A Phase Transition Study on the Mercerization of Cellulose

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Introduction

The mercerization of native cellulose has been investigated by Sisson and Saner[1] with the X-ray method from a phase transitional point of view. The native cellulose contains a crystalline lattice of cellulose I, which is transformed into that of celluose II by the mercerization process. It is well known that the degree of transition depends on both the concentration and the temperature of sodium hydroxide solution used as the mercerizing agent. Furthermore, the concentration range depends also on the origin of the cellulose sample[2].

In a preceding paper[3] the present author has investigated the changes in the lateral order distribution of the native cellulose on the mercerization process and concluded that the lowering of the lateral order is induced with a concentration of sodium hydroxide lower than that required to induce the phase transition. But it is necessary to obtain correct knowledge about the phase transition in order to discuss the transition mechanism.

The main purpose of this investigation is to confirm the concentration range

1) W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

2) B. G. Rånby and H. F. Mark, *Svensk Papperstidning*, **58**, 374 (1955).

3) Y. Tsuda and S. Mukoyama, This Bulletin, **30**, 271 (1957).

necessary to the transition and to obtain more information on the mercerization mechanism.

Experimental Procedure

a. Cellulose Samples.—Cotton linters pulp and sulfate and sulfite wood pulp were used. The analytical data of the samples were as follows:

(A) Cotton linters pulp, viscose grade, α-cellulose 98.3 %, degree of polymerization 610.

(B) Sulfate wood pulp, viscose grade, α-cellulose 94.3 %, degree of polymerization 690.

(C) Sulfite wood pulp, viscose grade, α-cellulose 95.7 %, degree of polymerization 1020.

b. Treatment with Sodium Hydroxide.—Before the treatment, the samples were disintegrated with a mixer, and then soaked at 20°C and 45°C in sodium hydroxide solution of various concentrations for two hours. The samples were recovered by suction on a glass filter, regenerated with 0.5 N acetic acid of the same temperature and washed with distilled water. The treated samples were dried with alcohol.

c. X-ray Diffraction.—The air dried samples, re-disintegrated with a mixer, were analyzed by Norelco Geiger counter-X-ray diffractometer (Copper K_α-radiation with Ni filter) with the specimen mounted by pressing in the specimen holder. The tubes were run at 35 kV. and with 15 mA emission current.

Measurement and Results

Figs. 1, 2 and 3 show the X-ray diffraction intensity curves of the untreated, completely mercerized and partially mercerized linters pulp respectively. The untreated linters pulp gives the pattern of cellulose I, the completely mercerized one that of cellulose II, and the partially mercerized one a mixed pattern of both. The absolute intensity of X-ray diffraction depends on the density of specimen pressed in the specimen holder, so that fluctuations of the absolute intensity in repeated measurements with the same sample were inevitable. Therefore it was impossible to utilize the absolute intensity itself to estimate the relative amounts of the two phases.

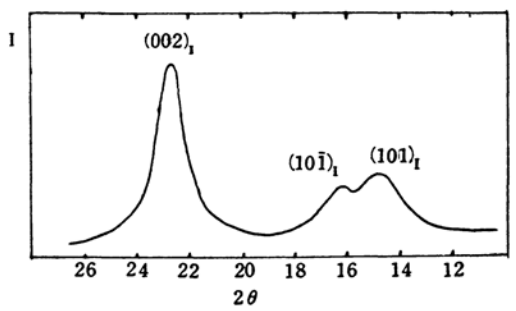

Fig. 1. X-ray diffraction intensity curve of the untreated linters pulp.

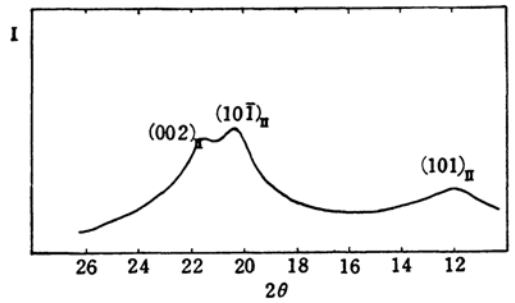

Fig. 2. X-ray diffraction intensity curve of the completely mercerized linters pulp.

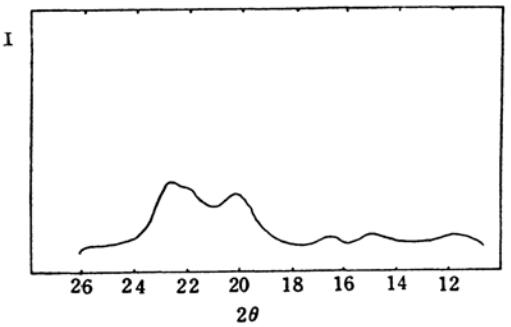

Fig. 3. X-ray diffraction intensity curve of the partially mercerized linters pulp.

