Cremonesi and D'Angiuro⁷⁻⁹ observed the formation of cellulose peroxide by treating sodium periodate-oxidized cellulose with an acetic acid-H₂O₂ mixture near 0°C. Thus, the introduction of peroxide groups has been shown to be possible for various cellulose derivatives.

Ozonization¹⁰⁻¹² is another known method of introducing peroxide into cellulose materials. However, this method is usually accompanied with severe scission of cellulose chains as the formation of peroxide proceeds. Furthermore detailed information on the stability and structure of the group has not been known.

For developing a novel polymer it seems important to introduce a group with high chemical reactivity into a known polymer. The purpose of this study was to prepare some polymer peroxides starting from cellulose materials. A method of treating with acid-H₂O₂ mixture was employed for the preparation, and the formation, stability, and structure of various cellulose peroxides were examined.

TABLE I
Effect of Solvent on Formation of CMC Peroxide^a

Solvent	Sulfuric acid	Peroxide,
		meq/100 g CMC
Water	absent	4.1
	present	7.5
Methanol	absent	3.8
	present	6.7
Acetic acid	absent	4.0
	present	15.8
Acetic anhydride	absent	4.2
	present	14.1
N,N-Dimethylformamide	absent	3.9
	present	6.6

^a Concentration of hydrogen peroxide, 0.4 mole/l.; concentration of sulfuric acid, 0.5*N*; liquor ratio (solvent, ml/CMC sample, g), 40; D.S. of sample, 0.42; time, 3 hr; temp., 25°C.

EXPERIMENTAL

Cellulose Derivatives

Fibrous carboxymethyl cellulose (CMC)¹³ with degrees of substitution (D.S.) of 0.15 on 0.42 was prepared by treating a commercial dissolving pulp from softwoods (NDP) with monochloroacetic acid and alkali. Graft copolymerization of acrylic acid (AA) on NDP was carried out using ceric salt^{14,15} as initiator to obtain AA-grafted cellulose. The AA-grafted cellulose was washed a few times with 0.1*N* hydrochloric acid to remove ceric salt¹⁶ from the sample and then used for further experiments. NDP was treated with an aqueous solution of various

TABLE II
Effect of Various Factors on Formation of CMC Peroxide^a

Factor	Time, hr	Temp., °C	Concn. of hydrogen peroxide, mole/l.	Concn. of sulfuric acid, <i>N</i>	Liquor ratio	Peroxide, meq/100 g CMC	
						D.S. = 0.15	D.S. = 0.42
Time	1	25	0.4	0.5	40	4.6	9.3
	3					7.0	15.5
	8					7.1	15.9
	18					7.2	16.1
	24					7.0	16.1
Temperature	3	0	0.4	3.0	40	8.1	21.2
		25				8.3	21.8
		40				8.3	20.4
Concn. of sulfuric acid	3	25	0.4	0	40	—	4.1
				0.5		—	15.5
				1.1		—	18.0
				2.0		—	20.0
				2.9		—	21.3
Concn. of hydrogen peroxide	3	25	0	3.9	20	0	0
			2.1			6.5	10.0
			5.2			10.5	30.0
			8.3			22.0	53.5

^a Solvent, acetic acid.

TABLE III
Effect of Kind of Acid on Formation of CMC Peroxide^a

Acid	Concn. of acid, N	Concn. of hydrogen peroxide, mole/l.	Peroxide, meq/100 g CMC		
			D.S. = 0	D.S. = 0.15	D.S. = 0.42
None	0	10.1	0	5.7	10.9
H ₂ SO ₄	3.9	8.3	0	21.9	54.7
CH ₃ SO ₃ H	4.6	7.2	0	20.8	59.4
<i>p</i> -C ₆ H ₅ SO ₃ H	2.1	7.2	0	13.8	31.7

^a Temperature, 25°C; time, 3 hr.

concentrations of periodic acid (liquid-to-material ratio 100:1) at 45°C for 60 min to obtain oxidized samples, which were termed aldehyde cellulose. Oxidation with periodic acid is a popular method for introducing aldehyde groups into cellulose.^{17,18} The hydroxylamine method¹⁹ was applied to the determination of carbonyl content of the sample.

