

Degradation of Poly(vinyl Alcohol) in Strongly Alkaline Solutions of Hydrogen Peroxide

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Synopsis

The action of hydrogen peroxide and sodium hydroxide independently as well as in combination together with stabilizer formulation—consisting of magnesium sulphate (5 g/L), ethylenediamine tetraacetic acid (2 g/L), gluconic acid (2 g/L), and nonionic/anionic wetting agent (1.5 g/L)—on poly(vinyl alcohol) (PVA) was investigated at 30°C and 95°C. The effect of sodium hydroxide (5–25 g/L) alone was to bring about an enhancement in the viscosity of PVA most probably due to gel formation. The latter was favored at higher sodium hydroxide concentrations and longer duration (30 min) of treatment. The opposite holds true when hydrogen peroxide (35% w/v) was used alone at concentrations ranging from 2 to 20 mL/L. The viscosity of PVA decreased as the hydrogen peroxide concentration increased. Nevertheless, hydrogen peroxide alone could not cause complete dissolution of PVA even at 95°C for 30 min. On the other hand, complete dissolution of PVA could be achieved under the influence of stabilized alkaline solutions of hydrogen peroxide at 95°C in less than 10 min. It was postulated that, under the conditions used, oxidation of PVA by hydrogen peroxide prevailed over gel formation under the influence of sodium hydroxide.

INTRODUCTION

Poly(vinyl alcohol) (PVA) has become the most commonly used sizing agent in textile industry especially for polyester and its blend with cotton.^{1–3} For effective size removal, PVA-sized fabrics must be subjected to water rinse at temperature not less than 90–95°C.⁴ PVA remaining on fabrics prevents proper bleaching and dyeing or printing; part of the residual PVA may be removed and then gelled and redeposited on the fabric during alkaline scouring. In addition, PVA gels can accumulate on equipment. Many investigators have tackled these problems.^{5–8}

Several studies^{7,8} have dealt with the action of H₂O₂ on poly(vinyl alcohol). They have disclosed that PVA undergoes oxidative degradation under the influence of H₂O₂ to yield PVA with lower viscosity and higher solubility. Nevertheless, very few studies⁶ have dealt with the action of H₂O₂ in strongly alkaline medium on PVA most probably because of the very fast decomposition of H₂O₂ in these media. Recently, we have shown that the decomposition of H₂O₂ in the latter can be regulated by making use of stabilizer formulation based on a combination of magnesium sulfate, ethylenediamine tetraacetic acid, gluconic acid, and nonionic/anionic wetting agent, and the effect of this on oxidative degradation of starch was reported.⁹

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The present work is undertaken with a view to study the action of H_2O_2 in strongly alkaline solutions stabilized by magnesium sulfate together with chelating agents on PVA. This is done as a prerequisite for establishment of a single stage process for desizing, scouring, and bleaching. In addition, the action of sodium hydroxide alone on PVA was examined.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) was supplied by Hoechst, W. Germany, under the commercial name Vinarol ST. Hydrogen peroxide (35% w/W) and sodium hydroxide tablets were of technical grade chemicals. Nonionic/anionic wetting agent was supplied by BASF, West Germany, under the commercial name Leuphen U. Magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), ethylene diamine tetraacetic acid (EDTA), and gluconic acid were of laboratory grade chemicals.

Preparation of PVA Solutions and Viscosity Measurements

Unless otherwise indicated, 16% of PVA solutions were prepared by adding the required amount of PVA powder to 500 mL deionized water at room temperature. Care was taken that the addition was done slowly while the liquor was in constant motion under the influence of a rapid stirrer (at least 60 rpm). The solution was then boiled for 20 min followed by cooling down to 30°C in an ice bath. To this solution, another 500 mL aqueous alkali solution containing H_2O_2 and the stabilizer was added to give PVA solution of 8%. Details of the H_2O_2 solutions are given in the text. Portions of the PVA solution (8%) were heated in water bath at specified temperature and for the desired time while stirring. These portions were then cooled down in an ice bath to 30°C and the viscosity was determined for each portion at 30°C as described earlier.⁹

RESULTS AND DISCUSSION

Figure 1 shows the effect of sodium hydroxide concentration on the viscosity of PVA at 30°C and 95°C for 30 min. It is seen that the viscosity of PVA increases significantly by increasing the sodium hydroxide concentration within the range studied, i.e., from 5 g/L to 25 g/L. Furthermore, the viscosity is higher the higher the temperature. Similar situation is encountered when PVA was treated with the same concentrations of sodium hydroxide but for different lengths of time at 95°C as shown in Figure 2. This could be interpreted in terms of gel formation. It is logical that sodium hydroxide causes significant (hydrolysis) of the acetyl groups of PVA. As a result, the tendency of PVA molecules to associate increases thereby enhancing the viscosity of PVA. It is understandable that presence of acetyl groups along the PVA molecules prevent the latter from congealing. Figures 1 and 2 show that higher concentration and temperature and long time of treatment with sodium hydroxide act in favor of gel formation. The latter is not observed when PVA is treated with water in the absence of sodium

