Morphological and Structural Formation of the Regenerated Cellulose Membranes Recovered from Its Cuprammonium Solution Using Aqueous Sulfuric Acid

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ABSTRACT: Morphological and structural formation of the regenerated cellulose membranes from its cuprammonium hydroxide solution by acid coagulation was investigated. Scanning electron microscopic observation revealed that the morphology of the membranes changed drastically as functions of both the cellulose concentration in the original cellulose solution C_{Cell} and the concentration of sulfuric acid as a coagulant C_{H2SO4}. It was found that at a constant polymer concentration (8 wt %) the membrane prepared by using 5 wt % aqueous sulfuric acid exhibits higher water flux, far smaller swelling anisotropy parameter L_t, and larger porosity P_r with a thinner skin structure, and these parameters were proven to be associated with lower $(1\bar{1}0)$ crystal plane orientation coefficient $f_{\|(1\bar{1}0)}$ compared with those for the membranes obtained by aqueous sulfuric acid with more than 10 wt %. On the other hand, at constant coagulant concentration (10 wt %) the membrane prepared by using the polymer solution with 5 wt % shows far greater P_r with practically no distinct skin structure; hence, a higher flux. The drastic changes in the morphology and structural parameters as functions of C_{Cell} and C_{H2SO4} were found to be well correlated with abrupt changes in material transportation (copper ion, ammonium ion, and water) from the polymer solution to aqueous coagulants as a function of C_{Cell} and C_{H2SO4}. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1669–1678, 1999

Key words: cuprammonium regenerated cellulose membrane; morphological distribution; sulfuric acid coagulants; material transportation; swelling anisotropy

INTRODUCTION

It has been demonstrated[1] that morphology of the regenerated cellulose membranes recovered from its cuprammonium hydroxide solution is categorized due to cationic species or pH of coagulants into typically four types, correlated with the changes in the circular dichroism (CD) spectra of the cellulose solution during its coagulation process. In this respect, it has been confirmed that cellulose exists as a δ chelate structure with coordination of cuprammonium ions to hydroxyl groups at C_2 and C_3 positions of the glucopyranose unit in cuprammonium hydroxide solution.[2] Of the coagulants used, aqueous sulfuric acid was proven to promptly decompose the original cellulose/cuprammonium hydroxide complex. In another line of study, authors[3] also have found that swelling anisotropy behavior of the regenerated cellulose membranes are closely correlated with crystal plane orientation (e.g., $(1\bar{1}0)$ plane orientation coefficient $f_{\|(1\bar{1}0)}$). In the literature, we also have mentioned that the membranes obtained from cellulose/aqueous cuprammonium

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hydroxide solution by aqueous sulfuric acid coagulation systems constitutes of one distinct group in view of the relation between porosity P_r and swelling anisotropy parameter L_t from other membrane groups, but unfortunately, refrained from detailed discussion due to lack of systematical experimental data. Thus, the swelling anisotropy behavior of aqueous sulfuric acid coagulation systems of membranes requires more detailed data, including the morphological observation.

On one hand, although the direct aqueous acid coagulation system towards the cellulose/cuprammonium hydroxide solution has not been applied in practice, this coagulation system has been known to give membranes with a gradient structure having a relatively large pore size, leading to a higher flux performance.[4] Such a membrane has been required to minimize the leucopenia associated with removability of β-2 microglobuline from the blood during hemodialysis using the membranes. Thus, the acid coagulation system has a potential applicability to produce membranes with a high flux if the membrane formation and structural formation by this coagulation system could be fixed.

This means that the change in the chelate or complex structure of cellulose during the coagulation process must be considered to discuss the morphological formation of the membrane besides a simple phase equilibrium study. Previously, Fushimi et al. discussed the relation between the interfacial potential in the coagulation of cuprammonium and the coagulation mechanism.[5] They classified the cuprammonium coagulation mechanism into three types—i.e., copper removal, Norman reaction, and ammonia removal—which were determined by interfacial potential. But the relation between the transportation of substances and the structure of postcoagulation have not been discussed. In addition, the transportation of substances during coagulation is also an important feature to clarify the morphological distribution in the cross-sectional (transverse) direction.

In this article, as an extension of the previous studies, we attempt to differentiate the morphologies and structures of the regenerated cellulose membranes prepared from its cuprammonium hydroxide solution using aqueous sulfuric acid coagulants as functions of the concentration of sulfuric acid and the polymer concentration in the cellulose solution, with special emphasis on swelling anisotropy and flux.

EXPERIMENTAL

Cellulose Solution

Cotton linter supplied by Peterdemings Co., Ltd., was dissolved in an aqueous cuprammonium hydroxide solution according to a known procedure[6] at a cellulose concentration of 8 wt %. The molar composition of the solution (cellulose/Cu/NH_3) was adjusted to constant as 0.08/0.029/0.61. We diluted this cellulose solution by water, and adjusted the cellulose concentration to 5, 6, and 7 wt %. The molar ratio of cellulose, NH_3, and Cu in these solutions was constant. The viscosity-average molecular weight of the cellulose recovered from the above solution by aqueous sulfuric acid was 1.7×10^5, as estimated by using the equation $[\eta] = 3.85 \times 10^{-2} M_w^{0.76}$ established for the cellulose/cadoxen system.[7]

Preparation of the Wet Regenerated Cellulose Membranes

Case I

The cellulose solution was cast on a glass plate (20×19.4 cm) to give a thickness of 250 μm, immersed into 500 mL of coagulants (aqueous sulfuric acid concentration C_{H2SO4} = 5–20 wt %) for 1 min, washed by water at 40°C for 1 min, and regenerated completely by 2 wt % aqueous sulfuric acid C_{H2SO4} for 5 min, followed by washing with water.