Formation of Cellulose Peroxides

In general cases, 0.50 g cellulose derivative, 10 ml aqueous H₂O₂ (35%), and 2 ml concentrated sulfuric acid were placed in a flask adjusted at 25°C for 3 hr. In the experiments of Tables I and II, an additional 10 ml of solvent was used to the above system. The influence of H₂O₂ concentration was examined in the systems using 10 ml acetic acid-H₂O₂ of various concentrations. The sample after reaction was washed with about 1 liter ice water followed by immediate determination of peroxide.

When the wet CMC sample was dried in a vacuum desiccator, the peroxide component was lost to a large extent. On the other hand, the peroxide on aldehyde cellulose was fairly stable and most of the peroxide remained as it was after drying.

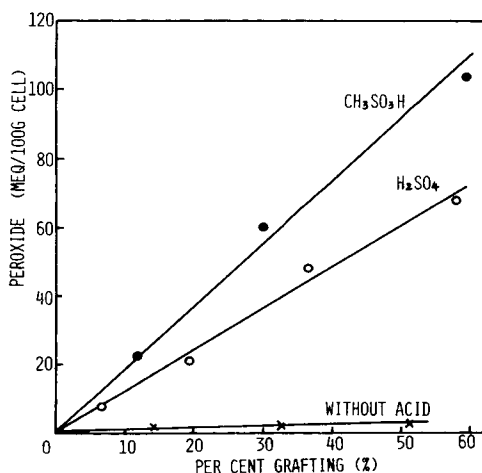


Fig. 1. Formation of peroxide on acrylic acid-grafted cellulose. Acrylic acid-grafted cellulose was treated at 25°C for 3 hr with 8.3 moles/l. aqueous solution of hydrogen peroxide. Concentrations of methanesulfonic acid and sulfuric acid were 4.6 and 3.9N, respectively.

Determination of Peroxide

A flask containing 0.50 g cellulose peroxide and 40 ml isopropyl alcohol, to which 10 ml isopropyl alcohol solution with saturated potassium iodide and 2 ml glacial acetic acid was added, was refluxed at 85°C for 15 min. After being cooled to room temperature, the liberated iodine was titrated with 0.01*N* sodium thiosulfate.

Thermal Decomposition of Cellulose Peroxides

A flask containing 0.50 g cellulose peroxide and 20 ml water was allowed to stand at 40°C for a given duration for thermal decomposition. After the treatment, the content was filtered to separate the fibrous part from the aqueous part. The amount of peroxide was determined for each part.

RESULTS AND DISCUSSION

Formation of Cellulose Peroxides

CMC sample was treated with a H₂O₂ mixture resulting in a product which is capable of isolating iodine from potassium iodide solution. The effect of solvent on the formation of peroxide on CMC is shown in Table I. The amount of peroxide group formed in the system without using sulfuric acid were almost the same, irrespective of the kind of solvent employed. The formation of peroxide for each solvent system increased with the use of sulfuric acid, which could be said to be a necessary factor in the formation of peroxide on CMC. The highest amount of peroxide was attained in the system using acetic acid. Effects of the reaction time, temperature, and concentration of sulfuric acid in the system using acetic acid were examined, and the results are summarized in Table II. The amount of peroxide reached nearly a maximum within the range of 1 to 3 hr, and

