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Application of GPC to Studies of the Viscose Process. II. The Effects of Steeping and Alkali-Crumb Aging*

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Summary

Changes in the distribution of degree of polymerization (DP) of cellulose during the steeping and alkali-crumb aging steps of the viscose process have been studied. A dissolving-grade pulp was used, and two mechanisms of degradation—oxidation and hydrolysis—were considered. Alkaline hydrolysis was relatively unimportant during the steeping, the major change in the DP distribution being a result of the much faster oxidative degradation. The extent of oxidation was determined by the solubility of oxygen in the alkali solution. Both oxidation and hydrolysis cause degradation during the aging of alkali crumb. Under the conditions used, hydrolysis was a slow, pseudo-first-order reaction, and oxidation a much faster zero-order reaction. Since there was a large difference in the rates of these reactions, the kinetics of degradation approached zero order.

INTRODUCTION

The production of fibers and film from cellulose by the viscose process is a multistep operation. Cellulose is converted to an alkali-soluble derivative by steeping pulp in aqueous sodium hydroxide and after aging the sodium cellulosate (alkali crumb), reacting it with

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carbon disulfide. The derivative (sodium cellulose xanthate) is dissolved, yielding a viscous solution (viscose). After aging, the viscose is extruded into an acid bath where the cellulose is recovered by coagulation and decomposition of the derivative.

The distribution of degree of polymerization (DP) is a variable which changes during the viscose process. Previously, the nature and extent of the changes had been inferred from measurements of the basic DP. Information about the DP distribution could only be obtained by combining several tedious determinations, e.g., osmometry, viscometry, and ultracentrifugation, or from complicated fractionation techniques. Gel permeation chromatography (GPC) affords a rapid method of studying these changes and evaluating the importance of this variable. The GPC method and its limitations have been described in Part I of this paper (*1*). In this Part II, the changes in DP distribution during steeping of pulp and aging of alkali crumb are considered.

The main objectives of the steeping process are (a) to convert the cellulose to a more reactive sodium cellulosate and (b) to remove the alkali-soluble material. In commercial practice, this is achieved either by a batch process where the pulp sheets are steeped in large steep presses or by a continual slurry steeping. An 18% aqueous sodium hydroxide solution is usually used in both systems.

Aging of alkali crumb results in a reduction of the basic DP. This is necessary because the solubility of the cellulose derivative is an exponential function of the reciprocal DP. The aging is usually carried out in large bins at controlled temperatures.

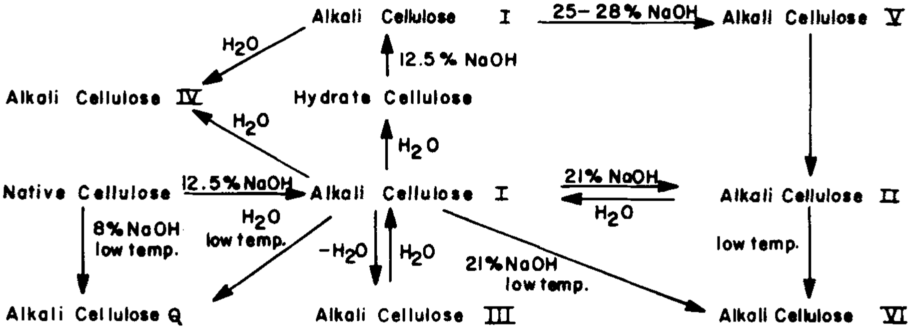
It is recognized that oxidation and hydrolysis cause degradation in both steeping and alkali crumb aging. Although there have been many studies of these process steps (*2*), the mechanisms of degradation are not understood.

RESULTS AND DISCUSSION

Steeping

To interpret the changes of DP distribution in cellulose during steeping, the chemical and physical reactions of cellulose in the presence of alkali solution and the design of the experiments were considered.

It has been established by x-ray diffraction that when cellulose is steeped in alkali, changes in its structure occur (*3*). Some of the possible transitions are outlined in Scheme 1. The changes are related to the alkalinity and temperature. In Scheme 1, there are nine forms of cellulose which may behave differently.



SCHEME 1. Some transitions of cellulose in alkali.