Case II

A similar membrane preparation procedure was applied to obtain membranes from the polymer solutions with different polymer concentrations C_{Cell} (=5–8 wt %) using a given aqueous sulfuric acid (C_{H2SO4} = 10 wt %), and the membranes are coded as C_kHs_n (k, polymer concentration; n, sulfuric acid concentration). The wet membranes were subjected to water permeability measurement and scanning electron microscopic observation for evaluation of porosity P_r and a rough estimation of skin (the phase with relatively smaller pore size)-core (the phase with relatively larger pore size) distribution in the thickness direction. The above wet membranes were immersed in acetone extracting water from the membrane, followed by drying in air. The dried membranes were subject to X-ray diffraction and mechanical relaxation measurement.

Cross-Sectional Morphological Distribution

The wet membranes were frozen in liquid nitrogen, and their fractured cross-section, sputtered

with gold, were subjected to scanning electron microscopy at an accelerating voltage of 5 kV (FE-SEM model S-800, Hitachi Co., Ltd., Japan). The five equally divided parts (dz_i, i = 1–5; $dz_i = d_w$, thickness of the membrane in wet state) in membrane thickness direction for the electron micrographs obtained above were analyzed by a high-resolution imaging treatment system (IP-1000, Asahi Chemical Ind. Co., Ltd., Japan) to evaluate the average pore size for each part r_i (i = 1–5) approximated as circular pores from the area S_{pi} of the pore part and the number of pores n_i, by extracting pore parts with monitoring the difference in brightness,[8] as $r_i = (S_{pi}/n_i\pi)^{1/2}$. The average pore size of five parts are defined as $r_1, r_2 \ldots r_5$ from the front surface. From the data porosity for each part P_{ri}, total average porosity $P_{r\mathrm{SEM}}$ was estimated as $P_{ri} = 100\, S_{pi}/S_i$ (%), and $P_{r\mathrm{SEM}} = 100\Sigma S_{pi}/\Sigma S_{si}$ (S_i, total area for each part) was estimated as follows.

Furthermore, skin-core distribution was approximated by d_{z1}/d_w, where d_w is the thickness in the wet state, and d_{z1} is the thickness of a distinctively quite dense phase having an average pore size less than 300 nm by assuming a circular pore from the front surface of the SEM micrographs. The porosity for this skin part P_{rz1} is also estimated in a similar manner described above. In this connection an apparent porosity P_{ra} can be estimated as $P_{ra} = 100(1 - \rho_a/1.52)$, where ρ_a is the apparent density of the membrane, and 1.52 (g/cm^3) is the density of the cuprammonium-regenerated cellulose fiber.[9]

Swelling Anisotropy Parameter of Dried Membranes and Water Permeability of the Wet Membranes

Swelling anisotropy parameters L_t (d_w/d_d, d_d is the thickness in the dried state), L_l (l_w/l_d, l_w, and l_d are lengths of the surface in the wet and dried state), and V_s (volumetric swelling degree) was measured according to a previous method.[3] Water permeability UFR of the wet membranes, with an area of 2.4 cm^2, was estimated from the water flux under the pressure difference of 400 mmHg at 25°C, and expressed as mL/h · m^2 · mmHg.

Transportation of Substances from the Original Cellulose Solution into Coagulants

To estimate the initial transportation rate of substances, 1 mL of each coagulant was poured over 3 g (=$W_{(0)}$) of the cellulose solution (cellulose concentration, $C_{Cell(0)}$) placed in a laboratory dish with an area of 4.5 cm^2, and stood for given contacting time (5 s to 5 min) at 26°C. After each run (at a given contacting time), the resulting coagulant was removed and subject to analysis for cupric ion and ammonia transported into coagulant ($W_{Cu(c)}$ and $W_{NH3(c)}$, respectively) as described later. At the same time, the weight of the resultant cellulose solution ($W_{(c)}$) was measured. Using the initial amounts of substances (Cu, $W_{Cu(0)}$; NH_3, $W_{NH3(0)}$; H_2O, $W_{H2O(0)}$) in the original cellulose solution, their transportation ratio are defined as follows:

$$\Delta W\ (\%) = 100W_{(c)}/W_{(0)} \tag{1}$$

$$\Delta Cu\ (\%) = 100W_{Cu(0)}/W_{Cu(0)} \tag{2}$$

$$\Delta NH_3\ (\%) = 100W_{NH3(c)}/W_{NH3(0)} \tag{3}$$

$$\Delta H_2O\ (\%) = 100(W_{(c)} - W_{(0)} - W_{Cu(0)} - W_{NH3(0)})/W_{H2O(0)} \tag{4}$$

Cellulose concentration ($W_{Cell(c)}$) after coagulation in the original solution is defined as

$$W_{Cell(c)}\ (\%) = 100\ C_{Cell(0)}/(100 - \Delta W) \tag{5}$$

Here, the transportation of H_2SO_4 in the coagulant into the cellulose solution was not considered. Therefore, $W_{Cell(c)}$ contains some error. In this article, ΔNH_3, ΔCu, and ΔH_2O were mainly discussed.

