

Decomposition of Peroxide on Carboxymethyl Cellulose and Its Ability to Initiate Graft Copolymerization

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Synopsis

The decomposition of the peroxide group on fibrous carboxymethyl cellulose (CMC) and its ability to initiate graft copolymerization were investigated. The peroxide on CMC liberated hydrogen peroxide when the sample was heated in an aqueous medium. The decomposition of the peroxide was markedly increased by the use of ferrous salt and the irradiation with light of $\lambda > 300$ nm. The grafting of methyl methacrylate on CMC peroxide was initiated by heating or irradiating with light, where the rate of grafting and the reciprocal of the average molecular weight of grafts in general were proportional to the square root of the peroxide content of the sample. The peroxide content of the sample was related closely to the number of grafts in initiation. The number was estimated as 17 times for thermal initiation and 6 times for photoinitiation at the maximum values. The CMC peroxide showed a marked activity toward photografting of acrylamide, acrylic acid, acrylonitrile, and vinyl acetate on the substrate.

INTRODUCTION

A large number of studies¹⁻¹⁵ on grafting induced by peroxide groups on polymers have been reported by various methods: irradiation with light^{1,2} and γ -ray³⁻⁵ under oxygen atmosphere, ozonization,⁶⁻¹¹ and auto-oxidation^{12,13} initiated by radical initiators such as α, α' -azobisisobutyronitrile and benzoyl peroxide.

The authors¹⁶ succeeded in introducing a peracid-type peroxide into fibrous carboxymethyl cellulose (CMC) by treating the substrate with an acid-hydrogen peroxide (H_2O_2) mixture. In the present paper, the decomposition of the peroxide on CMC and its ability to initiate graft copolymerization were investigated to clarify detailed features of CMC peroxide.

EXPERIMENTAL

Materials

Commercial pulp from softwoods was treated with monochloroacetic acid, resulting in a fibrous CMC sample¹⁷ with a degree of substitution of 0.42. Ferrous ammonium sulfate of reagent grade was used as ferrous salt. Methyl methacrylate (MMA), acrylic acid, acrylamide, acrylonitrile, and vinyl acetate were purified before use.

Preparation of CMC Peroxide

A flask containing 1.00 g CMC sample, 4 ml concentrated sulfuric acid, and 16 ml 35% aqueous solution of H_2O_2 was maintained at $25^\circ C$ for 3 hr. Thereafter, the product was washed with 2 liters of ice water to obtain a CMC peroxide in the wet state. The peroxide content of the sample was determined iodometrically.¹⁶

Decomposition of Peroxide on CMC

Thermal decomposition was carried out in a system consisting of 0.50 g CMC peroxide and 20 ml water or methanol at a given temperature. After the reaction, the content was filtered to separate the fibrous material from the aqueous medium, and then the amounts of peroxide in each part were determined. The effect of ferrous salt on the thermal decomposition of peroxide on CMC 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 CMC peroxide and 20 ml water was exposed to a high-pressure mercury lamp.

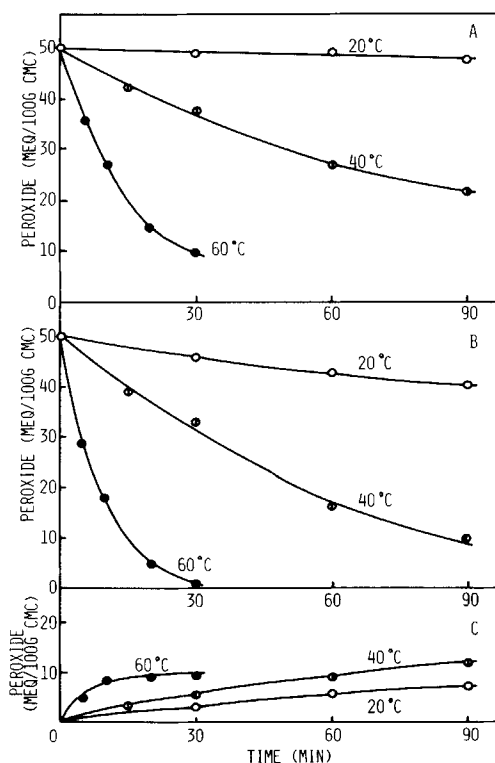


Fig. 1. Thermal decomposition of peroxide on CMC in aqueous medium. A, B, and C represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively.

