

Effect of Organic Peroxides on Initial Coloring of Poly(vinyl Chloride)*

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Synopsis

Suspension polymerization of vinyl chloride was studied using five organic peroxides which show similar polymerization rates. Initial coloring of polymers obtained depended on the kinds of peroxides and the amount of peroxides used. Initial coloring of PVC had no relation to water solubility of the peroxides, but depended greatly on their susceptibility to hydrolysis. Organic peroxides with susceptibility to hydrolysis remained low in the polymer, and yielded PVC showing preferable initial coloring.

INTRODUCTION

Many studies on the thermal decomposition of PVC have been reported, but studies related to initiators were few. Park and Skene¹ have studied the relation between the dehydrochlorination rate of PVC obtained by solution polymerization using four initiators. They reported that the dehydrochlorination rate decreased in the following order: lauroyl peroxide > diisopropylperoxydicarbonate > benzoyl peroxide > azobisisobutyronitrile.

They also found that the degradation rate of PVC increased with increasing initiator content.

Thermal stability, especially initial coloring of PVC, obtained by suspension polymerization depended on the kinds of initiators.² It is the object of this study to investigate the correlation between initial coloring of PVC obtained by suspension polymerization and the behavior of peroxides in aqueous systems.

EXPERIMENTAL

Polymerization

Peroxides, bis(2-ethoxyethyl)peroxydicarbonate (EE), bis(3-methoxy,3-methyl butyl) peroxydicarbonate (MM), bis(2-ethyl hexyl)peroxydicarbonate (EH), diisopropylperoxydicarbonate (IP), and *t*-butyl peroxyneodecanoate (BN) were of commercial grade (Nippon Oil and Fats Co., Ltd.).

Polymerization conversions were obtained at 55°C.³

In order to measure the behavior of pressure during polymerization and to

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obtain PVC for an initial coloring test, suspension polymerizations were done in a 3-L stainless autoclave. Polymerization conditions are as follows;

Vinyl chloride	700 g
Organic peroxide	1.01×10^{-3} mol
Part. sap. PVA	2.1 g
Water	1400 g
Polymerization temp	58°C

PVC was washed with water and dried under reduced pressure at 40°C.

Initial Coloring Test for PVC

PVC sheets of 5 mm thickness were prepared by rolling at 160°C for 5 min. and pressing at 160°C for 5 min. at 100 kg/cm² with 100 g PVC, 50 g dioctyl phthalate, 1 g dibutyl tin maleate, and 0.5 g stearic acid. Coloring of the sheets was measured as *b* values from phototransmission by a color meter (Diano Corp.).

The Influence of pH on the Decomposition Rate of Peroxides

10-mL benzene solution including 0.05M peroxide and 5-mL buffer solution with various pH in sealed glass ampoules were vigorously stirred. The analytical method for the amount of residual organic peroxide in benzene solution was iodometric titration.

Buffer solutions are as follows; pH 10: sodium carbonate/borax; pH 7: sodium phosphate/potassium dihydrogen phosphate; pH 4: acetic acid/sodium acetate.

Measurement of Hydrolysis of Peroxides

The hydrolysis rate was calculated from polymerization conversions obtained in the suspension polymerization of vinyl chloride as follows.

First, 120 g water, 0.15 g part. sap. PVA, 0.02 g peroxide and 40 g vinyl chloride monomer were charged in 300-mL autoclave and polymerization conversions were determined at 50°C.

Second, the same contents of water, part. sap. PVA and peroxide as the first

TABLE I
Decomposition Rate Constants of Peroxides in Toluene^a

Peroxides	$k \times 10^5 \text{ s}^{-1}$	
	45°C	55°C
EE ^b	2.15	7.74
MM	1.45	5.66
EH	1.44	5.78
IP	1.42	5.89
BN	1.29	5.29

^a All rates were determined by iodometric titration with initial concentrations of peroxides 0.05M.