Estimation of Copper Transported

Into a given volume of resulting coagulant 10 vol % of aqueous 15 wt % sulfuric acid solution was added to keep the pH of the sample solution below 2.0, and the absorbance of the solution at 810 nm was measured by a spectrophotometer (U-3400, Hitachi Co., Ltd., Japan), and the copper concentration was determined from the calibration curve obtained for aqueous cupric sulfate.

Estimation of NH_3 Transported

The given amount of resulting coagulant was colored by adding *o*-phthaladehyde, excited by light with a wave number of 390 nm, and the intensity of fluorescence at 450 nm was measured by a fluorescence photometer (F-4500, Hitachi Co., Ltd., Japan). The intensity was transformed to

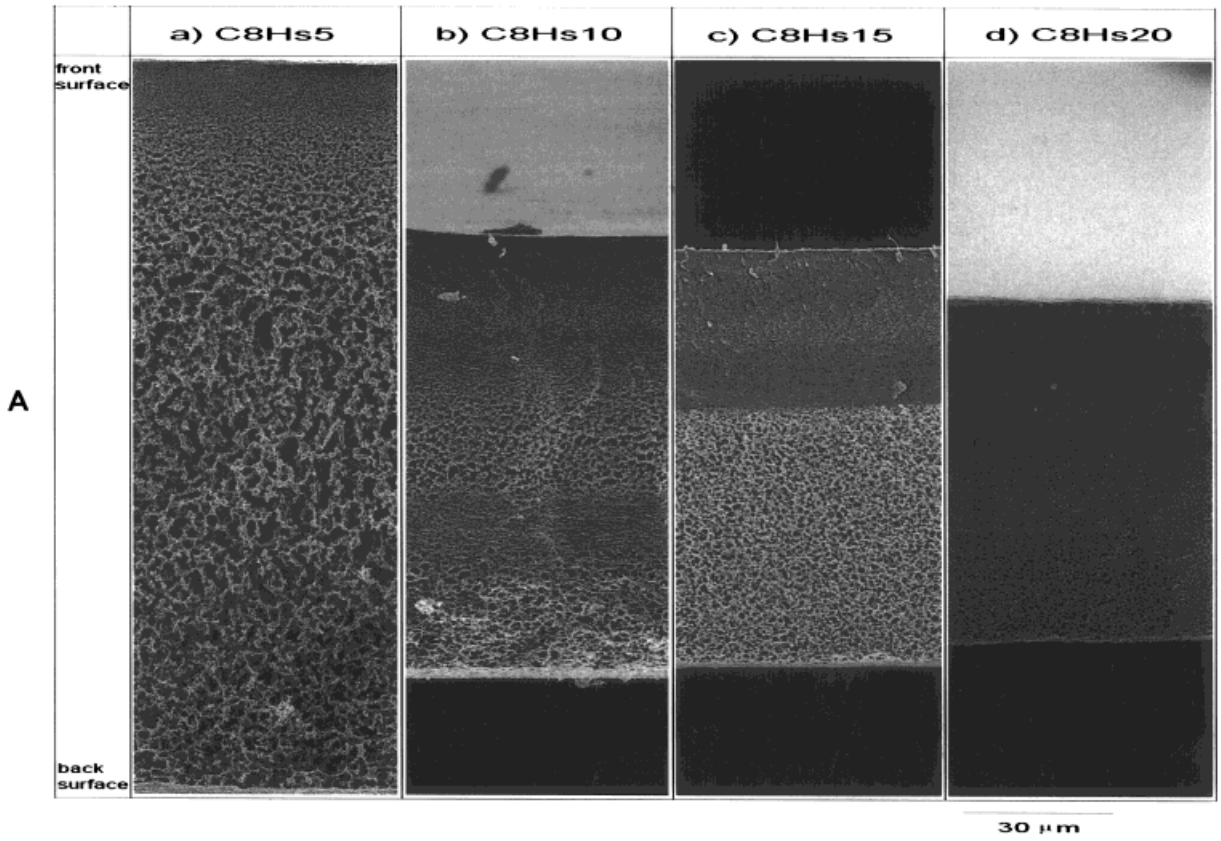

Figure 1 SEM micrograph of the cross section (thickness direction) of regenerated cellulose membranes: (A) Case I; a, C8Hs5; b, C8Hs10; c, C8Hs15; d, C8Hs20; (B) Case II; a, C5Hs10; b, C6Hs10; c, C7Hs10; d, C8Hs10.

the amount using the calibration curve obtained for aqueous ammonium chloride in advance.