In addition, heat is evolved during steeping (*4*). The heat effect ΔH_T can be separated into parts according to its origin.

(a)	Heat of wetting	ΔH_a
(b)	Heat of reaction (formation of alcoholate)	ΔH_b
(c)	Heat of possible lattice transition	ΔH_c
(d)	Heat of other reactions—degradation, oxidation, etc.	ΔH_R

$$\Delta H_T = \Delta H_a + \Delta H_b + \Delta H_c + \Delta H_R$$

The heat of steeping, approximately 2 cal/g with 18% NaOH, may cause local temperature variation of several degrees in the system. Dissipation of this heat to the steep liquor is a variable influenced by rate of filling the steep tank and packing of the pulp sheets, etc.

During steeping, the pulp sheets swell and absorb the alkaline solution (*5*). The amounts of swelling and absorption increase to a maximum at 18% sodium hydroxide. Above 18%, the swelling decreases slightly and is then unaffected by further increase in the alkalinity. The amount of alkali absorbed behaves similarly.

An initial drop in the basic DP is observed when pulp is steeped in alkali. This is most probably due to an oxidative degradation. It will thus depend on the concentration of oxygen both in the steep liquor and adsorbed on the pulp sheets. Although the latter factor should be similar for each pulp batch, the former depends on the alkalinity, the solubility of oxygen in alkali decreasing with increased alkalinity and temperature (*6*). After the initial drop in $\overline{\text{DP}}$, the degradation proceeds more slowly, and here the mechanism probably involves alkaline hydrolysis.

The removal of alkali-soluble material, hemicelluloses, and degradation products from the pulp sheets is related to the solubility of the material in the steep liquor and diffusion of this material into the steep. The solubility of cellulose in alkali is exponentially related to the reciprocal $\overline{\text{DP}}$. It is also dependent on the alkali concentration, being greatest around 10% NaOH (*7*). With commercial batch steeping, the extraction of alkali-soluble material is diffusion controlled, and the amount of material removed will be influenced by the temperature, alkalinity, nature of the pulp, time, etc.

Effect of Steep Alkali Concentration. To determine if alkali hydrolysis was a significant factor during steeping, a dissolving-grade pulp was immersed in aqueous sodium hydroxide solution of different dilutions. Five concentrations (6, 12, 18, 24, and 30%) were used. Each solution was saturated with nitrogen by bubbling the gas through the solution for 1 hr at room temperature to minimize oxidative degradation during the experiment.

One-gram samples of shredded pulp were steeped for 10 min in 50 ml of the alkali. After steeping, either the alkali crumb was washed with fresh portions of the original alkali to remove alkali-soluble material, or excess acetic acid was added to the mixture, neutralizing the alkali and precipitating the alkali-soluble material. Table 1 shows the average molecular weights after steeping.

The most significant change is the decrease (approx 10%) in the

TABLE 1

Influence of Steep Alkali Concentration on DP Distribution

% NaOH	$\bar{M}_n$		$\bar{M}_w$		$\bar{M}_z$		$\bar{M}_{z+1}$	
	NaOH	HOAc	NaOH	HOAc	NaOH	HOAc	NaOH	HOAc
6	455	429	978	1063	1854	2004	3000	3178
12	513	441	1056	1042	1823	2109	2818	3836
18	488		1074	1045	2012	1892	3596	3032
24	462	415	1081	1004	1836	1955		3456
30	416	416	1051	1013	2060	1858	3765	2877
Pulp	454		1145		2118		3050	

weight-average molecular weight from the pulp to the alkali crumb. This is attributed to oxidative degradation as a result of air in the pulp.

There is no evidence of any difference in the alkaline hydrolysis during the short steeping, as the $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_z$ values in the acetic-acid precipitated samples are unaffected by the alkali concentration. Extraction of the alkali-soluble material by NaOH affected the value of $\bar{M}_n$ only to an extent related to the solubility of cellulose in the alkali. There were significant differences for the number-average molecular weights, dependent on both the alkalinity of the steep and the method of sample preparation. The highest value of $\bar{M}_n$ was obtained at 12% NaOH consistent with the solubility characteristics discussed earlier.