In this experiment, to estimate the degree of the transition from cellulose I to cellulose II test experiments were made using samples containing known amounts of untreated and completely mercerized samples. The X-ray diffraction analyses of these samples were made with respect to the three pulp samples and then the degree of transition was followed taking the intensity ratio of (10$\bar{1}$) of cellulose II to (002) of cellulose I. In Figs. 4, 5 and 6 the

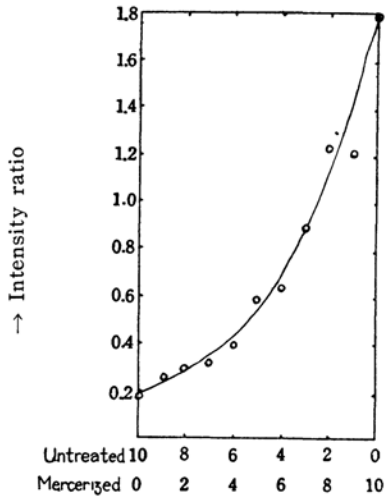

Fig. 4. Calibration curve for the linters pulp.

intensity ratio I $(10\bar{1})_{II}/I(002)_I$ is plotted against the relative amounts of the two phases. These calibration curves show that the gradient of curve increases with the increase in the amounts of cellulose I. Therefore it may be suggested that visual estimation of X-ray diffraction diagrams adopted by Sisson and Saner[1] leads to misunderstanding of the transition range. From the comparison of these figures it may be seen that the intensity ratio of the untreated linters pulp is lower than that for the untreated wood pulps, which is due to the higher lateral order of the native linters pulp.

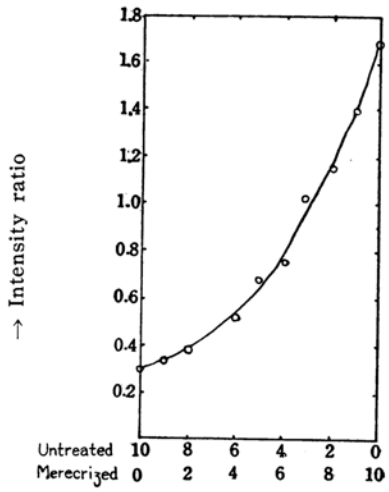

Fig. 5. Calibration curve of the sulfate pulp.

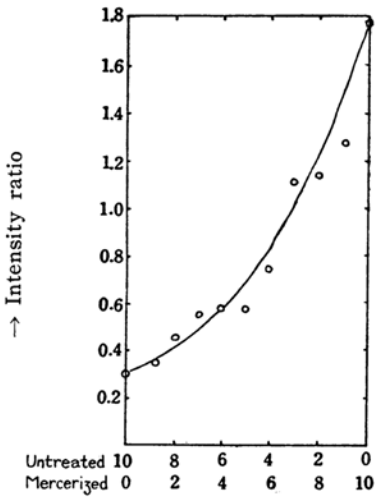

Fig. 6. Calibration curve of the sulfite pulp.

TABLE I

TRANSITION DATA OF SAMPLES TREATED AT 20°C

Linters Pulp			Sulfate Pulp			Sulfite Pulp		
NaOH[a] wt. %	I.R.[b]	D.T.[c] %	NaOH wt. %	I.R.	D.T. %	NaOH wt. %	I.R.	D.T. %
9.9	0.16	0	8.2	0.32	5	8.0	0.32	6
10.7	0.20	4	9.0	0.63	49	9.0	0.48	28
11.5	0.33	28	9.9	0.72	56	10.0	0.79	59
12.3	0.54	51	10.7	1.29	87	11.0	1.60	94
13.1	0.83	68	11.5	1.29	87	12.0	1.55	93
13.9	1.07	77	12.3	1.68	100			
14.6	1.23	82						
16.8	1.51	91						

TABLE II

TRANSITION DATA OF SAMPLES TREATED AT 45°C

Linters Pulp			Sulfate Pulp			Sulfite Pulp		
NaOH[a] wt. %	I.R.[b]	D.T.[c] %	NaOH wt. %	I.R.	D.T. %	NaOH wt. %	I.R.	D.T. %
10.0	0.21	8	9.0	0.28	0	9.0	0.30	0
11.0	0.26	16	10.0	0.38	18	10.0	0.36	12
12.0	0.31	25	11.0	0.58	44	11.0	0.74	54
13.0	0.33	28	12.0	1.07	75	12.0	1.04	72
14.0	0.56	52	13.0	1.13	78	13.0	1.40	86
15.0	1.18	81	14.0	1.25	83	14.0	1.63	96
16.0	1.38	87	15.0	1.56	95			
17.0	1.48	90	16.0	1.64	99			
18.0	1.59	94						

a) Concentration of NaOH used as the mercerizing agent.
b) Intensity ratio of I $(10\bar{1})_{II}$ to I $(002)_I$.
c) Degree of transition.