X-ray Diffraction Analysis

Orientation of crystal planes [$(1\bar{1}0)$ and (200)] of the dried membrane by substituting water in the wet membranes with acetone was analyzed by irradiating either perpendicular to the cross-section (that is, parallel to surface) or to the surface of the membranes by using an X-ray diffractometer (DIP100S, Mac Science Co., Ltd., Japan). Diffraction intensities ($I_{\parallel(1\bar{1}0)}$, $I_{\perp(1\bar{1}0)}$) at $2\theta = 12°$ and those ($I_{\parallel(200)}$, $I_{\perp(200)}$) at $2\theta = 21°$ were measured. The orientation factor $f_{\parallel(1\bar{1}0)}$ for the $(1\bar{1}0)$ plane to the parallel direction to the membrane surface was evaluated as described in an earlier article.[3]

RESULTS AND DISCUSSION

Morphological Formation

Figure 1(A) and (B) shows the electron micrographs of the wet membranes obtained by varying concentrations of sulfuric acid C_{H2SO4} as the coagulant, using a polymer solution with a constant polymer concentration C_{Cell} (= 8 wt %) (A) (Case I) and of those obtained by varying polymer concentrations C_{Cell} (= 5–8 wt %) using a given coagulant (C_{H2SO4} = 10 wt %) (B) (Case II).

Here, the front and back surfaces (the upper and the bottom sides in the photographs, respectively) mean the surfaces contacting the coagulant and glass plate, respectively. Obviously, polymer particles are mutually connected to form pores. Figure 1(A) reveals that (1) the thickness of the membranes d_w drastically decreases when C_{H2SO4} goes up from 5 to 10 wt %, then continues to decrease gradually with an increase in C_{H2SO4}; (2) the gradient pore structure is seen for all membranes from the front surface to the inside, but the pore size in the middle to the back surface seems to be almost constant for each membrane; and (3) all membranes have skin structure along the front surfaces. Figure 1(B) reveals that (1) the membrane thickness decreases with an increase in C_{Cell}, approaching an asymptotic thickness in

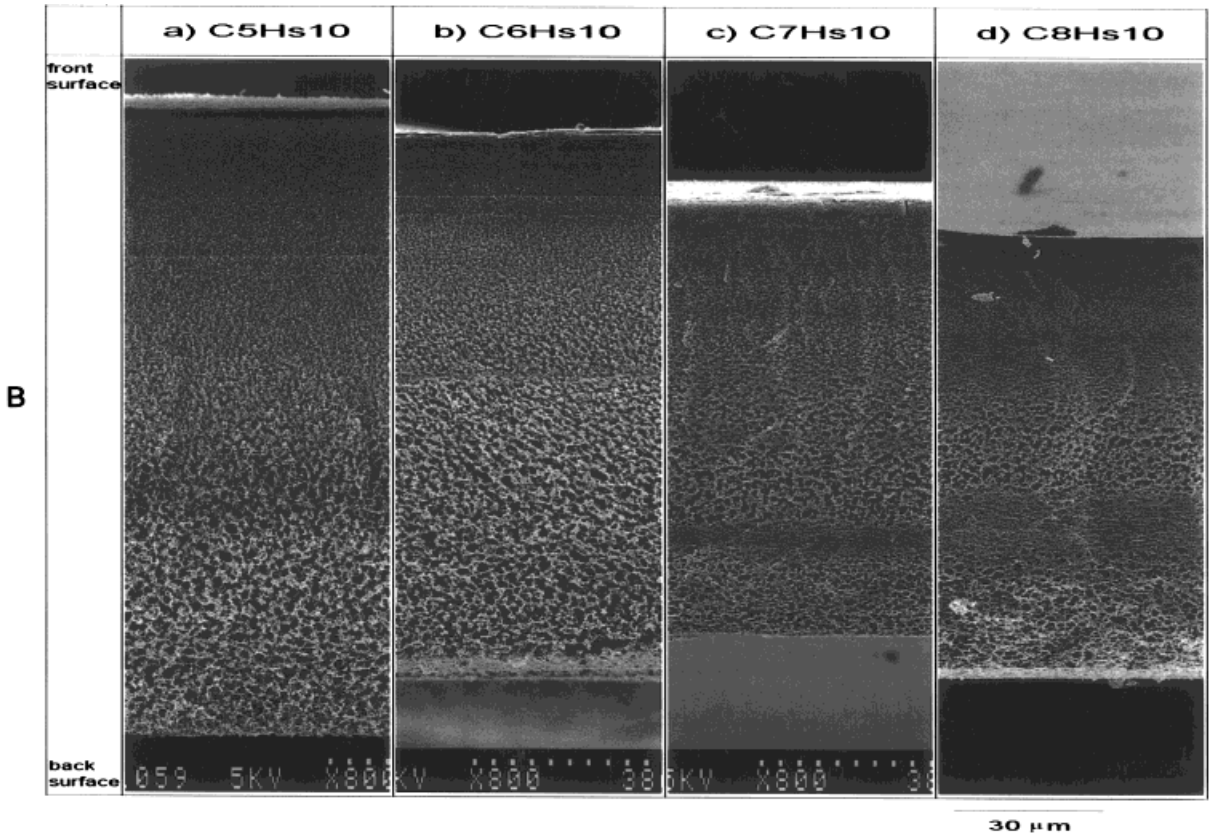

Figure 1 (*Continued from the previous page*)

$C_{Cell} \geqq 7\%$; and (2) all the membranes exhibit a typical gradient structure with relatively thin skin, compared with those in Figure 1(A). The dark and dense phase seen in the middle part of C7Hs10 might be formed during the freezed–dry process of the membrane. The skin phases are marked as d_{z1}, d_{z1}/d_w, and the porosity P_{rSEM}, P_{rz1} estimated from the micrographs are shown in Table I as well as the sample preparation conditions, thickness in wet d_w, water permeability UFR, apparent porosity P_{ra}, and swelling parameters L_t and V_s.