^b With 1.0M styrene.

step were charged in the autoclave and stirred at 30°C for 30 min. After vinyl chloride monomer was charged, polymerization conversions were determined at 50°C.

In order to calculate the remaining peroxide concentration after hydrolysis, polymerization conversions in the first step were plotted according to the Talamini equation⁴ (Polym. conv.) $\propto t/(I_0)^{0.5}$, where I_0 = initial concentration of peroxide and t = polymerization time. Their coefficients of correlation are greater than 0.98 for all five peroxides. The remaining peroxide contents were calculated according to each Talamini relation. The amount of hydrolyzed peroxide may be calculated from the amounts of peroxides before and after hydrolysis.

RESULTS AND DISCUSSION

Initial Coloring of PVC

Five organic peroxides with similar decomposition rates and polymerization activities (Table I and Fig. 1, respectively) were chosen.

Polymerization was carried out at 58°C until the pressure dropped to 5.5 kg/cm² and initial coloring of PVC was observed.

Initial coloring was measured by a color meter; shades of yellow were indicated by b value: the higher the b value, the stronger the color.

Initial coloring development of PVC obtained with EH as initiators increases with increasing amounts of peroxide (Fig. 2).

In suspension polymerization of vinyl chloride, the thermal stability, especially initial coloring of PVC obtained at the same temperature, actually depends on the kinds of initiators used.

Initiators affecting initial coloring have been considered as follows:

- (1) effect of initiator fragments attached to PVC molecules;
- (2) effect of initiators remaining in PVC;
- (3) difference in the formation of the polymer particles, depending on the kinds of initiators.

However, these effects have not been confirmed because of complexity. Our results (Fig. 2) showed that peroxide remaining in PVC causes unpreferable

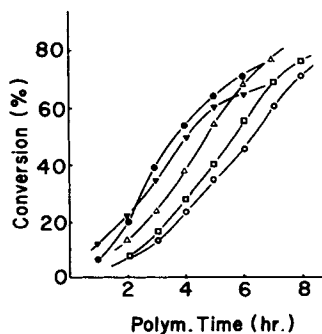


Fig. 1. Plots of conversion vs. time for peroxide-initiated suspension polymerization of vinyl chloride at 55°C. Peroxide concentration: 9.05×10^{-5} mol/mol VCM. Peroxide: (▼) EE; (□) MM; (△) EH; (●) IP; (○) BN.

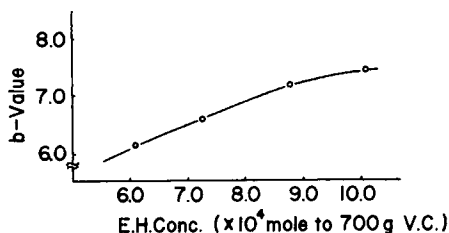


Fig. 2. Initial coloring (b value) of PVC (5 mm thickness) obtained with various concentrations of EH.

initial coloring of PVC. The b -values for initial coloring of PVC, initiated by an equimolar amount of the peroxides, are summarized in Table II. The b values varied from 6.9 to 10.2, depending on the kinds of peroxides.

The Behavior of Pressure during Polymerization

The change in the pressure (Fig. 3) is plotted vs. time during suspension polymerization of vinyl chloride at 58°C . The polymerization time, until the pressure begins to drop, decreases with increasing thermal decomposition rate of peroxide.

However, the time for the subsequent pressure drop does not depend on the thermal decomposition rate. The time for the pressure drop to 6 kg/cm^2 may be affected by the concentration of undecomposed peroxide remaining in the polymerization system. Both the time for the subsequent pressure drop and the initial coloring development are affected by the amount of peroxide in the final stage of polymerization, but they are independent of the thermal decomposition rate. Monomer concentration is low in the final stage of polymerization and the remaining peroxide has a greater opportunity to make contact with the aqueous phase than in the middle stage of polymerization. It is the interaction between peroxide and water, especially hydrolysis of peroxide, is most important for initial coloring of PVC.