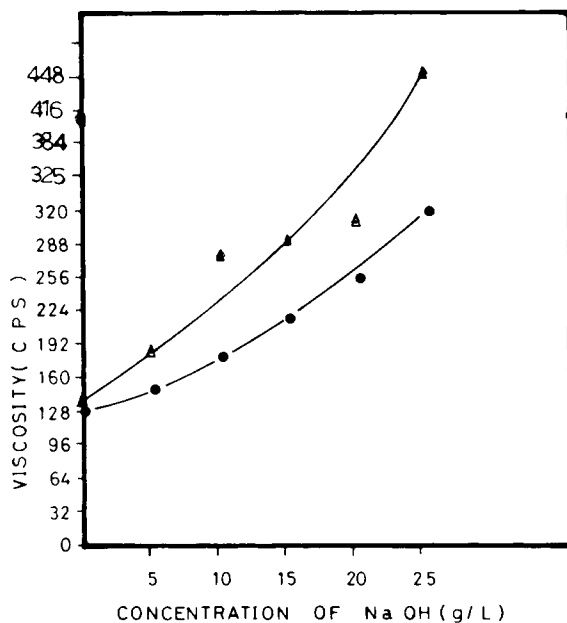


Fig. 1. Effect of sodium hydroxide concentration on the viscosity of 8% poly(vinyl alcohol) solution after 30 min at 30°C (●) and 95°C (△).

hydroxide at 95°C for up to 30 min as can be seen from Figure 2. Indeed, earlier studies^{3,6} have disclosed that sodium hydroxide could gel PVA if used in desizing process in absence of H₂O₂.

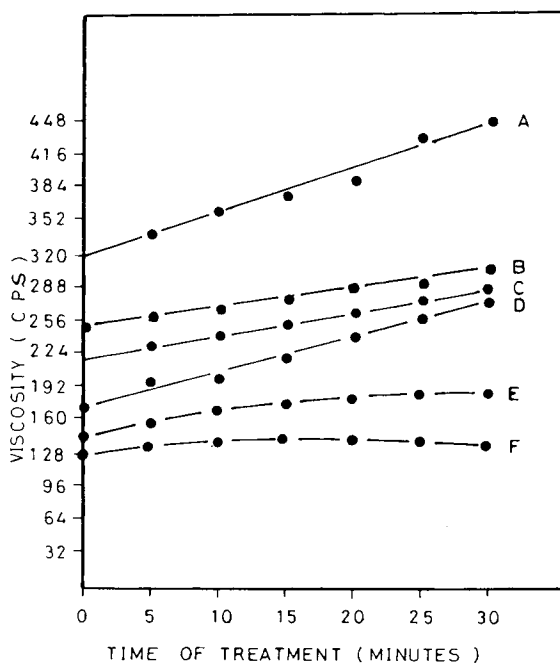


Fig. 2. Effect of sodium hydroxide concentration on the viscosity of 8% poly(vinyl alcohol) solution at 95°C. [NaOH] (g/L): (A) 25; (B) 20; (C) 15; (D) 10; (E) 5; (F) without NaOH.

Figure 3 shows the effect of hydrogen peroxide at different concentrations in alkaline solution (20 g/L sodium hydroxide) stabilized by magnesium sulphate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) at 30°C and 95°C for 30 min on the viscosity of PVA. Figure 4 shows similar results but when the treatment was carried out at 95°C for different lengths of time.

It is seen (Figs. 3 and 4) that the viscosity of PVA decreases sharply by increasing the H_2O_2 concentration. This is observed regardless of the temperature and time of the treatment. Nevertheless, for a given H_2O_2 concentration, the reduction in the viscosity is determined by the temperature and the time of the treatment. For instance, a solution containing hydrogen peroxide (16 mL/L) and sodium hydroxide (20 g/L) along with the stabilizers in question could not induce complete dissolution of PVA at 30°C even after 30 min. On the contrary, the same solution at 95°C expedites complete dissolution of PVA within 5 min. This indicates that H_2O_2 not only impedes the gel formation induced by sodium hydroxide but also cause intensive depolymerization of PVA via oxidation. Oxidative degradation of PVA has been reported to occur at 1,3 and/or 1,2 positions along the PVA backbone.²

Figure 5 shows the effect of sodium hydroxide at different concentrations along with constant concentration of hydrogen peroxide (4 mL/L) stabilized by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L) and EDTA (2 g/L) at 30°C for 30 min on the viscosity of PVA. Obviously, the viscosity of PVA increases by increasing the concentration of sodium hydroxide up to 10 g/L remains almost constant up