Flux Properties

Table I tells us that UFR, d_w and d_{z1}/d_w dramatically changes as a function of C_{H2SO4} for Case I when C_{H2SO4} goes up from 5 to 10 wt %. UFR for

Table I Preparation Conditions, Morphological, Structural, Flux, and Swelling Parameters of the Regenerated Cellulose Membranes

	Preparation Conditions										Transportation Parameters				Swelling Parameters	
Sample	C_{Cell}/ wt %	C_{H2SO4}/ wt %	d_w/ μm	d_w/ C_{Cell}	UFR/ mL/m²/h/ mmHg	P_{ra}/ %	P_{rSEM}/ %	P_{rz1}/ %	d_{z1}/ d_w/ %	P_{rz1}/ d_{z1}	Cu/ %	NH_3/ %	H_2O/ %	$f_{\|(1\bar{1}0)}$	L_t	V_s
C8Hs5	8	5	160	20.0	159.0	71.9	43.1	13.3	15.2	0.88	20.4	27.9	−1.0	0.236	1.41	1.53
C8Hs10	8	10	120	15.0	27.0	31.2	27.1	11.2	31.2	0.36	28.2	36.4	9.3	0.463	1.65	1.90
C8Hs15	8	15	106	13.3	8.8	44.0	23.2	6.0	33.7	0.18	29.8	38.0	15.5	0.451	1.67	1.86
C8Hs20	8	20	105	13.1	7.1	36.1	16.4	4.1	34.4	0.12	33.9	45.2	17.5	0.498	1.64	1.89
C7Hs10	7	10	96	13.7	30.7	38.3	30.4	15.2	14.6	1.04	23.6	30.8	7.1	0.414	1.92	2.01
C6Hs10	6	10	97	16.2	113.0	47.9	28.5	13.3	11.3	1.18	27.1	30.5	4.6	0.424	1.83	1.93
C5Hs10	5	10	104	20.8	672.0	64.6	34.3	18.9	14.0	1.35	28.3	30.5	2.0	0.252	1.83	1.96

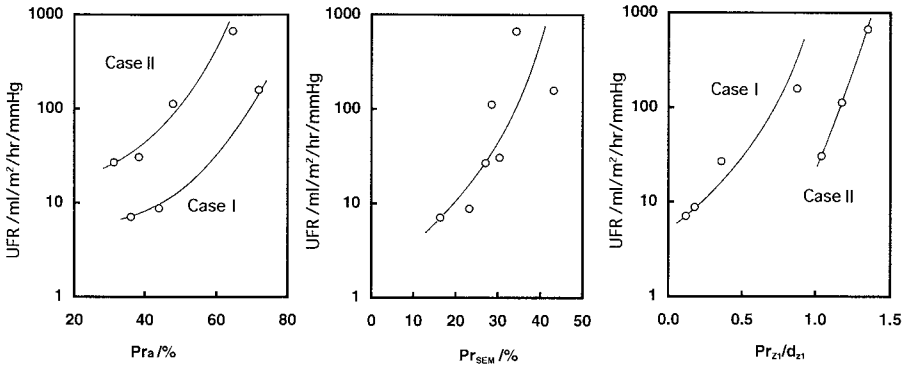

Figure 2 Dependence of total flux UFR on P_{ra}, $P_{r\mathrm{SEM}}$, and P_{rz1}/d_{z1}.

Case II becomes large, as expected, with the decrease in C_{Cell}, and there seems to be some critical and drastic change between C_{Cell} = 6 and 5 wt %, giving five times the UFR, although such a drastic change is not observed for d_w and d_{z1}/d_w, rather, showing a critical change at C_{Cell} = 8 and 7 wt %. Note that the difference in C_{Cell} leads to the different equilibrium—dissolved state of the cellulose/cuprammonium hydroxide complex with other components (especially H_2O) in the solution when the copper and ammonia are fixed at constant molar ratio against cellulose, as suggested by Miyamoto and Okajima et al.[10]

The total flux UFR is one of interest in the present study, and then it is plotted against P_{ra}, $P_{r\mathrm{SEM}}$, and P_{rz1}/d_{z1} in Figure 2. Obviously, UFR gives two master curves on P_{ra} due to C_{H2SO4} and C_{Cell} dependences, indicating that there is another factor controlling UFR. $P_{r\mathrm{SEM}}$ failed to differentiate the UFR for Case II. UFR-P_{rz1}/d_{z1} seems to give two master curves. Case II showed a larger P_{rz1}/d_{z1} value than Case I. This means that Case II has more of a porous skin phase than Case I. The porosity of the skin phase was considered to control the UFR. The cellulose membrane with a high flux could more easily be obtained by decreasing the cellulose concentration in the solution.