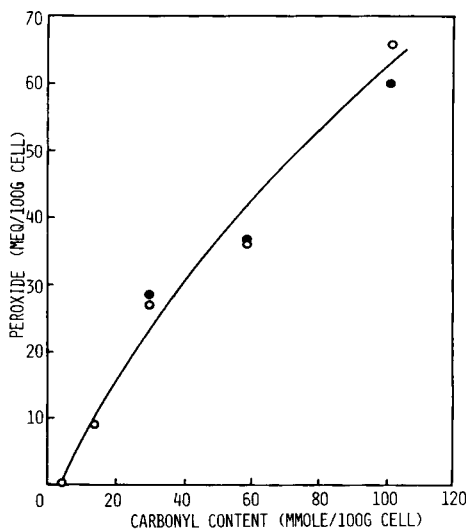


Fig. 2. Formation of peroxide on aldehyde cellulose in the presence (O) or absence (●) of sulfuric acid (3.9 *N*). Aldehyde cellulose was treated at 25°C for 3 hr with 8.3 mole/l. aqueous solution of hydrogen peroxide.

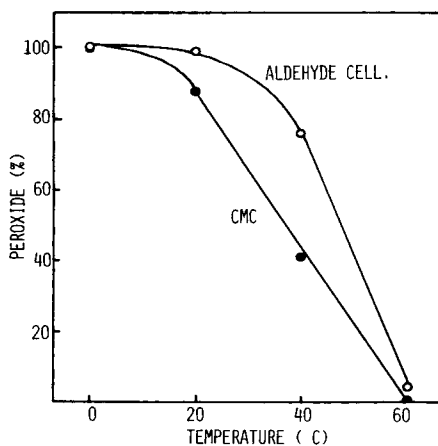


Fig. 3. Stability of cellulose peroxides. Initial amounts of peroxide were 47.5 and 42.8 meq/100 g cell. for CMC and aldehyde peroxides, respectively. Wet sample was maintained at given temperatures for 3 hr.

almost no difference was observed within the range of 0° to 40°C. Therefore, it can be said that a low temperature is not always required for peroxide formation on CMC with the acid-H₂O₂ system, indicating that the reaction at room temperature is rather favorable for an easy formation of peroxide. As the concentration of sulfuric acid increased, the formation of peroxide showed a tendency to increase gradually. It seemed that no marked scission of main chain of the cellulose material took place in the concentration range of sulfuric acid used, as the CMC peroxide prepared in this way was still fibrous.

As shown in Table II, it was found that a higher concentration of H₂O₂ was advantageous for the formation of CMC peroxide. Higher D.S.s of CMC sample were found to be effective. Organic acid such as methanesulfonic acid and *p*-toluenesulfonic acid as well as inorganic acid were found effective catalysts for the formation of CMC peroxide, which is shown in Table III. Thus, it is clear that the presence of acid, the concentration of H₂O₂, and the D.S. of CMC are important factors for the formation of peroxide. With an adequate combination of these factors, an introduction of peroxide group into CMC material up to about 30% equivalent mole carboxyl content of the sample was achieved in this study.

Results for AA-grafted cellulose are shown in Figure 1. A considerable amount of peroxide was formed proportional to the percent grafting of the sample with the aid of acids, while the formation of peroxide was very low in the absence of acid. This tendency was quite similar to the case of CMC sample, which contains carboxyl group in the substrate. Consequently, the formation of peroxide seems to be caused by the reaction of carboxyl group in AA-grafted cellulose.

TABLE IV
Comparison of Peroxide Content Before and After Drying^a

Cellulose peroxide	Peroxide, meq/100 g cell.	
	Before drying	After drying
CMC	45.8	0
Aldehyde cellulose	36.5	23.1

^a Cellulose peroxides were dried under reduced pressure at 20°C for 24 hr.

As seen in Figure 2, the peroxide was also introduced into aldehyde cellulose with the use of a sulfuric acid-H₂O₂ mixture. The higher the carbonyl content of the sample, the higher amount of peroxide observed. Contrary to the cases of CMC and AA-grafted cellulose, the formation of peroxide on aldehyde cellulose was not influenced by the presence of sulfuric acid in the reaction system.