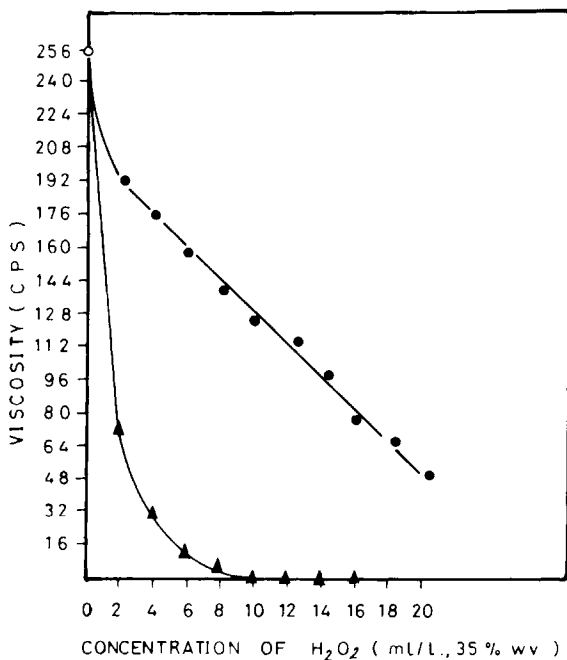


Fig. 3. Effect of hydrogen peroxide at different concentration in alkaline solution (20 g/L sodium hydroxide) stabilized by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) on the viscosity of poly(vinyl alcohol) (8%) after 30 min at 30°C (●) and 95°C (▲).

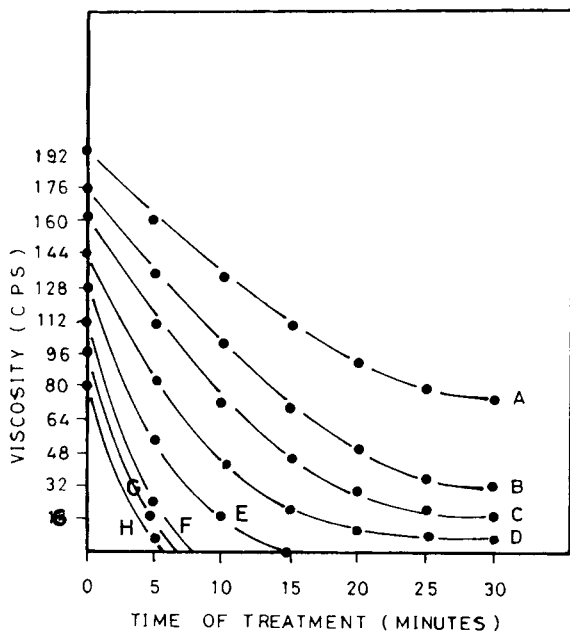


Fig. 4. Effect of concentration of hydrogen peroxide stabilized in alkaline solution (20 g/L sodium hydroxide) by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) on the viscosity of poly(vinyl alcohol) solution (8%) at 95°C. [H₂O₂] (mL/L): (A) 2; (B) 4; (C) 6; (D) 8; (E) 10; (F) 12; (G) 14; (H) 16.

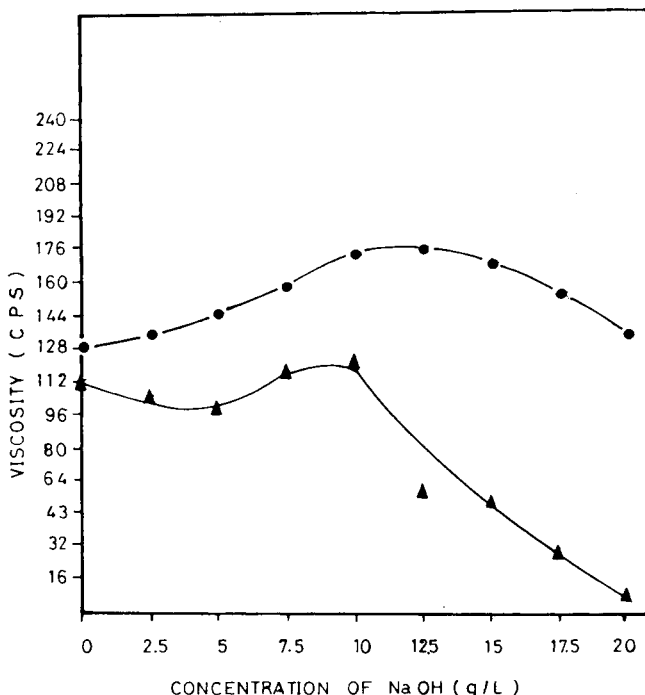


Fig. 5. Effect of sodium hydroxide at different concentration along with hydrogen peroxide (4 mL/L, 35% w/v) stabilized by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) on the viscosity of poly(vinyl alcohol) (8%) after 30 min at 30°C (●) and 95°C (▲).