Orientation Parameters

Figure 3(A) and (B) shows the X-ray diffraction patterns of the dried membranes obtained by varying C_{H2SO4} and C_{Cell}, respectively, which have been taken at different irradiation directions. The diffraction peak for the $(1\bar{1}0)$ crystal plane of cellulose II crystals appearing at $2\theta = 12°$ orients selectively parallel to the film surface. From the figures we obtained diffraction intensi-

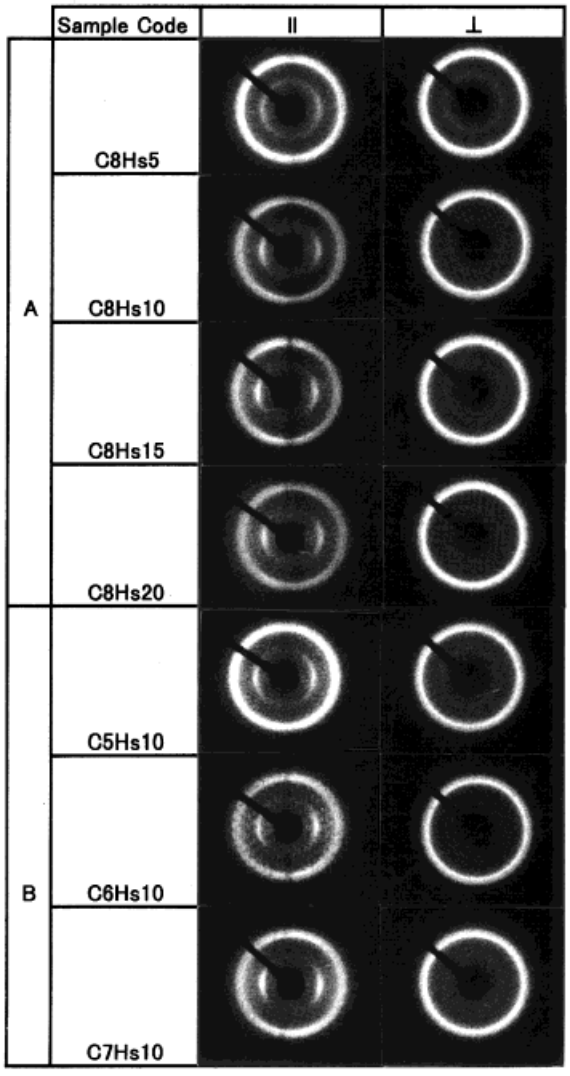

Figure 3 X-ray diffraction patterns of the dried membranes obtained by varying C_{H2SO4} and C_{Cell} taken at parallel (∥) and perpendicular (⊥) directions to membrane surface: (A) case I; (B) case II.

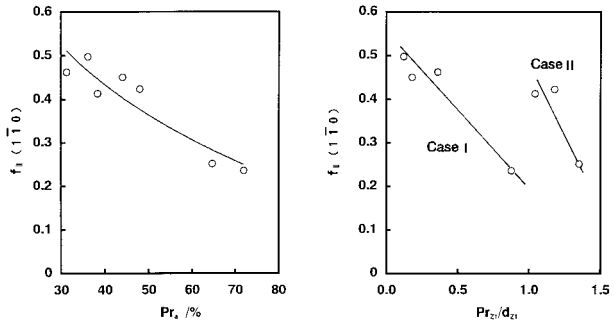

Figure 4 Dependence of the orientation parameter $f_{\|(1\bar{1}0)}$ on P_{ra} and P_{rz1}/d_{z1}.

ties. The orientation factor of the $(1\bar{1}0)$ plane to the parallel direction against the membrane surface $f_{\|(1\bar{1}0)}$ was estimated and is collected in Table I. The $f_{\|(1\bar{1}0)}$ seems drastically changed as a function of C_{H2SO4} and C_{Cell} in the same way observed for the morphological observation. Figure 4 shows that $f_{\|(1\bar{1}0)}$ decreases with an increase in P_{ra}. The reciprocal of P_{ra} is one of the measures of volumetric contraction by coagulants, that is, a bulk dimension decreases selectively in thickness during the sample preparation, as discussed on viscose rayon films by Takahashi.[11] The $f_{\|(1\bar{1}0)} - P_{rz1}/d_{z1}$ gives two master curves for Case I and Case II. This suggests that Case I differs from Case II in the mechanism of volumetric contraction.

Swelling Anisotropy

In our previous work, the swelling anisotropy parameter L_t correlates well with $f_{\|(1\bar{1}0)}$. In addition, we attempted to find other parameters influencing L_t using the data in Table I. The L_t was plotted against P_{ra} and $f_{\|(1\bar{1}0)}$ in Figure 5. L_t

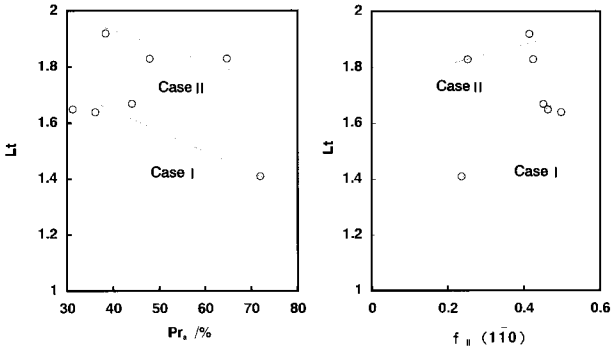

Figure 5 Dependence of the swelling anisotropy parameter L_t on P_{ra} and $f_{\|(1\bar{1}0)}$.

