

Hydroxypropylcellulose—The Reaction of Alkali Cellulose with Propylene Oxide

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Synopsis

Several methods for the hydroxypropylation of alkali cellulose have been investigated to obtain a uniformly substituted material soluble in dilute alkali and regenerable in dilute acid. The reaction in which alkali cellulose is reacted with a 60% concentration of liquid propylene oxide based on the cellulose content was found to be reproducible giving a film-forming derivative of 6% substitution with minimum by-products in less than 2 hr. During the course of this work, hydroxypropylcellulose solutions and films were prepared and evaluated. A valid comparison of the physical properties with those of hydroxyethylcellulose and viscose solutions and films has been made.

INTRODUCTION

The hydroxyalkylation of cellulose yields products which may be alkali soluble or water soluble, or soluble in organic solvents; they may even be thermoplastic depending on the kind and degree of structural change effected by the alkylating agent.¹

Of particular interest to us was the reaction of propylene oxide with alkali cellulose to form a derivative, soluble in dilute alkali and regenerable from dilute alkali.

The hydroxyethylation of alkali cellulose has been thoroughly investigated¹⁻⁹; however, very little has been reported on the hydroxypropylation.^{10,11} Froment¹¹ has investigated the heterogeneous reactions of both ethylene and propylene oxide with NaOH-cellulose in acetone solvent at 30°C in a hermetically sealed shredder. The products from those reactions were of low substitution and of varied solubility in dilute sodium hydroxide. Furthermore, these reactions were not reproducible and presumably the products were nonuniformly substituted.

A reproducible process for the preparation of a film-forming hydroxyethylcellulose product with a degree of substitution of 4.15% has previously been reported.^{6,12} This process is carefully controlled to prevent the formation of a complex hydroxyethyl structure of high M.S. whose regeneration is difficult.

We expected the analogous reaction of alkali cellulose with propylene oxide as the alkylating agent to be more easily controlled because propylene

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oxide is less reactive than ethylene oxide. Furthermore, side reactions might be eliminated because of the less reactive secondary alcohol groups produced.

Initially, a product of 5.5% M.S. was sought based on the 4.15% film-forming hydroxyethyl derivative. However, during this investigation, it was found that a product of 6% to 6.5% M.S. had better physical and chemical properties. Empirical and qualitative methods such as the solubility, filterability, and film-forming qualities of the products were employed to describe the uniformity of each batch. The physical properties of the films cast from filtered solutions was a further confirmation of product uniformity.

Our efforts to establish optimum laboratory reaction conditions for the uniform hydroxypropylation of alkali cellulose led us to investigate several methods of reaction. The reactions of propylene oxide with alkali cellulose as a gas-solid reaction and as a liquid-solid reaction at atmospheric pressure and under vacuum were found to be the most efficient methods leading to uniform products.

EXPERIMENTAL

The products from all propoxylations were worked up to evaluate solution and film properties, by-product formation, and reaction efficiencies. One half of the hydroxypropylcellulose crumb was swelled with cold water and directly dissolved by addition of 50% caustic solution at 0° to obtain the solution concentrations desired (8% HPC 7% NaOH). The amount of water and caustic used was calculated on the basis of the cellulose content, the alkalinity of the alkali cellulose used in the reaction, and on the Zeisel number. The Zeisel number, which expresses the amount of propylene oxide substitution of the cellulose, was determined by the method of Morgan.¹⁸

The remaining half of the hydroxypropylcellulose crumb was neutralized with 10% acetic acid, washed free of acid with water, and extracted with chloroform to remove organic soluble by-products. The neutral crumb was dried under vacuum at 70°C. The dry product was dissolved in dilute caustic to a final concentration of 8% solids, 7% sodium hydroxide. The regeneration efficiency was determined from the weight of dry film regenerated from a known weight of dissolved crumb. Reaction conversions and yields were calculated on the basis of propylene oxide converted to product.

These solutions were filtered through a 2-ounce filter cloth of 1.6-cm diameter under 40 psig air pressure. Films, approximately 8 × 11 in., were cast by pouring the deaerated solutions of hydroxypropylcellulose on glass plates and spreading the mixture with a stainless steel casting bar. The films were regenerated at room temperature from baths containing 12.5% sulfuric acid and 20% sodium sulfate. After regeneration for 3 min, the films were washed in running tap water at room temperature for

several hours. The wet films were dried on glass plates after securing the edges of the film with tape to prevent shrinkage and curling.