The observed intensity ratio and the corresponding degree of transition estimated from the calibration curves are tabulated in Table I and II.

In Fig. 7 and 8 the obtained degree of transition is plotted against the concentration of alkali. The main transition ranges are tabulated in Table III. As shown in Fig. 7 and Fig. 8, the higher resistance against the mercerization is characteristic of the linters pulp, whereas no difference between the sulfate and the sulfite pulp is observed in the transition behavior. The elevation of the temperature of the alkali treatment induces the increase in the concentration of the main transition range.

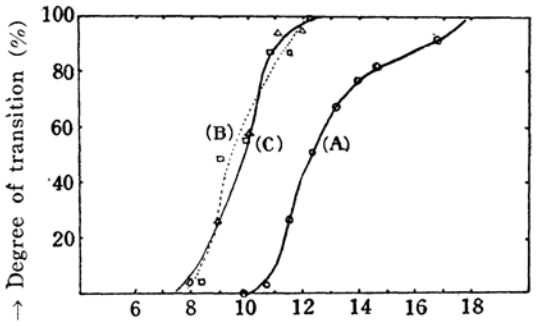

Fig. 7. Phase transition curves (at 20°C).
(A) the linters pulp
(B) the sulfate pulp
(C) the sulfite pulp

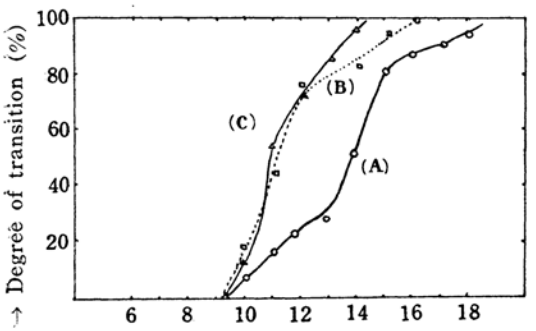

Fig. 8. Phase transition curves (at 45°C).

TABLE III
THE MAIN TRANSITION RANGE (EXPRESSED IN THE CONCENTRATION OF NaOH)

Pulp Samples	Temperature of Treatment	
	20°C	45°C
Linters Pulp	11-16	10-17
Sulfate Pulp	8-11	10-15
Sulfite Pulp	8-11	10-13

Discussion

The results reported here were based on the assumption that the decrystallization, which accompanies the mercerization, proceeds in proportion to the degree of transition. This assumption may contradict the results obtained in the preceding paper[3,4], but it must be mentioned that the pattern of cellulose II appears only for the sample whose cellulose II content is more than 40 per cent., according to the results of the test experiment. Therefore the decrystallization could not be discriminated from the phase transition by such an empirical method.

The transition range of the sulfate pulp is not different from that of the sulfite pulp, which is in good agreement with the lateral order distribution reported in the the preceding paper[4]. On the contrary, Rånby and Mark[2] reported that the sulfate pulp shows a higher resistance against the mercerization than the sulfite pulp. This difference may be due to the difference in the fine structure of both sulfate pulps. According to the results obtained here, it may be concluded that the crystalline structure of the sulfate pulp is not different from that of the sulfite pulp.

As shown in Fig. 8 all pulp samples show at 45°C an increased resistance against the complete mercerization. This tendency is in agreement with the results obtained by Sisson and Saner[1].

The variation in the lateral order distribution on the mercerization process which was reported in the previous paper[3] should be discussed again with the knowledge of transition obtained here. The variation range of lateral order distribution of the linters pulp at 20°C almost corresponds to the transition range obtained here, so that the preceding conclusion must be altered as follows: on the mercerization process the lowering of the lateral order is accompanied simultaneously with the phase transition; in other words, the former does not precede the latter. The misunderstanding of the transition range in the previous paper[4] was due to the visual estimation of the X-ray diffraction diagrams.

One may obtain further information on the mercerization mechanism, comparing the phase transition behavior with the the variation in the lateral order distribution acompanying it.

4) Y. Tsuda and S. Mukoyama, This Bulletin, **29**, 748 (1956).

Summary

The phase transition ranges were obtained at 20°C and 45°C for the linters pulp, the sulfate pulp and the sulfite pulp. It was concluded that the resistance of the linters pulp against the mercerization is higher than those of the wood pulp, where as no difference is observed between the sulfate and the sulfite pulp.

It was suggested also that the visual estimation of the X-ray diffraction diagrams may lead to a misunderstanding of the phase transition range.

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