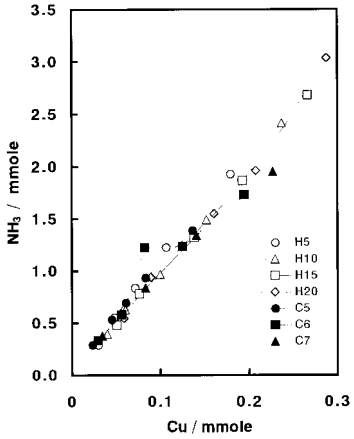

Figure 6 The relative transportation ΔNH_3 against ΔCu from the original solution into coagulants at various coagulation time until 5 min: ○, C8Hs5(H5); △, C8Hs10(H10); □, C8Hs15(H15); ◇, C8Hs20(H20); ●, C5Hs10(C5); ■, C6Hs10(C6); ▲, C7Hs10(C7).

tends to decrease with an increase in P_{ra} for both cases, and to increase with an increase in $f_{\|(1\bar{1}0)}$, showing two master curves for Case I and Case II. The hydroxyl groups of cellulose molecules locate on the $(1\bar{1}0)$ plane surfaces of cellulose II crystal, as pointed by previous work.[11] The $(1\bar{1}0)$ plane orientation was considered to cause water molecule retaining between the $(1\bar{1}0)$ plane stabilized by hydrogen bonding. Then anisotropic swelling occurred, specifically at the membrane thickness, as showed previously.[3] The larger volumetric contraction causes the larger $f_{\|(1\bar{1}0)}$ and L_t.

Transportation Properties

Figure 6 shows that the relation between the molar number of NH_3 and that of Cu at a given coagulation time up to 5 min for Case I and Case II is almost the same relation. Previously we showed the molar ratio of NH_3/Cu for various kinds of coagulants.[1] The order of the transported molar ratio for the sulfuric acid coagulant was about 10. This coagulation system was considered to decompose the complex of cellulose with cuprammonium hydroxide (regeneration). As an index of removability of components, the estimated percentage or each component at coagulation time $t_c = 5$ min are also complied in Table I. In the cellulose solution, the largest amount of component is water (over 80 wt %). The transportation parameters ΔH_2O is considered to the index of the volumetric contractive power of the structure. We select ΔCu as the index of coagulation

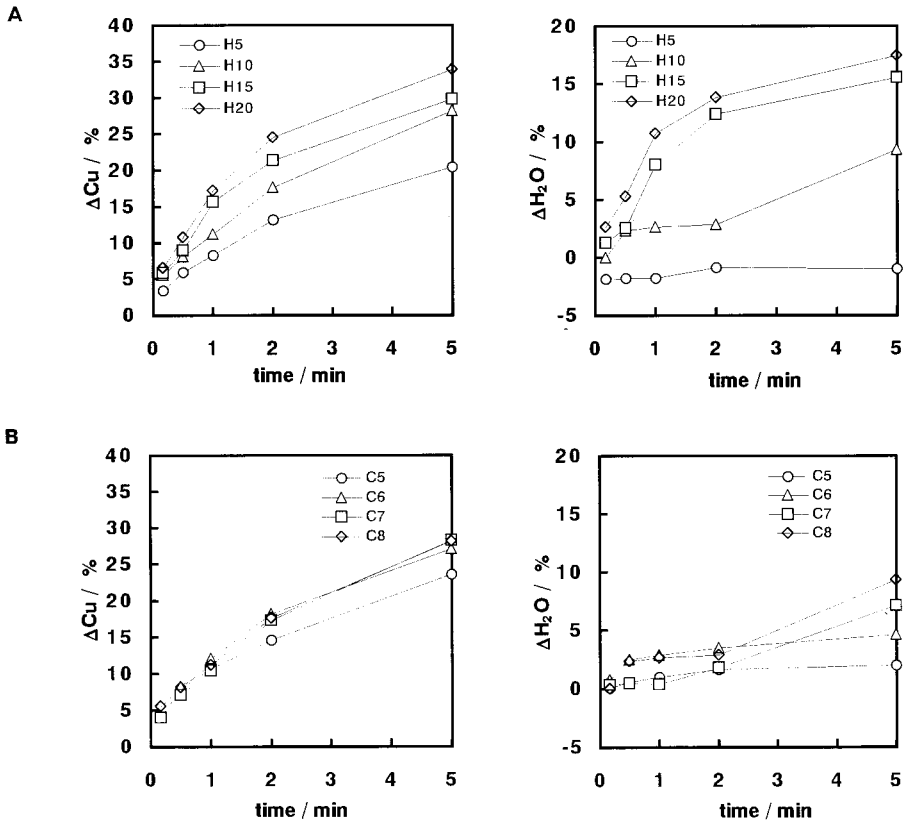

Figure 7 Material transportation (copper ΔCu and water ΔH_2O) from the original solution into coagulants against coagulation time *tc:* (A) Case I; ○, C8Hs5(H5); △, C8Hs10(H10); □, C8Hs15(H15); ◇, C8Hs20(H20); (B) Case II; ○, C5Hs10(C5); △, C6Hs10(C6); □, C7Hs10(C7); ◇, C8Hs10(C8).

and regeneration, ΔH_2O as the index of degree of volumetric contraction, as follows.