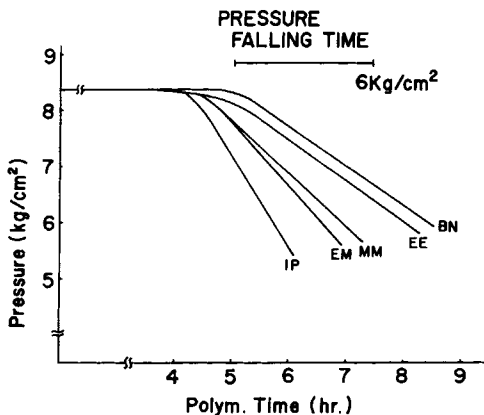


Fig. 3. Polymerization pressure during suspension polymerization of vinyl chloride at 58°C .

Hydrolysis of Peroxide

The reactivities of the peroxides with water were examined. In order to simulate the mechanism of peroxide decomposition in the middle stage of polymerization, the effect of pH on the decomposition rate of the peroxide in benzene/water = 2/1 suspension system is shown in Table III. The decomposition of peroxide was not significantly affected by pH of the suspension (Table III). Hence, the thermal decomposition of peroxide is predominant and the hydrolysis may not proceed in the middle stage of polymerization where many monomers remain.

In the final stage of polymerization, both concentrations of peroxide and monomer are very low. The amounts of peroxide preferable for polymerization after hydrolysis were given (Table IV) together with solubility of peroxides in water at 20°C.

These results indicate that the peroxides are remarkably hydrolyzed in water containing dispersant. Hydrolysis rates of both EE and BN are very rapid and the rate of IP is not. PVC obtained with both EE and BN show preferable initial coloring. This is mainly due to the rapid hydrolysis of EE and BN while IP,

TABLE II
b Values of Initial Coloring of PVC,^a Initiated by Peroxides at 58°C

Peroxide	EE	MM	EH	IP	BN
b Value	6.9	7.2	7.4	10.2	7.0

^a The ranges of polymerization conversions were 85 ± 2%, respectively.

TABLE III
Thermal Decomposition Rate of Peroxides in Buffer Solutions^a

Peroxide	Temp (°C)	Thermal decomposition rate [<i>t</i> _{1/2} , time (h)]			
		pH 4.15	pH 7.04	pH 10.37	No buffer solution
IP	40	11.7	11.3	10.7	10.8
	45	5.7	5.7	5.2	5.2
BN	45	19.0	15.0	15.1	15.2
	50	6.3	7.0	6.9	7.5

^a Peroxide concentration: IP, 0.05M, BN, 0.1M.

TABLE IV
Water Solubility and Hydrolysis of Peroxides

Peroxide	Solubility of peroxide into water at 20°C (wt %)	Hydrolysis of peroxide at 30°C, 30 min (%)
EE	0.55	98.0
MM	0.16	67.1
EH	0.04	45.1
IP	0.16	35.7
BN	0.03	78.1

which has a slow hydrolysis rate, is apt to remain in PVC, and unpreferable initial coloring of PVC may result.

The kinetic and thermodynamic parameters for decomposition of IP were determined experimentally.

$$\Delta H^* = 5.0 \text{ kcal/mol}$$

$$\Delta S^* = -59 \text{ e.u.}$$

These are similar to the values previously reported⁵ for the hydrolysis of diethylcarbonate in water. Therefore, these peroxides mainly decompose due to the hydrolysis in dilute aqueous solution.

CONCLUSION

The effect of organic peroxides on the initial coloring of PVC obtained in suspension polymerization was studied:

- (1) The remaining peroxide affected initial coloring development of PVC.
- (2) In the middle stage of polymerization, where many monomers remain, the peroxides predominantly thermally decompose and act as polymerization initiators. And then, in the final stage of polymerization, the peroxides are exposed to hydrolysis.
- (3) The peroxides which are susceptible to hydrolysis give PVC of preferable initial coloring.
- (4) Water solubility and decomposition rate of peroxides do not immediately affect initial coloring development.

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