Mechanical Properties of Paper Sheets Prepared from Partially Cyanoethylated Wood Pulp

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Synopsis

Cyanoethylated of wood pulp was carried out at different conditions including acrylonitrile concentration, time, and temperature of the reaction. Some mechanical properties of paper sheets prepared from the cyanoethylated wood pulp were examined. Cyanoethylated paper sheets acquired higher breaking length, fold number, and burst factor than the untreated paper sheets irrespective of the conditions used for cyanoethylation. On the other hand, the tear factor of cyanoethylated paper sheets was generally lower than that of the untreated control though under certain conditions cyanoethylation brought about substantial improvement in tear factor. The water retention value and beating time are decreased depending upon the condition of cyanoethylation used.

INTRODUCTION

Chemical modification of cellulose via cyanoethylation has gained considerable importance in the field of cellulose chemistry particularly that of cotton.[1] Cellulose (Cell—OH) reacts with acrylonitrile in presence of strong alkalis in a manner typical of primary and secondary alcohols to form cyanoethyl ether.[2] The reaction between the cellulose hydroxyls and acrylonitrile may be presented as follows:

$$\text{Cell—OH} + \text{CH}_2{=}\text{CHCN} \rightarrow \text{Cell—OCH}_2\text{—CH}_2\text{—CN}$$

A variety of products with different properties may be obtained depending upon the length of the cellulose molecules and the availability of the hydroxyl groups for reaction. With care, high values of degree of substitution (D.S.) may be achieved.[3]

Miller and Flowers[4] were the first to report on the cyanoethylation of paper. According to them, very low degree of cyanoethylation improved the fold[5] and tear[6] strength. Other advantages could be obtained on the treated paper such as heat resistance[7,8] and rot resistance.[7]

The present work is undertaken with a view of studying (a) the susceptibility of wood pulp to cyanoethylation and (b) some mechanical properties of paper sheets prepared from the cyanoethylated wood pulp.

EXPERIMENTAL

Preparation of Partially Cyanoethylated Wood Pulp. Wood pulp (20 g) was mixed with 100 mL of 2% sodium hydroxide solution containing 2% of urea for 15 min at 10°C, then 3.25 g (0.5 mol) of acrylonitrile was added. Mixing was continued for the desired time while gradually raising the

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temperature to 40°C. The sodium hydroxide was then neutralized by adding 30 mL of 10% acetic acid solution, while continuing the mixing. At this end, the mixture was successively washed under vigorous stirring with 50% ethanol (500 mL) and water to obtain a white fibrous product. The latter was finally dried at ambient condition.

The extent of the cyanoethylation reaction was expressed as percent nitrogen. The latter was determined according to a method described elsewhere.[9]

Preparation of Hand Sheets. The cyanoethylated wood pulp was beaten to 50°SR using Jakro mill. Hand sheets were made from the above pulps according to the Swedish Standard Method (SCA). Strength properties of the produced sheets were tested according to Tappi Standard. The WRV[10] of the prepared sheets were also determined.

RESULTS AND DISCUSSION

Bleached commercial paper grade wood pulp was used as a starting material. Chemical analysis showed that this wood pulp consists of ash 0.28%, lignin 0.96%, Pentosan 8.5% and α-cellulose 85.16%. Time of beating to 50°SR for this wood pulp amounted to 22 min.

Figure 1 shows the relation between the reaction time and the nitrogen content of cyanoethylated wood pulp at 40°C and 60°C using two acrylonitrile concentrations, a low concentration of 0.5 mol and a high concentration of 1 mol. It can be seen that, at 40°C, the nitrogen content increases by increasing the time of the reaction up to 90 min. Thereafter, the nitrogen content decreases by further increasing the reaction time. This is observed regardless of the acrylonitrile concentration used. Nevertheless, the extent of reaction, i.e., nitrogen content is higher at higher than at lower acrylonitrile concentration. Similar observations are recorded when the cyanoethylation reaction was carried out at 60°C except that the extent of the reaction tends to decrease by increasing the reaction time from 15 to 120 min upon using the low concentration of acrylonitrile.

The enhancement in the extent of the cyanoethylation reaction by increasing the concentration of acrylonitrile or the initial reaction time could be associated with higher availability of acrylonitrile molecules in the proximity of cellulose hydroxyls. It is anticipated that longer reaction time and/or higher acrylonitrile concentration would act in favor of an abundance of acrylonitrile molecules in the interior of the cellulose fibers. This is rather a prerequisite for the reaction to occur because of the immobility of the hydroxyl groups of the cellulose.

The decrement in the extent of the cyanoethylation during the later stages of the reaction suggests partial hydrolysis of the cyanoethyl groups to carboxyethyl groups under the influence of the alkaline medium of the reaction. Current data (Fig. 1) further suggest that this partial hydrolysis seems to be favored at higher temperature, i.e., at 60°C, particularly upon using low acrylonitrile concentration.