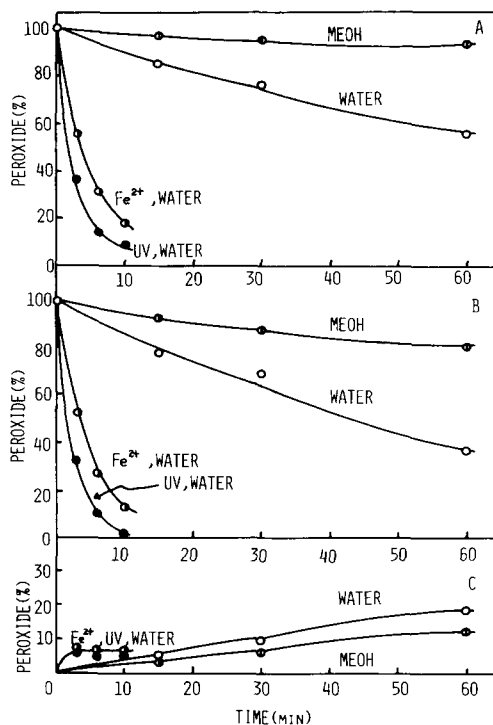


Fig. 2. Decomposition of peroxide on CMC at 40°C. A, B, and C represent amounts of peroxide in total system, in fibrous material, and in aqueous medium, respectively.

Grafting

Thermal grafting was carried out under nitrogen in a Pyrex glass tube containing 0.50 g CMC peroxide, 20 ml water, and 2 ml monomer (2.0 g of acrylamide) at 60°C. Photografting was carried out at 30°C, irradiating the above system with a high-pressure mercury lamp. Polymer products were washed with water and extracted with acetone, *N,N*-dimethylformamide, and hot water to remove homopolymers. The percent grafting, the graft efficiency, and the total conversion of monomer were defined by the following equations:

$$\text{percent grafting (\%)} = \frac{\text{weight of grafts}}{\text{weight of CMC peroxide}} \times 100$$

$$\text{graft efficiency (\%)} = \frac{\text{weight of grafts}}{\text{weight of homopolymer and grafts}} \times 100$$

$$\text{total conversion (\%)} = \frac{\text{weight of homopolymer and grafts}}{\text{weight of monomer}} \times 100$$

Determination of Average Molecular Weight of Grafted Poly(methyl Methacrylate)

Graft copolymer was treated with 72% sulfuric acid¹⁸ to isolate poly(MMA) as grafts. The average molecular weight of the grafts was determined by the viscosity of benzene solution at 30°C using the equation proposed by Fox et al.¹⁹ The molar number of grafts per 100 g CMC peroxide calculated from the percent

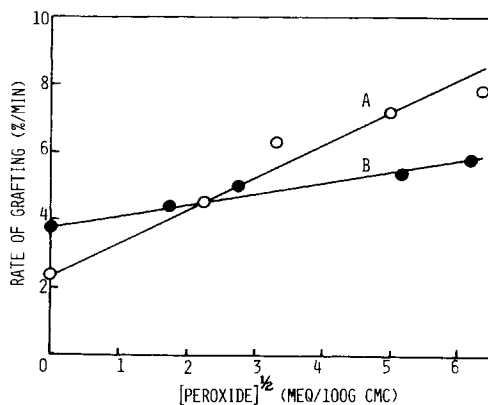


Fig. 3. Relationship between rate of grafting and peroxide content of sample in thermal grafting of MMA at 60°C (A) and photografting of MMA at 30°C (B).

