

# Formation of Peroxide on Poly(vinyl Alcohol) and Its Characteristics

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## Synopsis

Peroxide formed on poly(vinyl alcohol) (PVA) fiber due to hydrogen peroxide ( $H_2O_2$ ) treatment was examined in terms of formation conditions, decomposition behavior, and function of graft initiation. By treating aqueous sodium hypochlorite- or periodic acid-oxidized PVA with  $H_2O_2$ , formation of peroxide on the substrates was observed which was not on unoxidized PVA. The amount of peroxide increased proportionally to the carbonyl content of the sample, the level of which was higher for NaClO- than for  $HIO_4$ -oxidized sample. The peroxide was decomposed by warming the sample in water to separate the  $H_2O_2$ . The reaction was easier for the  $HIO_4$ - than the NaClO-oxidized sample. The structure of peroxide was assumed to be the  $\alpha$ -hydroxy hydroperoxide type for both NaClO- and  $HIO_4$ -oxidized samples, which should be distinguished in respect to the location of the group. It is inferred that the peroxide on the NaClO-oxidized sample is situated along the chain of PVA and that the one on the  $HIO_4$ -oxidized sample is located mainly at the end of the chain. It was also observed that the peroxides formed on NaClO- and  $HIO_4$ -oxidized samples are capable of initiating graft copolymerization of methyl methacrylate by means of heat or light.

## INTRODUCTION

In previous papers<sup>1,2</sup> the introduction of peracid- and hydroxy hydroperoxide-type peroxides on carbonyl- and aldehyde-containing celluloses by means of hydrogen peroxide ( $H_2O_2$ ) treatment was reported. On the other hand, the authors<sup>3</sup> observed the formation of  $H_2O_2$  in aqueous poly(vinyl alcohol) (PVA) solution under UV irradiation in the presence of oxygen, the intermediate of which was supposed to be an  $\alpha$ -hydroxy hydroperoxide group formed on PVA. Niki et al.<sup>4</sup> also reported the formation of peracid as well as  $H_2O_2$  in UV-irradiated aqueous PVA solution.

In the present study, PVA was employed as a substance related to cellulose, and the factors affecting the formation of peroxide due to  $H_2O_2$  treatment were examined. The resulting peroxide was investigated in terms of stability, decomposition, and graft initiation.

## EXPERIMENTAL

### Materials

Commercial Vinyon fiber (4–5 denier) was cut to a length of 1 cm and extracted with boiling water; it was named unoxidized PVA sample. Oxidized PVA samples of various carbonyl contents were prepared by treating the unoxidized sample with aqueous solutions of periodic acid ( $HIO_4$ ) (5–40 mmole/liter) or alkaline sodium hypochlorite (NaClO) at 50°C for 60 min (PVA/solution = 1

g/100 ml). The carbonyl content of the samples was determined by hydroxylamine method.<sup>5</sup>

### Formation of Peroxide

A conical flask containing 0.5 g PVA sample and 10 ml 35% aqueous H<sub>2</sub>O<sub>2</sub> solution was maintained at given temperatures for peroxidation reaction. Thereafter, the product was washed with 1 liter ice water and the peroxide content of samples was determined by iodometry.<sup>1</sup>

### Decomposition of Peroxide

Thermal decomposition was performed in a system containing 0.5 g peroxide sample and 20 ml water. After keeping the system at a given temperatures, the fiber part was separated from the water. The amount of peroxide in each part was determined. The effect of ferrous salt on the decomposition was examined employing 20 ml of a 1 mmole/liter aqueous ammonium ferrous sulfate solution. Photodecomposition was carried out in a Pyrex glass system at 40°C.

### Grafting

For thermal grafting, a Pyrex glass tube containing 0.5 g peroxide sample, 20 ml water, and 2 ml methyl methacrylate (MMA) was swept out with nitrogen and maintained at 60°C. For photografting, the above system was irradiated with UV light at 40°C. The product was washed with water and extracted with acetone to remove homopolymers. Percent grafting and graft efficiency determinations were as those mentioned in the previous paper.<sup>6</sup>