RESULTS

Gas-Solid Propoxylation at Atmospheric Pressure

Initial reactions were carried out with 10 g alkali cellulose at 25° and 35°C in a 500-ml thermostated, three-necked flask. These experiments showed that propylene oxide flow rates greater than 10 cc/hr were required to obtain products of 5-6% substitution in 3-4 hr. Propoxylation was then carried out at 35°C in a 1500-ml reactor with 20 g and 60 g alkali cellulose. Propylene oxide entered the reactor through a side arm connected to a coarse sintered glass disk at the bottom of the reactor. Reproducible flow rates were maintained by passing a measured flow of nitrogen gas through a Moore flow control unit and through a calibrated Brooks rotameter before passage through a propylene oxide reservoir. Samples of the product were removed from the reactor at half-hour intervals during the reaction and analyzed. The Zeisel numbers were plotted as a function of time (Fig. 1) for a series of propylene oxide flow rates. These curves

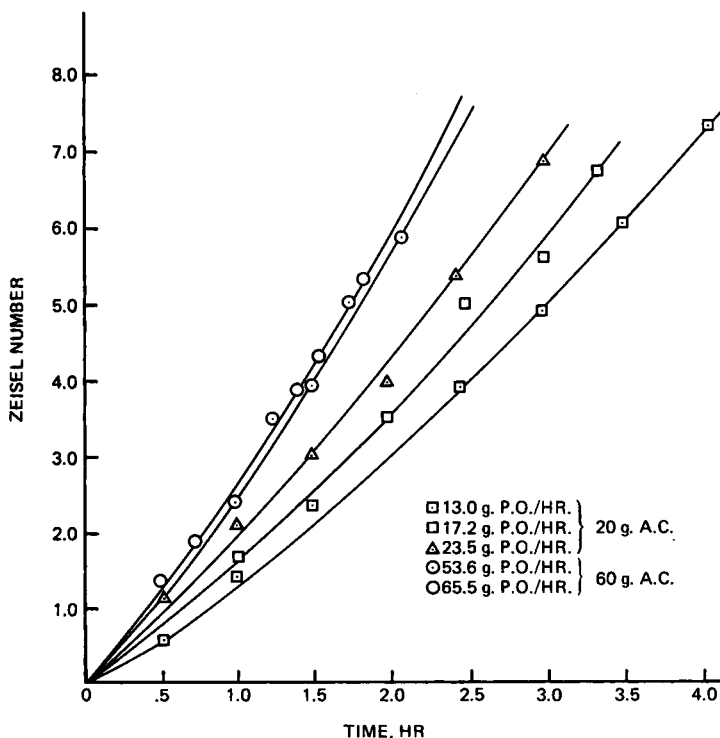


Fig. 1. Zeisel number-time curves for different propylene oxide flow rates. Gas-solid reaction in the 1550-ml reactor at 35°C.

showed that the rate of propoxylation increased with increasing propylene oxide throughput and that a product of 5.5–6% M.S. could be obtained in 2 to 3.5 hr.

Liquid–Solid Reaction at Atmospheric Pressure

Propylene oxide was added to 200 g alkali cellulose inside a 3.5-liter cylindrical stainless steel vessel fitted with a gas-tight cover. This quantity of alkali cellulose filled two thirds of the reactor and permitted good mixing of the reactants on a roller mixer inside a thermostated cabinet. These experiments were carried out at 25° with 30%, 40%, and 60% concentrations of propylene oxide based on the cellulose content of the alkali cellulose. A product of 5.5% to 6% M.S. was obtained in 2 hr using a 60% propylene oxide concentration, whereas products of low M.S. were obtained at the 30% and 40% concentrations. In all following work a 60% propylene oxide concentration was therefore used.