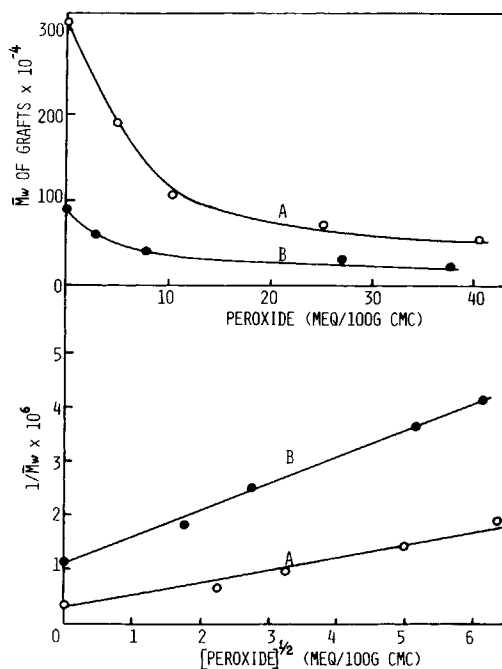


Fig. 4. Relationship between average molecular weight of grafted poly(MMA) and peroxide content of sample in thermal grafting (A) at 60°C for 90 min and photografting (B) at 30°C for 40 min.

grafting and the average molecular weight of the grafts was indicated as the number of grafts.

Photoirradiation

Irradiations with a high-pressure mercury lamp (400 W) was carried out in a Riko rotary photochemical reactor RH400-10W, around which Pyrex glass tubes rotated.

RESULTS AND DISCUSSION

Decomposition of Peroxide on CMC

Figure 1 presents the thermal stability of the peroxide on CMC in aqueous medium. The amount of peroxide on the fibrous material (*B*) showed a tendency to decrease with the lapse of time; while the increasing formation of H_2O_2 was observed in the aqueous medium (*C*), showing a reinforced tendency at a higher temperature. The total amount of peroxide, the sum of those on fibrous material and in aqueous medium, is presented as the curves (*A*) (Fig. 1). The loss due to thermal decomposition appeared to rise at an elevated temperature, which was determined at 80% of the initial amount for the system treated at $60^\circ C$ for 30 min.

The thermal decomposition of the peroxide on CMC in methanol medium (Fig. 2) and the formation of H_2O_2 in the medium are slower than in aqueous medium.

The O—O bond of organic peroxides yields oxygen radicals when heated. The peracid on CMC is thermally decomposed according to eqs. (1) and (2). On the other hand, the formation of H_2O_2 was observed when CMC peroxide was warmed in aqueous medium. This phenomenon can be explained by the reverse reaction of the formation of CMC peracid as shown in eq. (3). Reactions of eqs. (1)–(3) were restrained by the use of methanol medium (Fig. 2). H_2O_2 formed, eq. (3), might be decomposed further, leading to the formation of radicals:

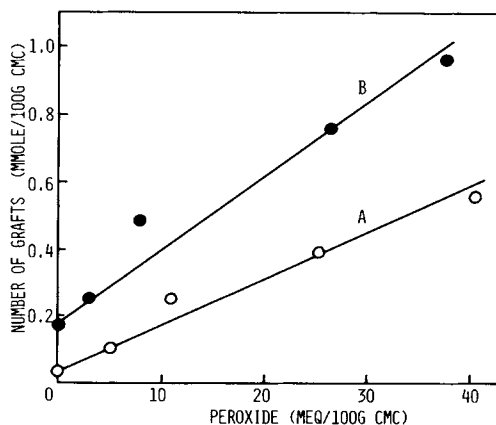
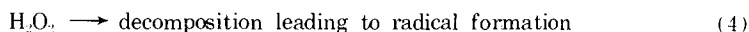
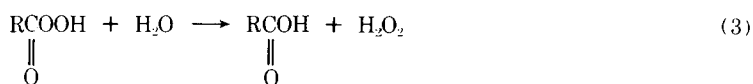
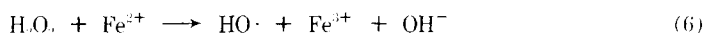
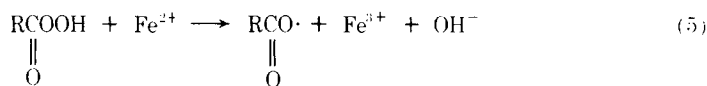


Fig. 5. Relationship between number of grafts and peroxide content of sample in thermal grafting (A) at $60^\circ C$ for 90 min and photografting (B) at $30^\circ C$ for 40 min.