TABLE I  
Effect of Various Factors on Peroxide Formation on PVA<sup>a</sup>

Factor	Time, hr	Temperature, °C	Concentration of hydrogen peroxide, mole/liter	Peroxide, mgq/100 g PVA	
				NaClO <sub>4</sub> -oxidized PVA	HIO <sub>4</sub> -oxidized PVA
Time	1	25	9.4	17.6	11.2
	3	25	9.4	18.1	12.0
	5	25	9.4	18.2	12.1
	7	25	9.4	17.7	12.5
Temperature	3	0	9.4	11.0	8.1
	3	25	9.4	18.1	12.0
	3	50	9.4	18.0	12.8
Hydrogen peroxide	3	25	1.0	12.4	9.4
	3	25	2.1	14.2	10.0
	3	25	5.1	15.3	10.5
	3	25	9.4	18.1	12.0

<sup>a</sup> Liquor ratio, 20; solvent, acetic acid; Carbonyl content (mmole/100 g PVA): NaClO<sub>4</sub>-oxidized PVA, 18.0; HIO<sub>4</sub>-oxidized PVA, 21.7.

### Photoirradiation

Irradiations with a high-pressure mercury lamp (400 W) were carried out in a Riko Rotary Photochemical Reactor RH400-10W, around which Pyrex tubes were set to rotate.

## RESULTS AND DISCUSSION

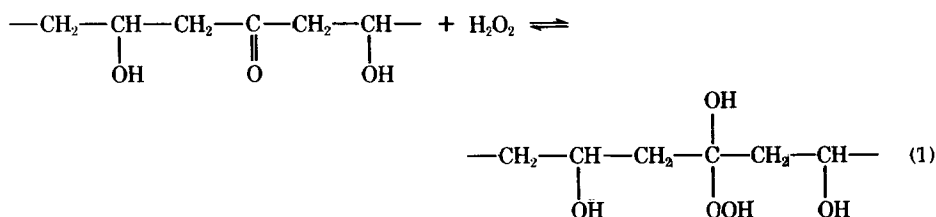
### Formation of Peroxide

Oxidized PVA containing carbonyl groups introduced by NaClO and HIO<sub>4</sub> yielded peroxide groups by a treatment with H<sub>2</sub>O<sub>2</sub>, whereas unoxidized PVA did not. The effects of reaction time, temperature, and concentration of H<sub>2</sub>O<sub>2</sub> are summarized in Table I. The amounts of peroxide formed in the reaction reached their maximum levels within 1–3 hr, which increased with increasing temperature of the reaction. The concentration of H<sub>2</sub>O<sub>2</sub> also affected the formation of peroxide.

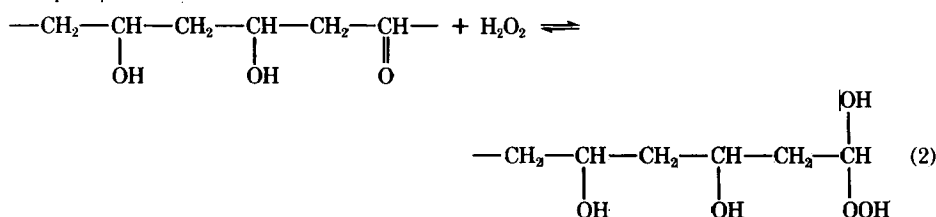
The relationship between carbonyl content of oxidized PVA sample and amount of peroxide formed is shown in Figure 1. In the figure it is clear that the formation of peroxide increases with increasing carbonyl content of the sample. It is certain therefore that the carbonyl group of the sample participates in the formation of peroxide on PVA. However, the amount of peroxide for NaClO-oxidized PVA indicated somewhat higher levels as compared with that for HIO<sub>4</sub>-oxidized PVA, which seems to suggest a difference in the oxidized states of the two types of oxidized PVAs.

It is generally known that aldehyde and/or ketone types of carbonyl groups can be introduced on PVA substrates by ordinary oxidation treatments. By treatment with NaClO solution<sup>7</sup> ketone is reported to be the main group introduced on the PVA chain. On the other hand, the HIO<sub>4</sub>-oxidized PVA supposedly bears the aldehyde group at the chain end due to the oxidative cleavage at the small amount of 1,2-glycol group<sup>8</sup> contained in the PVA sample. Ikada et al.<sup>9</sup> reported the formation of aldehyde groups during oxidation of PVA with ceric salt. It is therefore naturally assumed that the reactions of PVA with H<sub>2</sub>O<sub>2</sub> follow eqs. (1) and (2):