Effect of Steeping Time. To determine the effect of steeping time on the DP degradation, only one alkali concentration was used. No attempt was made to remove oxygen from the system. The results obtained for different steeping time are given in Table 2. After the initial drop in basic DP—to an extent probably related to the consumption of oxygen in the system—degradation proceeds very slowly. Rates of hydrolysis could not be calculated because the changes observed were within the precision limits of the method.

TABLE 2

Influence of Steeping Time on DP Distribution (18% NaOH at 25°C)

	$\bar{M}_n$		$\bar{M}_w$		$\bar{M}_z$		$\bar{M}_{z+1}$	
Min	NaOH	HOAc	NaOH	HOAc	NaOH	HOAc	NaOH	HOAc
5	457	439	954	961	1783	1738	3213	2711
10	541	379	1034	901	2001	1756	3879	2925
60	504	402	1093	908	2037	1759	3437	2986
120	395	322	913	976	1933	2175	3770	3694

Alkali Crumb Aging

The largest change of basic DP and distribution of DP occurs during the aging af alkali crumb. The extent of degradation is determined by the temperature, alkali concentration, oxygen content, and handling. Normal commercial practice is to hold these constant and vary the time to attain a specific basic DP.

Effect of Aging Time. To separate the effects of oxidation and hydrolysis, the reduction of DP and the DP distribution in alkali crumb was studied in oxygen and nitrogen atmospheres. To prepare the alkali crumb, the pulp was shredded in a Waring Blendor and then steeped in 18% aqueous sodium hydroxide for 10 min. The alkali crumb was transferred to a sintered-glass filter funnel, and excess steep liquor removed by suction. The crumb was again shredded in the Waring Blendor to ensure uniformity and divided into two equal portions. The batches were placed in 1 liter Erlenmeyer flasks sealed with rubber stoppers carrying two 7 mm i.d. glass tubes. The contents of the flasks were then aged at room temperature (25°C) for 10 days. A flow of oxygen was passed through one of the flasks, and a flow of nitrogen through the other. The flow rate was approximately 1 ml/5 min. To prevent loss of moisture from the crumb during aging, the gases were bubbled through distilled water before entering the flasks. Periodically, samples were removed for analysis. Although in the presence of oxygen the degradation was faster, the alkali crumb remained white. Under nitrogen, the alkali crumb became yellow, eventually turning brown. The DP distribution results are given in Table 3. Many more low DP molecules are formed in the oxygen environment, and with 4 or more days' aging, the DP distribution was extremely narrow.

TABLE 3

DP Distribution for Alkali Crumb Aged at 25°C in Oxygen and Nitrogen

Age (days)	$\bar{M}_n$		$\bar{M}_w$		$\bar{M}_z$		$\bar{M}_{z+1}$		Viscometric DP	
	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2	N_2	O_2
0	389	330	1015	1008	2151	2264	3849	3926	1040	1045
1	396	375	936	758	1768	1504	2882	3208	970	755
2	371	304	843	567	1545	913	2444	1387	870	535
4	479	184	800	337	1382	563	2588	844	740	350
7	348	151	656	215	1133	302	2057	404	660	245
10	330	125	602	178	981	248	1430	329	600	200

Integral or cumulative amount curves for the samples aged in nitrogen are shown in Fig. 1. The degradation was slow. Initially, 30% of the sample had a DP greater than 1200, and 12% was less than 200. After 10 days at 25°C, there was still 11% above DP 1200 and only 15% below DP 200. The differential curves for these samples