to 15 g/L and then decreases by further increase in sodium hydroxide concentration to 20 g/L to attain a value which is comparable with that obtained with H_2O_2 in the absence of sodium hydroxide. This suggests that, at such a low temperature and low concentration of H_2O_2 , sodium hydroxide could gel PVA, thereby increasing its viscosity. This increment in viscosity could be counterbalanced at higher concentration of sodium hydroxide (20 g/L) most probably due to enhanced rate of H_2O_2 decomposition. It is understandable that the rate of decomposition of H_2O_2 increases by increasing the sodium hydroxide concentration as reported earlier.⁹

Figure 6 shows the effect of sodium hydroxide at different concentrations together with a constant concentration of H_2O_2 (4 mL/L) stabilized by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) at 95°C for different lengths of time on the viscosity of PVA. The effect of H_2O_2 alone under similar conditions on the viscosity of PVA is also given in the same figure. It is seen that the viscosity of PVA decreases by increasing the sodium hydroxide concentration within the range studied, i.e., from 2.5 g/L to 20 g/L. Prolonging the duration of treatment exerts similar effect. At such high temperature, i.e., 95°C, PVA can presumably form a gel under the influence of sodium hydroxide. Concurrently with this, PVA can be oxidized by H_2O_2 decomposition products. Gel formation would bring about an increment in viscosity of PVA while oxidation would cause a decrement. Current data suggest that oxidation prevails over gel formation under the conditions used, in contrast with the

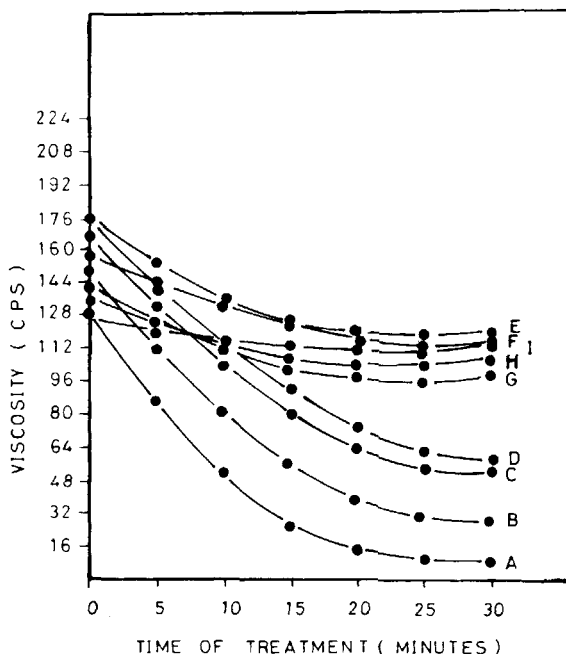


Fig. 6. Effect of sodium hydroxide at different concentration along with hydrogen peroxide (4 mL/L, 35% w/v) stabilized by magnesium sulfate (5 g/L), anionic/nonionic wetting agent (1.5 g/L), gluconic acid (2 g/L), and EDTA (2 g/L) on the viscosity of poly(vinyl alcohol) solution (8%) at 95°C. [NaOH] (g/L): (A) 20; (B) 17.5; (C) 15; (D) 12.5; (E) 10; (F) 7.5; (G) 5; (H) 2.5; (I) without NaOH.

corresponding conditions at 30°C. Hence at 95°C the decrease in viscosity of PVA, observed regardless of the concentration of sodium hydroxide used, is a direct consequence of the higher rate of decomposition of H₂O₂ and, therefore, higher rate of oxidation at this temperature. Indeed, the higher decrement in viscosity at higher than at lower sodium hydroxide concentrations as compared with the decrement in viscosity brought about by H₂O₂ alone during the later stages of the treatment substantiates this.

Based on the above, it is obvious that sodium hydroxide alone could gel PVA; the higher the sodium hydroxide concentration, the greater the gel formation and, therefore, the viscosity. This is the case at 30°C and 95°C. Incorporation of H₂O₂ at certain concentrations together with the stabilizers in question not only impedes gel formation but rather prevails over provided that the treatment is carried out at 95°C. As a result complete dissolution of PVA occurs within less than 10 min via oxidative degradation of PVA. Utilization of H₂O₂ at a concentration as low as 4 mL/L along with different concentrations of sodium hydroxide at 95°C does reduce the viscosity of PVA drastically. However, complete dissolution could not be achieved, even after 30 min. Hence, the concentrations of sodium hydroxide and H₂O₂ as well as time and temperature of the treatment should be exercised to achieve complete dissolution of PVA.

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Received June 14, 1984

Accepted September 6, 1984