NaClO-Oxidized PVA:



HIO<sub>4</sub>-Oxidized PVA:



Low molecular weight aldehyde and ketone compounds<sup>10</sup> are known to yield various types of peroxide by a treatment with  $H_2O_2$ . We<sup>2</sup> noted the formation of  $\alpha$ -hydroxy hydroperoxide-type peroxide at the aldehyde group introduced on cellulose substrate by  $H_2O_2$  treatment. Therefore, eqs. (1) and (2) signify the formation of peroxide along the PVA chain and at the end of chain for  $NaClO$ - and  $HIO_4$ -oxidized PVAs, respectively.

### Stability of Peroxide

Table II shows the stability of peroxide formed on  $NaClO$ -oxidized PVA. In the wet state, no large change in the peroxide content was recorded after three to six days of standing at  $5^\circ C$ . However, the content was reduced to about 74% of that of the starting material after standing for six days at room temperature. A wet PVA peroxide sample yielded one in the dry state with some loss in peroxide content by drying under reduced pressure. The dry sample lost about 37% of the initial peroxide content by standing 5 hr at  $40^\circ C$ , whereas only a small loss was observed after five days at  $5^\circ C$ . Thus, the peroxide on PVA proved to be fairly stable at a low temperature and also to be available in either wet or dry state as the occasion calls.

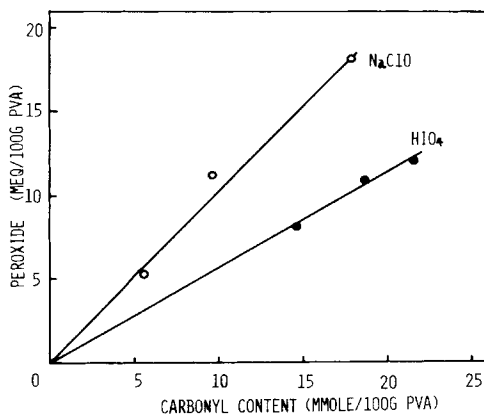


Fig. 1. Formation of peroxides on  $NaClO$ - and  $HIO_4$ -oxidized PVA fibers. Time, 3 hr; temperature,  $25^\circ C$ ; concentration of hydrogen peroxide, 9.4 mole/liter.

TABLE II  
Stability of Peroxide on  $NaClO$ -Oxidized PVA Fiber

Sample	Temperature, $^\circ C$	Time, days	Peroxide meq/100 g PVA
Wet state	—	0	18.6
	5	3	18.7
	5	6	18.0
	room temp.	6	13.7
Dry state	—	0	16.6
	5	5	16.8
	room temp.	5	15.2
	40	5	10.4

### Decomposition of Peroxide

Figure 2 shows the thermal decomposition of the peroxide on NaClO-oxidized PVA. The peroxide content of the fiber part decreased with elapse of time, whereas the formation of  $H_2O_2$  took place in the water part, which increased as the temperature was raised. However, the difference between the total sums of peroxide in systems before and after the thermal treatment was rather small. When methanol or acetone was used instead of water as a medium, the amount of  $H_2O_2$  formed was decreased from 50% to 10% by thermal treatment of  $40^\circ C$  for 60 min. Thus, it is clear that part of the peroxide on PVA was decomposed to form  $H_2O_2$  by the warming in water.

The thermal decomposition of peroxide groups is generally known to proceed according to eq. (3):



The reverse reactions of eqs. (1) and (2) forming  $H_2O_2$  might also be added in this case. Similar phenomena were observed for peroxides of carboxymethyl cellulose<sup>6</sup> and and aldehyde cellulose.<sup>2</sup>

The effects of UV irradiation and ferrous salt on the decomposition of the peroxide are shown in Figure 3. By adding 1 mmole/liter ferrous salt to the system standing at  $60^\circ C$ , the total amount of peroxide was decreased sharply. A similar phenomenon was also observed in the system irradiated with light of  $\lambda > 300$  nm. Ferrous salt seems to contribute to the redox-type decomposition, and light seems to accelerate the reaction of eq. (3). In a system employing both ferrous salt and UV irradiation, the decomposition of  $H_2O_2$  itself seems to be accelerated sharply, too.