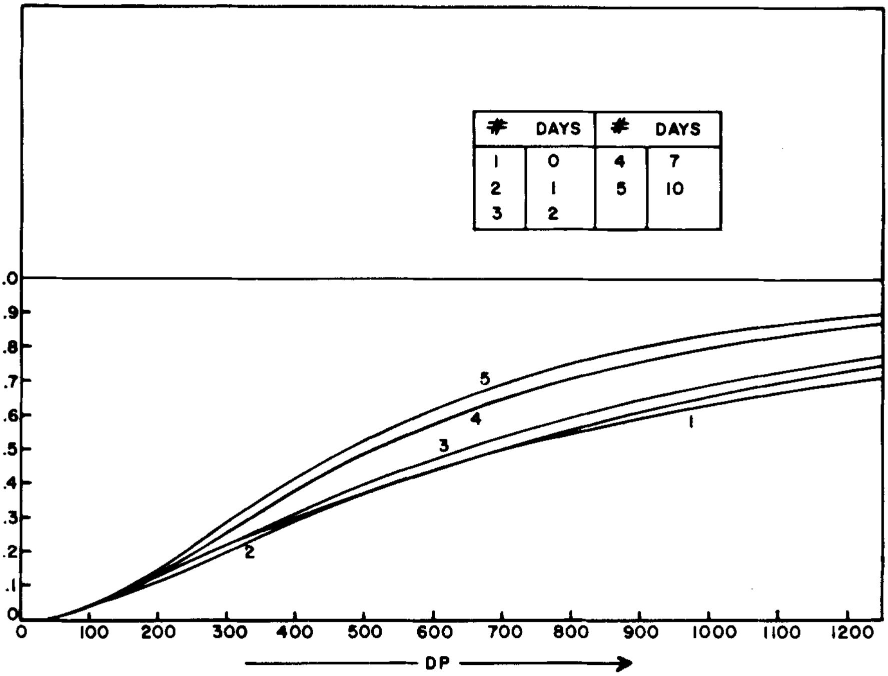


FIG. 1. Integral curves, alkali crumb aged at 25°C in nitrogen.

are illustrated in Fig. 2. The distributions are all relatively broad, although the shoulder due to low-DP material present in the initial sample is gradually obscured by the formation of more small molecules by degradation.

Although there are significant differences in the distribution as a result of aging the alkali crumb under nitrogen, it is not possible to separate the effects of random scission and end clipping (end-group attack). However, as the greatest change in the differential curve was between DP 100 and DP 700, the sample probably originated from a random scission of the cellulose molecules.

In oxygen, the degradation was much faster. The integral curves (Fig. 3) show that although initially 30% of the sample had a DP above 1200 and 12% below 200, after 10 days at 25°C there were no molecules present with a DP above 700, and 68% of the sample had a DP below 200. This is reflected in the differential curves (Fig. 4); after 7 days, the distribution was narrow. The distribution shown in these curves may be the result of random scission and/or end clipping.

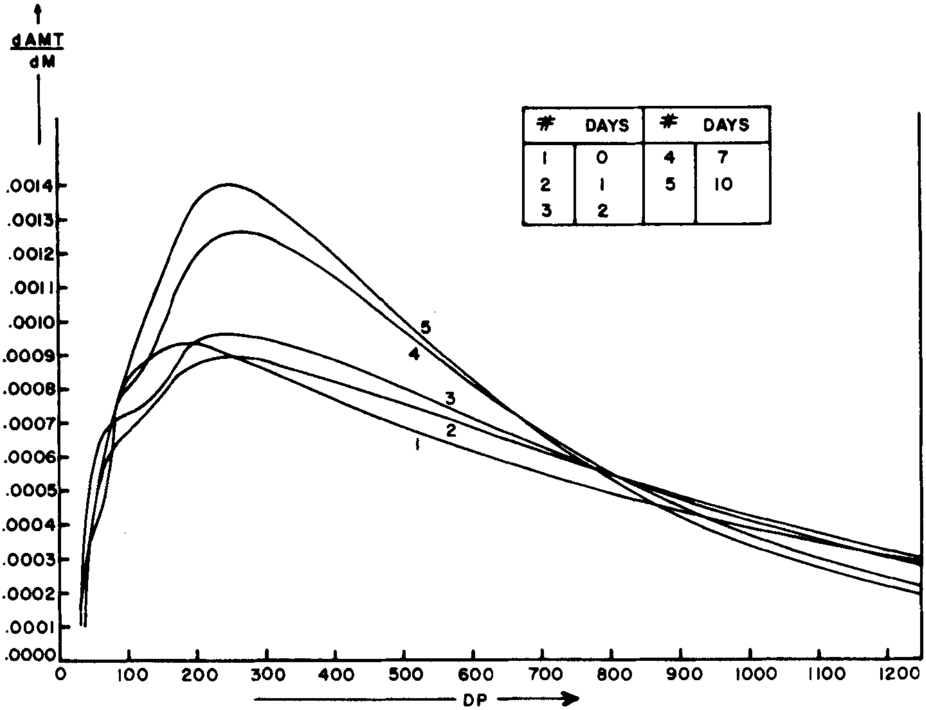


FIG. 2. Differential curves, alkali crumb aged at 25°C in nitrogen.

