Cellulose Degradation in Xanthate Process

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Synopsis

Changes in degree of polymerization (DP) of cellulose during the viscose process were investigated by determining the number average molecular weight ($\overline{M}_n$), weight average molecular weight ($\overline{M}_w$), and polydispersity ($\overline{M}_w/\overline{M}_n$) giving molecular weight distribution (MWD). In general, a reduction in DP from the pulp stage to the final filament stage was noticed. Maximum degradation was observed to take place during xanthation and not during aging as sometimes claimed. Among the four methods used for gel permeation chromatography (GPC), Universal calibration HDV method, not involving viscosity measurement, gave the best and most reproducible values.

INTRODUCTION

Viscose processing has been the subject of investigation in understanding changes in the state of cellulose and the underlying mechanism. Changes in DP and MWD at different steps of viscose manufacture were of particular interest in the present study. GPC offers a precise and rapid technique of determining these parameters. Although cellulose MWD at various stages was studied by Agg and Yorke,[1] it was not examined at the xanthation stage. Cellulose MWD at this important step was an integral part of the present investigation.

EXPERIMENTAL

Unmodified cellulose is insoluble in most common organic solvents. Conversion of cellulose to the soluble derivative, therefore, becomes necessary for analysis by GPC. All the data presented here were obtained with cellulose nitrate samples prepared according to ASTM method D-1716-60T. The cellulose samples at different stages of viscose manufacture, namely, pulp, soda cellulose (before and after aging), viscose (in the form of film), and viscose yarn, were obtained from a commercial plant.

The soda cellulose samples were neutralized immediately with $1N$ sulfuric acid and washed with cold water followed by hot water. Viscose solution was cast in the form of film using $1N$ sulfuric acid bath and subsequently washed with 0.6% sodium sulphide to remove sulfur. The nitrated cellulose samples were stored under absolute ethyl alcohol in the refrigerator prior to use.

A sample was air dried at room temperature and a 0.1% solution in tetrahydrofuran (THF) was prepared by shaking mechanically for 6 h and allowing to stand overnight. The solution was filtered through 0.5 millipore filter before use. Waters gel permeation chromatograph Model 201 was used
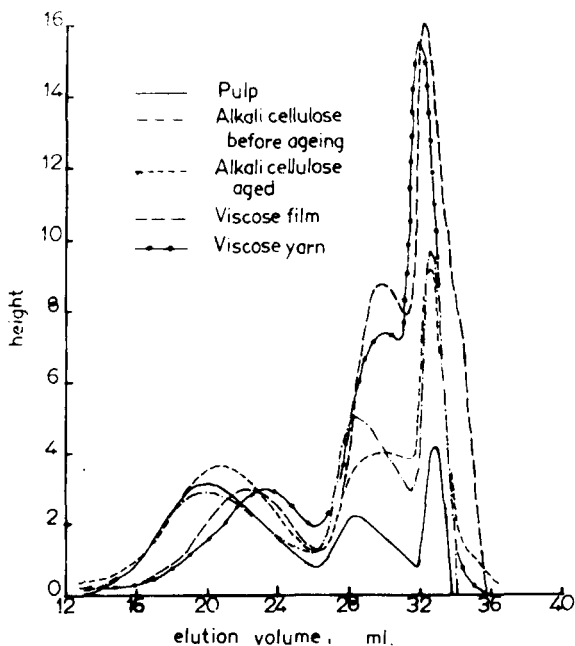
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CHROMATOGRAM

Fig. 1. GPC curves of cellulose samples at different stages of the viscose process: (—) pulp; (- · -) alkali cellulose before aging; (- - -) alkali cellulose aged; (— —) viscose film; (-··-) viscose yarn.

with styragel columns. The columns were calibrated with known molecular weight polystyrene samples from Waters Associates.