Both ferrous salt and light irradiation accelerated the decomposition of peroxide on CMC in aqueous medium. The function of the two factors in the reaction system was especially noted for the decomposition of H_2O_2 in aqueous medium (Fig. 2). In the presence of ferrous salt, decomposition of peracid and H_2O_2 underwent the following redox reactions:



On the other hand, light irradiation contributes to the decomposition according to eqs. (1) and (4). H_2O_2 is easily decomposed by means of light.²⁰⁻²²

Grafting Induced by Peroxide on CMC

Grafting of MMA on CMC peroxide was examined in thermal initiation and photoinitiation systems, (Figs. 3-5). Figure 3 shows the relationship between the rate of grafting and the peroxide content of CMC. CMC itself though it does not contain a peroxide group, initiates the grafting of MMA by heat or light. However, a somewhat higher level of grafting rate in the same initiation system was observed for CMC peroxide, which showed a nearly linear relation with the square root of the peroxide content of the sample. Both graftings were characterized by a relatively low formation of homopolymer, and the graft efficiencies were in the range of 80% to 90%.

The average molecular weight of grafted poly(MMA) showed a tendency to decrease with increasing amount of peroxide (Fig. 4). A lower molecular weight of grafts was obtained for the photoinitiation system as compared to the thermal system. A straight-line relationship was obtained between the reciprocal of average molecular weight of grafts and the square root of the peroxide content of the substrate.

The number of grafts increased in proportion to the peroxide content (Fig. 5). However, the number of grafts was higher for the copolymer obtained in the photoinitiation system than that in the thermal system. The number of grafts on the CMC substrate increased by introducing the peroxide group. Values of 17 and 6 times were recorded for CMC peroxide with thermal initiation and photoinitiation, respectively.

TABLE I
Photografting^a of Vinyl Monomers on CMC Peroxide

Monomer	Peroxide, meq/100 g CMC	Total conversion, %	Percent grafting, %	Graft efficiency, %
Acrylamide	0	61.9	214.3	84.8
	34.9	100	365.3	89.5
Acrylic acid	0	—	88.0	—
	34.2	—	205.1	—
Methyl methacrylate	0	29.7	102.4	90.3
	34.6	41.1	152.2	96.9
Acrylonitrile	0	15.7	42.9	83.0
	31.5	69.4	191.6	84.0
Vinyl acetate	0	10.5	32.0	80.1
	35.0	54.0	178.8	86.9

^a Photoirradiation was carried out at 30°C for 15 min in a Pyrex glass tube.

The information on the rate of grafting and the average molecular weight of grafts suggests that the mechanism for grafting induced by the peroxide on CMC is by radical polymerization. CMC radicals $\text{RCO}\cdot$, and $\text{R}\cdot$, eqs. (1) and (2), initiate



grafting. Perbenzoic acid²³ and peracid-type resin²⁴ have an ability to initiate polymerization of MMA.

On the other hand, the decomposition of CMC peroxide induced by heat and light also results in the formation of hydroxyl radicals eq. (1). It is conceivable that the hydroxyl radical may contribute to the initiation of polymerization leading to the formation of homopolymers. However, the graft efficiencies in the thermal grafting and the photografting on CMC peroxide were observed at high levels of 80%–90%. Consequently, the activity of CMC radicals initiating polymerization is fairly high (Fig. 5).

Table I shows the results of the photografting of various monomers on CMC peroxide. The total conversion of monomer and the percent grafting were high on CMC peroxide. Graft efficiencies were observed in the range of 80% to 90% for all monomers. Grafting of MMA, acrylonitrile, and acrylamide on CMC using ceric salt^{25–27} as an initiator has been reported. In this study, various vinyl monomers, such as acrylonitrile, acrylamide, acrylic acid, MMA, and vinyl acetate, were effectively grafted on CMC peroxide with short irradiation.

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