It must be emphasized at this point that the GPC data is only representative of the distribution in the sample as injected into the GPC equipment. It is possible that low-DP material is lost during sampling, handling, and preparation. This would be relatively unimportant if only the change in basic DP were used—it would not affect $\bar{M}_z$ or $\bar{M}_{z+1}$ and have only a slight effect on $\bar{M}_w$—there would, however, be a significant effect on $\bar{M}_n$. The effects of end clipping and random scission can only be separated if the low DP degradation products are retained in the sample.

There are at least two chemical reactions that will result in degradation of the DP; hydrolysis and oxidation. When oxygen is excluded from the system, only hydrolysis occurs. A semilogarithmic plot of the number-average DP as a function of the aging time under nitrogen was linear. Although the reaction is second order, under the conditions used it was pseudo-first order.

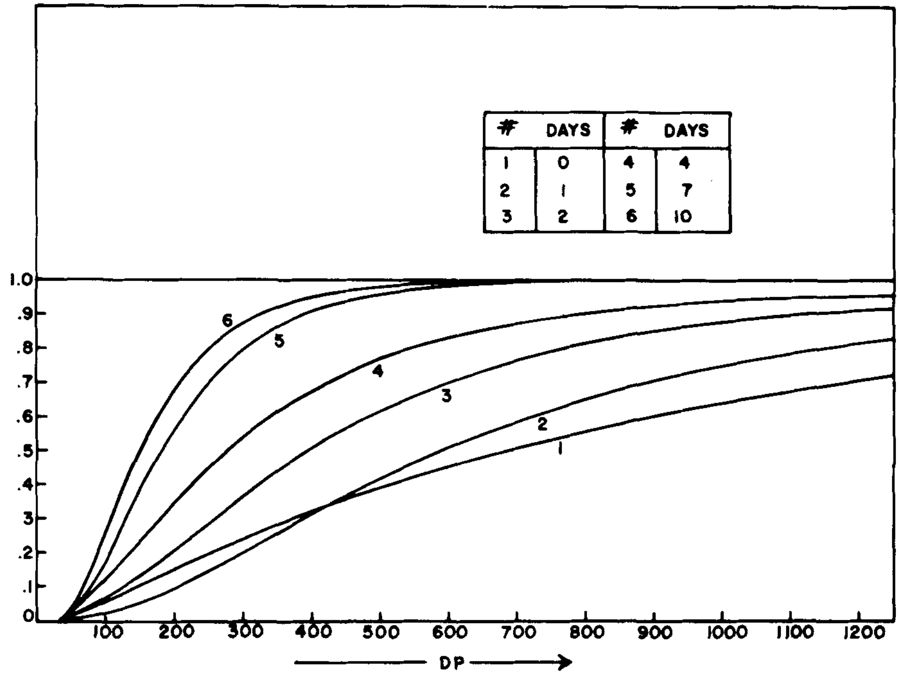


FIG. 3. Integral curves, alkali crumb aged at 25°C in oxygen.

In the presence of oxygen, it may be assumed that both oxidation and hydrolysis occur. The rate of oxidation is related to the solubility of oxygen in sodium hydroxide and will be almost independent of the oxygen concentration in the atmosphere around the alkali crumb. The oxidation can be represented as a reaction of zero order. Thus kinetics of degradation is the result of two competing reactions, one zero order and one second order. Hydrolysis, the second-order reaction, is slow compared to oxidation. Consequently, a zero-order plot of the data will only approach linearity as shown in Fig. 5. Results obtained for the reciprocal of the weight-average DP of the cellulose after aging the alkali crumb under nitrogen are shown for comparison. The changes are much smaller, and this curve also approaches linearity.