Large-Scale Propoxylations of Alkali Cellulose

The liquid–solid reaction was then studied in a 15-gallon drum reactor to determine whether the propoxylation was reproducible on a larger scale. The reactor was fitted with three baffles to permit better mixing of the reactants. The open end was sealed by a cover and gasket which was fastened with a steel clamp. The inlet tube was perforated with many small holes and extended 25 in. inside the reactor. An outlet tube and a thermometer well were sealed into the other end of the drum. Mixing was obtained by rolling the drum on a roller mixer whose speed was controlled by a variable chain drive motor. Temperature control was achieved by passing a stream of water over the drum as it turned. A rubber and Teflon bearing arrangement attached to the inlet and outlet tubes permitted the addition of propylene oxide while the drum rotated. In all experiments, 5 pounds of alkali cellulose and 1.1 pounds of propylene oxide (60% concentration) were used. The propylene oxide was added under several pounds of nitrogen pressure through a 500-ml addition funnel. The exit end of the reactor was connected to a cold water condenser and remained open during the reaction which was carried out at 25°. These modifications were incorporated here to safeguard against unexpected heat build-up due to possible rapid exothermic homopolymerization or other undesirable side reactions. Reactions were carried out for 2 to 2.5 hr. A product of 6% substitution was obtained in 2.25 hr, thereby confirming the results obtained in the 3.5-liter reactor. These results permitted further scale-up to a 37-gallon hexagonal baratte.

Propoxylations in a 37-Gallon Baratte

To improve the efficiency of the propoxylation, several new techniques were incorporated as standard operating procedure: The 37-gallon baratte with its 12.1 pounds of alkali cellulose was evacuated to 27 in. vacuum and heated to 25°; 2.7 pounds of liquid propylene oxide (60% concen-

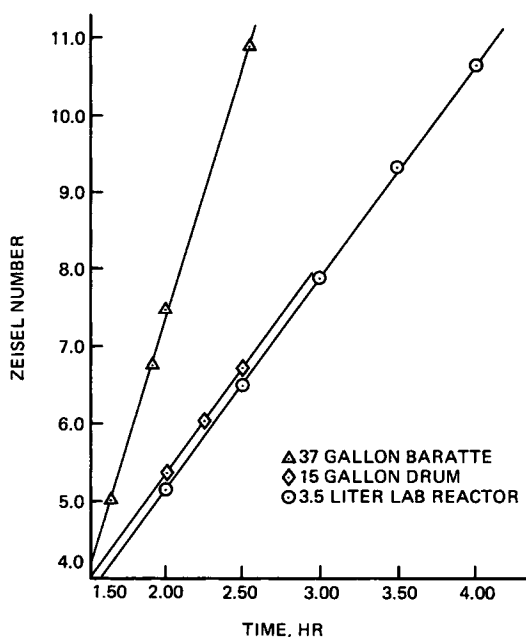


Fig. 2. Comparison of reactor efficiencies.

tration) was added to the evacuated baratte as it turned and the temperature was raised to 30° during the reaction. An overpropoxylated product of 10.9% was obtained in the initial experiment at 2.5 hr using this technique which indicated that the reaction was more efficient than in either the laboratory or the 15-gallon reactors. Other propoxylations confirmed this. Reactions were carried out for 1.6 and 1.9 hr giving substituted products of 5.0% and 6.8%, respectively. The Zeisel number-time plots for the three reactors are compared in Figure 2, indicating that the desired substitution level of 6% can be achieved in 1.7 hr at 30° by use of a baratte-type reactor.

Additional Propoxylations

Further experiments were carried out to determine the effect of reaction time on the conversion of propylene oxide to hydroxypropylcellulose with the objective to increase the conversion and to reduce the amount of propylene oxide required to obtain the D.S. desired for product solubility and uniformity.

Using only 30% propylene oxide based on cellulose, advantage was taken of the aging time of alkali cellulose to permit increased reaction time of propylene oxide at 30°. Propylene oxide was added to alkali cellulose by injection into the baratte similarly to the injection of carbon disulfide at the end of the alkali cellulose aging cycle or in effect during the aging cycle. A series of experiments were thus carried out with 20% and 30% propylene oxide using different reaction times ranging from 2 to 6 hr. The data of

TABLE I
Propoxylation of Alkali Cellulose at 30°C

Propylene oxide, %	Reaction time, hr	Viscosity, sec	Cellulose, %	Alkalinity, %	D.P.	PO, % substituted
30	2	336	8.25	7.15	260	7.55
30	4	270	8.29	7.01	255	7.35
30	6	243	8.45	7.12		
20	2	335	7.56	7.09	242	4.30
20	2	328	8.62	7.01	249	5.00
20	4	208	7.59	7.01	245	4.81
10	4	300	7.54	7.03	245	3.06
25	4	427	8.96	6.09	241	6.62

Table I show that with 30% propylene oxide a 2-hr reaction time is quite sufficient to obtain a very high D.S. of 7.5% propylene oxide; little or no depolymerization occurs under these conditions. Using only 20% propylene oxide based on cellulose, a 4-hr reaction time is required for adequate substitution and filterability at a 7.0% alkalinity level.