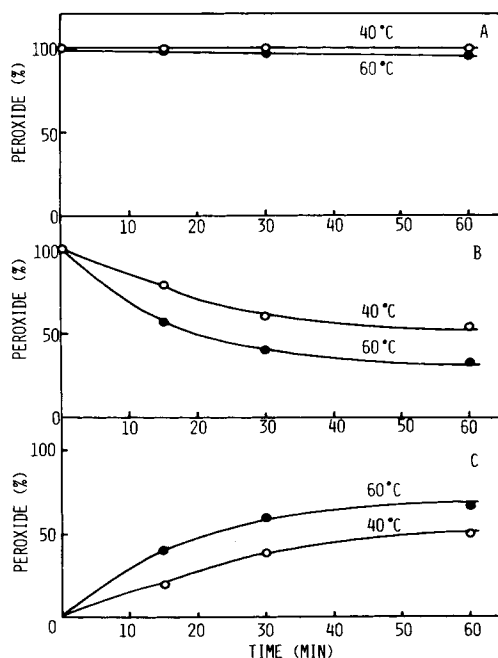


Fig. 2. Thermal decomposition of peroxide in aqueous medium. NaClO-oxidized PVA (16.4 meq peroxide/100 g PVA). A, B, and C represent amount of peroxide in total system, in fiber part, and in water part, respectively.

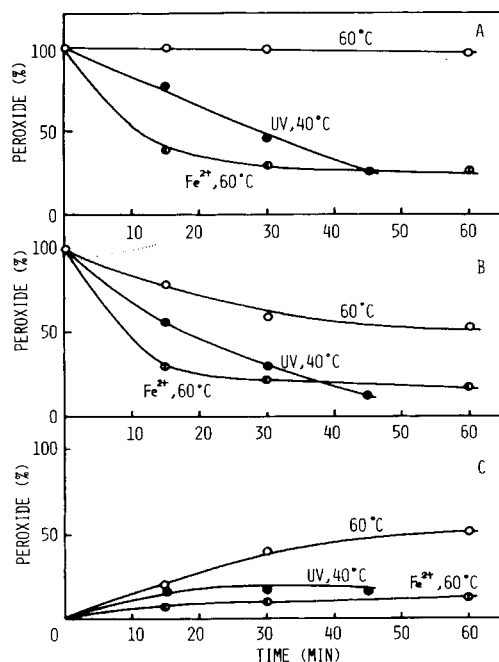


Fig. 3. Decomposition of peroxide in aqueous medium. NaClO-oxidized PVA (11–16 meq peroxide/100 g PVA); concentration of ferrous ion, 1 mmole/liter; UV;  $\lambda > 300$  nm. A, B, and C represent amounts of peroxide in total system, in fiber part, and in water part, respectively.

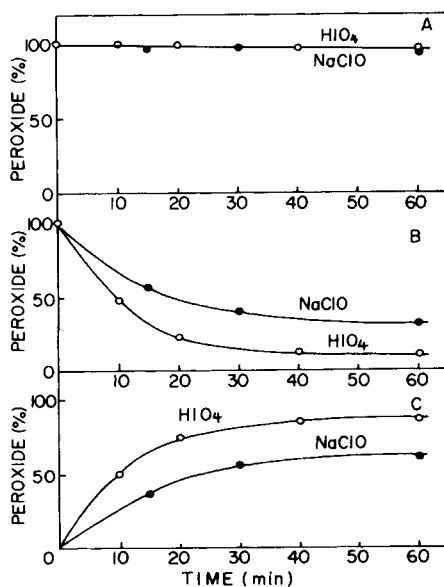


Fig. 4. Comparison of thermal decomposition of peroxides on NaClO- and HIO<sub>4</sub>-oxidized PVAs. Peroxide (meq/100 g PVA); NaClO-oxidized PVA, 11.5; HIO<sub>4</sub>-oxidized PVA, 11.4. A, B, and C represent amounts of peroxide in total system, in fiber part, and in water part, respectively.

In Figure 4, thermal decompositions of peroxides on NaClO- and HIO<sub>4</sub>-oxidized PVA samples are compared. The peroxide on NaClO-oxidized PVA was decomposed more easily than that on HIO<sub>4</sub>-oxidized PVA, resulting in a higher formation of H<sub>2</sub>O<sub>2</sub> in water for the former sample. It is therefore conceivable that the reverse reaction of eq. (1) takes place more readily than that of eq. (2).