To obtain data for the third curve (air) in Fig. 5, alkali crumbs were aged in a sealed can and exposed to the air only when samples were removed. This represents a situation where the available oxygen was consumed and then replenished when the can was opened. The

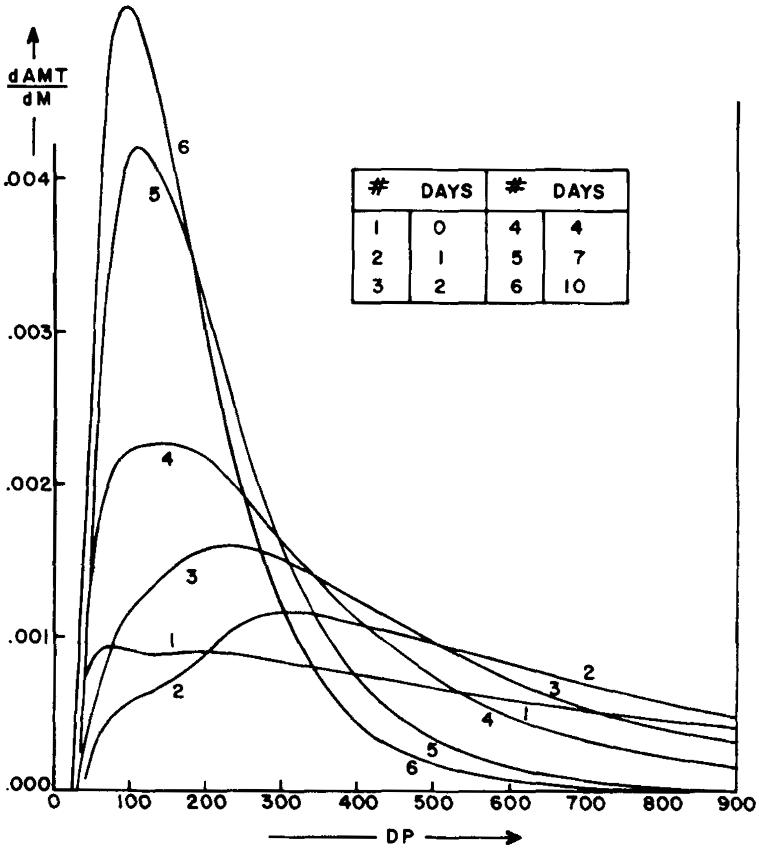


FIG. 4. Differential curves, alkali crumb aged at 25°C in oxygen.

reciprocal weight-average DPs were more scattered and were intermediate to those obtained in oxygen or nitrogen atmospheres.

CONCLUSIONS

Gel permeation chromatography can be used to study the distribution of DP of cellulose during the steeping and alkali-crumb aging steps of the viscose process. Oxidation and hydrolysis are the two mechanisms of degradation with oxidation being much faster. During steeping, the extent of oxidation is determined by the amount of oxygen dissolved in the system. After consumption of the available oxygen, steeping time is relatively unimportant.

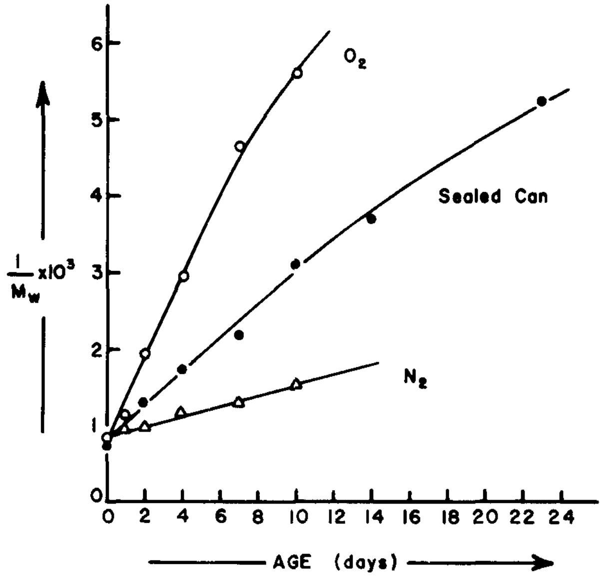


FIG. 5. Effect of alkali crumb aging time at 25°C.

In alkali-crumb aging, hydrolysis is by a pseudo-first-order reaction and oxidation by a zero-order reaction. As there is a large difference in the rates of these reactions, the kinetics of degradation under normal conditions will approach zero order.

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