Table I shows the effect of cyanoethylation of wood pulp under the conditions employed on some mechanical properties of the paper sheets prepared therefrom. It is seen that cyanoethylation exerts a considerable

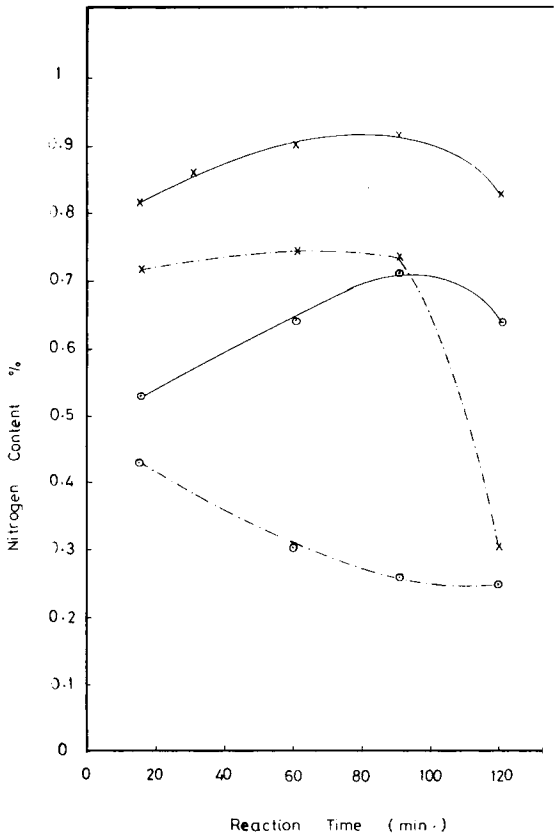

Fig. 1. Relation between reaction time and nitrogen content of cynoethylated wood pulp. Temperature (°C):(—)40, (- - -) 60; concentration: (⊙) low, (X) high.

influence on fold number, tear strength, burst factor, breaking length, and WRV of the paper sheets, being dependent upon the conditions of cyanoethylation used. Cyanoethylation causes significant improvement in the fold number regardless of the condition used for cyanoethylation. Nevertheless, the magnitude of this improvement is manipulated by the condition used. The highest improvement in the fold number could be achieved when cyanoethylation was carried out at 60°C for 90 min using acrylonitrile concentration of (1 mol) whereas the lowest improvement is observed under similar conditions but at 40°C, assuming two reactions taking place simultaneously, i.e., cyanoethylation and partial alkaline hydrolysis, the results would imply that creation of carboxyethyl groups along with substantial amount of cyanoethyl groups in the cellulose molecules accentuates the fold number of the cyanoethylated paper sheets.

Burst factor of the paper sheets increases by cyanoetheylation of the wood pulp prior to the sheet preparation (Table I). However, for the two sets of reaction conditions at 40°C, there is a tendency for the burst factor to decrease, by increasing the extent of cyanoethylation, i.e., nitrogen content, whereas, with cyanoethylation at 60°C, no clearcut relation between the burst factor and nitrogen content could be observed. This reflects the effect of the conditions of cyanoethylation on the burst factor of the paper sheets

TABLE I
Mechanial Properties of Paper Sheets Prepared from Partially Cyanoethylated Wood Pulp

Acrylonitrile concn (mol)	Temperature (°C)	Time (min)	Double fold number	Tear factor	Burst factor	Breaking length (m)	WRV (%)	N_2 content (%)	Time of beating (min)
0.5 (low concn)	40	—	11	36	18.75	3107.63	210.2	0	22
		15	37	44	33.30	4513.88	224.5	0.537	19
		30	54	32	32.81	4722.22	208.6	0.644	12
		90	48	36	28.65	4774.3	206.0	0.713	11.5
1 (high concn)	40	15	32	40	30.21	4895.83	197.5	0.82	11
		30	24	34	24.48	4531.25	194.0	0.908	11
		90	20	32	21.61	4305.55	192.7	0.919	11
0.5 (low concn)	60	15	35	36	25.26	4079.86	196.0	0.434	10.3
		30	39	34	25.78	4340.27	197.8	0.303	10.2
		90	35	34	24.69	4330.60	194.1	0.263	10.1
1 (high concn)	60	15	48	32	25.82	4738.3	203.9	0.724	10
		30	50	32	27.84	4423.05	203.2	0.755	10
		90	64	36	26.27	4713.01	201.9	0.741	9.5

and calls for the excersize of these conditions for better improvement in burst factor.

Table I shows that the tear factor of cyanoethylated paper sheets is higher than that of the untreated sheet (control) only when cyanoethylation was carried out at 40°C for 15 min. Prolonging the reaction time at 40°C or carrying out the cyanoethylation at 60°C for varying lengths of time brings about sheets the tear factor of which are lower than that of the control. This may be taken to indicate that partial alkaline hydrolysis of cyanoethylated cellulose occuring during the course of cyanoethylation reaction adversely affects the tear factor of the paper sheets, since minimum alkaline hydrolysis would be expected at 40°C for short reaction time.

Variations of the breaking length of paper sheets with the conditions of cyanoethylation are shown in Table I. Obviously, cyanoethylation causes a significant increment in breaking length irrespective of the conditions used, but the magnitude of this increment is governed, to some extent, by the conditions of cyanoethylation used. Cyanoethylation at 40°C for 15 min using 1 mol acrylonitrile brings about the highest increment in breaking length, while those at 60°C for the same time but using 0.5 mol acrylonitrile produces the lowest.

The water retention value (WRV) decreased depending upon the condition of cyanoethylation used, because the functional groups are rendered more hydrophobic. This is due to the bulky arrangement of the substituents, which force the cellulose structure open and decrease to close order of the molecules on drying.

The beating time is decreased according to the condition of cyanoethylation used.

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