### Grafting

Results of grafting of MMA on PVA peroxide are shown in Tables III and IV. The peroxide was found to have an ability to initiate grafting, as there resulted always a higher percent grafting in any of the thermal, redox, and photochemical initiating systems as compared with the sample without peroxide. In the comparison of oxidized PVAs, the HIO<sub>4</sub>-oxidized one yielded a relatively lower percent grafting and graft efficiency than the NaClO-oxidized samples.

In the grafting system, free H<sub>2</sub>O<sub>2</sub> does exist, which originates from PVA peroxide following the reverse reactions of eqs. (1) and (2). H<sub>2</sub>O<sub>2</sub> is often used as an initiator in the case of grafting on cellulose<sup>11-13</sup> and PVA<sup>14</sup> with the coexistence of ferric salt. Therefore, the liberated H<sub>2</sub>O<sub>2</sub> as well as the peroxide on PVA can be considered as an effective initiator in the grafting system of the present study.

Figure 5 shows the results of thermal grafting of MMA on NaClO-oxidized PVA in various initiating systems. The thermal grafting on NaClO-oxidized

TABLE III  
Grafting of MMA Initiated by Peroxide on NaClO-Oxidized PVA<sup>a</sup>

System	Temperature, °C	Ferrous ion	Peroxide, meq/100 g PVA	Percent grafting, %	Graft efficiency, %
Thermal grafting	60	without	0	35.5	94.6
	60	without	18.5	140.0	95.5
	60	with	0	95.0	81.3
	60	with	17.5	185.0	76.6
Photo-grafting	40	without	0	184.3	78.1
	40	without	15.6	212.3	74.7

<sup>a</sup> Grafting was carried out for 60 min. Concentration of ferrous ion, 1.0 mmole/liter.

TABLE IV  
Grafting of MMA Initiated by Peroxide on HIO<sub>4</sub>-Oxidized PVA<sup>a</sup>

System	Time, min	Temperature, °C	Ferrous ion	Peroxide, meq/100 g PVA	Percent grafting, %	Graft efficiency, %
Thermal grafting	150	60	without	0	16.2	69.8
	150	60	without	11.8	46.7	72.4
	60	60	with	0	35.8	81.9
	60	60	with	10.7	68.5	89.4
Photo-grafting	60	40	without	0	17.8	22.4
	60	40	without	10.7	46.6	47.4

<sup>a</sup> Concentration of ferrous ion, 1 mmole/liter.

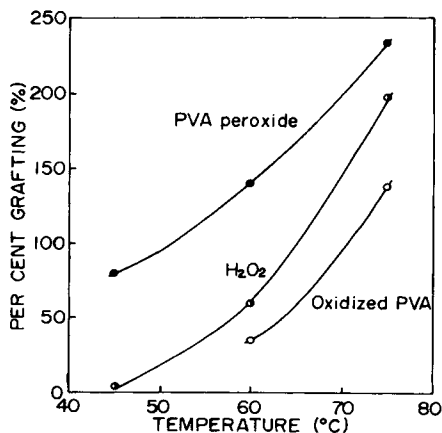


Fig. 5. Thermal grafting of MMA on NaClO-oxidized PVA fiber in various initiation systems. Polymerization time, 60 min; peroxide content of sample, 18.5 meq/100 g PVA; amount of H<sub>2</sub>O<sub>2</sub> in the system, 20.3 meq/100 g PVA.

PVA<sup>15</sup> was initiated irrespective of the presence of initiator, which was promoted with the use of H<sub>2</sub>O<sub>2</sub> in the system. However, a higher percent grafting was attained by PVA peroxide as compared with a system of NaClO-oxidized PVA and H<sub>2</sub>O<sub>2</sub> with the same mole equivalent of the peroxide as the former sample. PVA peroxide can therefore be said to initiate grafting easier than H<sub>2</sub>O<sub>2</sub> existing in the system.

It was already shown in Figure 4 that peroxide on HIO<sub>4</sub>-oxidized PVA is decomposed easier than that on NaClO-oxidized PVA. In the grafting system the same tendency may also be true. Consequently, the lower percent of grafting of HIO<sub>4</sub>-oxidized PVA should mainly be attributed to the easier decomposition of peroxide on the sample.

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