The conditions used were as follows: (1) columns used, 1×10^5, 1×10^4, 1×10^3 Å Styragel; (2) sample volume, 100 mL, for polystyrene, 2 mL, for nitrated cellulose; (3) solvent flow rate, 1.0 mL/min; (4) R.I. detector sensitivity, 8 power; (5) temperature, 25°C.

Viscosity measurement of the samples was done using Ostwald capillary viscometer having an efflux time of 45 s for THF at 25°C.

RESULTS

Figure 1 shows a chromatogram of the nitrated cellulose samples collected at different stages. The GPC curve consists of three peaks. A broad peak on higher molecular weight side is the one of principal interest. The sharp peak on the lower molecular weight side with a prominent shoulder corresponds to hemicelluloses with DP not more than 10. Main interest in these is their relative intensities as compared with that of the broad prominent peak, to show the extent of low molecular weight fraction present as a result of treatments in regeneration.

Table I shows the average parameters obtained by using Universal calibration HDV method. This method does not involve viscosity value and is found to give the best results among the four methods[2-5] tried here for measure-

TABLE I
Universal Calibration Hydrodynamic Volume Method without Viscosity Measurement

Sample no.	Sample	$\overline{M}_n$	$\overline{M}_w$	DP	Polydispersity $\overline{M}_w/\overline{M}_n$	Intrinsic viscosity (dL/g)
1	Pulp	62,777	2,26,277	760	3.60	10.5
2	Alkali cellulose before aging	57,750	2,20,277	742	3.81	10.0
3	Alkali cellulose aged	53,800	2,03,119	683	3.78	6.0
4	Viscose film	39,200	1,22,401	412	3.12	4.0
5	Viscose yarn	31,935	1,13,242	380	3.54	2.4

ment. DP was calculated as $\overline{M}_w/297$, where 297 is the molecular weight of nitrocellulose.

Table I shows that there is a moderate drop in DP after steeping and shredding of pulp. The chromatogram also shows increased height of lower molecular weight peaks and broadening of MWD.

A significant drop in DP is observed as a result of aging of the alkali cellulose crumb as indicated by the average parameters in steps (2) and (3), and also by the shift of main broad peak toward the lower molecular weight side.

When the cellulose sample collected after xanthation, dissolution, and ripening was analyzed by GPC, a sudden fall in the average parameters was noticed [compare steps (3) and (4)]. This is also evident from significant skewing of the curve toward the lower molecular weight side with increase in the height of the lower molecular weight peaks. Lower polydispersity shows uniformity of chain length in viscose.

It is recognized that oxidation and hydrolysis cause degradation in both steeping and alkali crumb aging, wherein the oxidation with simultaneous cleavage of glycosidic linkings takes place by air oxygen present in the system or entering from outside. Although there have been many studies[6-12] of the processing steps, the mechanisms of degradation are not yet clear. Phifer and Dyer[13] attempted to separate the effects of oxidation and hydrolysis but were unsuccessful. A slight decrease in $\overline{M}_n$ with significant decrease in $\overline{M}_w$ indicates that during aging, degradation occurs mainly by random scission.

It is known that there is practically no degradation occurring in the viscose solution phase comprising the stages of mixing, filtering, and ripening.[14,15] It can, therefore, be said that maximum degradation, in the viscose process, occurs during xanthation. This can be explained as:

1. Cellulose is a heterochain compound containing acetal bonds which are most liable to oxidative degradation. The essential prerequisites for oxidation, namely, alkali and oxygen, are both present during xanthation, and even a small amount of oxygen is sufficient to cause a considerable degradation by oxidation.

2. The formation of xanthate ester, xanthate being a bulky group, breaks some of the interchain H-bonds and makes cellulose more susceptible to attack for oxidation and hydrolysis to take place rapidly.

During xanthation, cellulose is not only subjected to chemical degradation, but also to mechanical degradation. Constant rotation of the container wherein the cellulose is subjected to mechanical comminution during xanthation also contributes to the degradation. This, however, may only be a minor contribution.

In conclusion, cellulose degradation in the viscose process is maximum during xanthation, and is more than that occurring during aging.

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