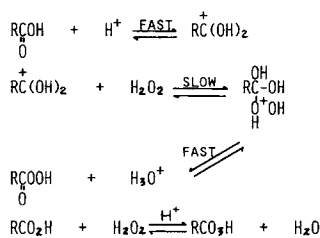
Stability of Cellulose Peroxides

Figure 3 shows the change of peroxide content by letting cellulose peroxide samples stand in the wet state for 3 hr at given temperatures. The ordinate indicates the percentage of the peroxide content after the treatment. The peroxides on CMC and aldehyde cellulose were reasonably stable at 0°C but became unstable as the temperature rose and were completely decomposed at 60°C. The peroxide on aldehyde cellulose was more stable than that on CMC, and about 75% of the initial amount remained in the sample after standing for 3 hr at 40°C.

Table IV shows results of the thermal decomposition of peroxide in aqueous medium. The peroxide on CMC decreased in amount gradually with lapse of time while formation of H₂O₂ was observed in the aqueous medium. The total amount of decomposed peroxide was indicated as the difference between the initial amount and the sum of the amounts remaining in the sample and formed in the aqueous medium. The value reached about 50% of the initial amount after 90 min of decomposition. In case of the peroxide on aldehyde cellulose, the estimated amount of peroxide lost in the sample was almost equal to that formed in the aqueous medium, so that the total loss of peroxide was very small for aldehyde cellulose.

Thus, it was proved that the peroxides on CMC and aldehyde cellulose have the property of releasing H₂O₂ from the substrates by thermal decomposition in aqueous medium. However, there was a clear difference in the resistance to thermal decomposition between the two peroxides, suggesting that a different structure should be assigned to each.

1. CMC AND AA-GRAFTED CELLULOSE



2. ALDEHYDE CELLULOSE

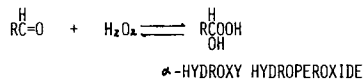


Fig. 4. Formation of cellulose peroxides.

TABLE V
Thermal Decomposition^a of Peroxide on Cellulose Materials in Aqueous Media at 40°C

Cellulose peroxide	Time, min	Peroxide, meq/100 g cell.		
		Sample part	Water part	Total system
CMC	0	49.6	0	49.6
	30	33.3	4.6	37.9
	90	9.9	11.7	21.6
Aldehyde cellulose	0	46.0	0	46.0
	30	37.2	8.5	45.7
	90	25.5	18.7	44.2

^a Cellulose peroxide, 0.5 g; water, 20 ml.

Structure of Cellulose Peroxides

As the formation of peroxide was related to the D.S. of CMC and the percent grafting of AA-grafted cellulose, the carboxyl group in the samples is believed to contribute to the formation of peroxide (Table III and Fig. 1). It is well known that a carboxyl group in low molecular weight compounds^{20,21} generally reacts with H₂O₂ in the presence of acid to form a peroxide of the peracid type according to eqs. (1) and (2), as shown in Figure 4. The formation of peroxide on CMC and AA-grafted cellulose was markedly promoted by the use of acids (Table III and Fig. 1). It is therefore natural to consider that the carboxyl group in both samples can also be converted to a peroxide of the peracid type according to reactions similar to eqs. (1) and (2). Takagi²² observed that peracid-type resins were obtainable when carboxylic acid-type ion exchange resins were treated with H₂O₂ in the presence of acid.

On the other hand, it is supposed that the aldehyde group in the sample has an ability to form a peroxide in the case of aldehyde cellulose, where the peroxide type of α -hydroxy hydroperoxide seems to be most probable according to eq. (4). Aldehyde and ketone compounds²¹ of low molecular weight have been observed to react with H₂O₂ resulting in such a type of peroxide.

As seen in Table IV, warming cellulose peroxides in water resulted in the formation of H₂O₂ in the aqueous medium. This is based on the reverse reaction of eqs. (3) and (4). The reaction was more conspicuous for the α -hydroxy hydroperoxide than for the peracid. It was concluded that the structure of the peroxide introduced into cellulose derivatives by treating them with an acid-H₂O₂ mixture should be either of the peracid or α -hydroxy hydroperoxide type.

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