Since a lower alkalinity level is more economical, a 25% propylene oxide concentration and 4 hr reaction time is probably required to obtain uniform and sufficient substitution to permit the lowering of alkalinity to 6.0% while increasing the cellulose content. Additional experiments confirmed this, giving us more economical processing conditions desired for producing hydroxypropylcellulose film. These data are also included in Table I. They lead us to conclude that by proper choice of reaction time and reaction temperature, hydroxypropylcellulose of uniform substitution and good filterability can be obtained employing cellulose-to-alkalinity ratios which are equivalent to those used in the viscose process.

Properties of Hydroxypropylcellulose

Solution Preparation and Properties: The large quantities of product obtained in the 37-gallon baratte were worked up to evaluate solution and film properties which are a direct reflection of the hydroxypropylcellulose quality and a measure of the efficiency of the propoxylation. The two methods of dissolution described earlier were used to prepare final solutions of 8% solid-7% caustic. Homopolymer formation during hydroxypropylation appears to be insignificant, for only negligible amounts of by-products were extracted from the reaction products.

Film Preparation and Properties: A sufficient number of physical test data were obtained for 27 sets of HPC films ranging in Zeisel number from 4% to 11% in order to make a valid comparison of some of the critical factors such as gel swelling and dimensional stability of unsoftened films. These data and comparable data for laboratory and commercial hydroxyethylcellulose (HEC) and viscose films are given in Table II, III, and IV.

The data of Tables II and III show that HPC films have a lower gel swelling, a slightly higher deformation than HEC films, and a permanent

TABLE II
Comparison of the Dimensional Stabilities of HPC, HEC, Ethynier, and Viscose Films^a

Film type	Gel swelling index	No. of sets of film	Deformation, % ^b		Perm. set. % ^b	
			MD	TD	MD	TD
HPC	725	27	1.6	1.6	2.5	2.5
HEC	788	26	1.3	1.3	1.5	1.4
Ethynier ^c	770-820	13	1.4	1.3	1.5	1.5
Viscose	400-440	17	2.3	2.4	3.1	3.2

^a Prepared in the laboratory (unsoftened films).

^b Two determinations for each film set.

^c Obtained from Rayonier, Inc.

TABLE III
Comparison of Average Physical Properties of HPC, HEC, Ethynier, and Viscose Films—Unsoftened Films

Film type	No. of sets of film	Tenacity, lb		Elongation, %		Stress flex	Gauge, mils
		MD	TD	MD	TD		
HPC ^a	20	22	22	4	4	4	0.96
HEC ^a	18	24	22	5	4	4	0.91
Ethynier ^b	4	27	30	6	6	5	0.81
Viscose	15	27		5		11	1.08

^a Prepared in the laboratory.

^b Obtained from Rayonier, Inc.

TABLE IV
Comparison of Average Physical Properties of HPC, HEC, Ethynier, and Viscose Films—Softened Films

Film type	Softener, %	Tenacity, lb		Elongation, %		Stress flex	Gauge, mils
		MD	TD	MD	TD		
HEC ^a	24.9	15	17	18	15	34	1.13
HPC ^b	30.8	14	14	28	20	30	1.10
Ethynier	10-50	10-20	8-15	4-20	4-20	4-16	1.00
Viscose	10-30	32-34	22-28	15-17	18-46	14-66	0.80-0.90

^a One set of films—Zeisel No. 6.21%.

^b Two sets of films.

set between that of HEC and viscose, indicating inferior dimensional properties to HEC. All other properties of these films such as tenacity, elongation, and stress flex (Tables III and IV) are equivalent for both the softened and unsoftened films.

CONCLUSIONS

The hydroxypropylation reactions reported here lead us to conclude that uniform HPC products can be obtained of sufficient substitution to

be alkali solution and film forming on acid regeneration. These products have properties similar to the corresponding HEC and viscose films. However, process economics for HPC is less favorable than that of HEC while the dimensional stability properties are below those of hydroxyethylcellulose. Thus hydroxypropylation of cellulose to produce a novel film for the packaging industry cannot be considered as commercially attractive at this time.

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