All the morphological changes and structural formations, discussed later, should be related to the material transportation (copper ΔCu and water ΔH_2O) from the original solution, and these are plotted against coagulation time t_c in Figure 7(A) and (B). For Case I, the removability of H_2O is increasing when C_{H2SO4} goes up from 5 to 10 wt %, clearly corresponding to the above phenomenological observation. For Case II, ΔCu and ΔH_2O also seem to slightly increase from C_{Cell} = 5 to 6 wt %, corresponding again to the above phenomenological observations for this system. The removability of components increased rapidly at an early stage, and then slightly with coagulation time, except for C_{H2SO4} = 5 wt %. It seems that the delay of coagulation occurs at the inside position from the interface of the coagulant and this may cause the formation of gradient pore-size distribution with a larger pore on back side contacted with the glass plate.

Effects of Transportation Parameters on Morphological and Structural Formation

It is now important to know the determinants of the morphological and structural formation, and we attempted to examine this in view of material transportation. In Figure 8 the apparent porosity P_{ra}, the membrane thickness in wet d_w, as normalized by cellulose concentration C_{Cell} of the solutions used d_w/C_{Cell}, and the skin-core parameter d_{z1}/d_w are plotted against transportation parameters ΔH_2O listed in Table I. Naturally, the larger ΔH_2O showed the lower P_{ra} and d_w/C_{Cell} for both Cases I and II. However d_{z1}/d_w for Case I monotonously increases with an increase in ΔH_2O, while that for Case II is independent of this. The reciprocal of P_{ra} is one of the measures of a volumetric contractive power of coagulants as described before in this article. In this case, two types of contraction mechanisms seem to occur: one is thickening of the skin phase (Case I), another is a gradual densification of network struc-

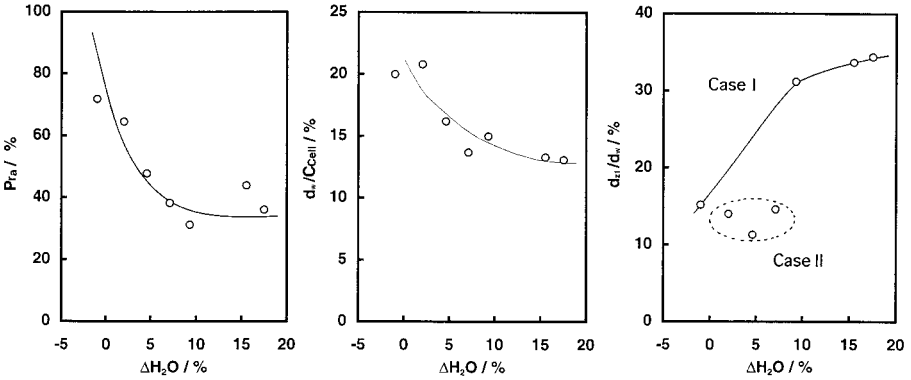

Figure 8 Dependence of the apparent porosity P_{ra}, d_w/C_{Cell} and the skin-core parameter d_{z1}/d_w on transportation parameter ΔH_2O.

ture of the thickness direction (Case II). For Case II, the distance between cellulose molecules in the solution may change with the cellulose concentration. If the limitation of the molecular distance (density) of the cellulose molecules in the solution control the bonding power with other molecules during coagulation, the starting point of the thickening of the skin phase may be over 8 wt % cellulose concentration under the same coagulation condition.

The orientation parameter $f_{\|(1\bar{1}0)}$ is similarly plotted in Figure 9. The $f_{\|(1\bar{1}0)}$ increased with an increase in the transportation parameters (ΔCu and ΔH_2O) in general for both cases. Dehydration power represented by ΔH_2O during coagulation controlled the $f_{\|(1\bar{1}0)}$. Especially, C5Hs10 gives the low $f_{\|(1\bar{1}0)}$, regardless of the larger ΔCu. This means that the degree of completeness of the $(1\bar{1}0)$ plane formation may be different from others. Because Cu ion coordinated with hydroxyl groups at the C_2 and C_3 position of the glucopyranose unit in cuprammonium hydroxide solution as a δ chelate form,[12] the change in the cellulose–cuprammonium hydroxide complex in a low polymer concentration solution might effect the formation of the $(1\bar{1}0)$ crystal plane by steric hindrance despite the larger ΔCu.

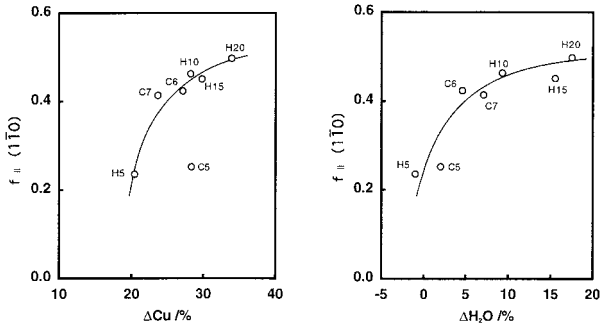

Figure 9 Dependence of the orientation parameter $f_{\|(1\bar{1}0)}$ on the transportation parameters ΔCu and ΔH_2O.

CONCLUSION

Morphological and structural formation of the regenerated cellulose membranes from its cuprammonium hydroxide solution by acid coagulation was investigated in connection with the water flux and the dimensional stability of the membrane against water. Scanning electron microscopic observation revealed that the morphology of the membranes changes drastically as functions of both the cellulose concentration in the original cellulose solution C_{Cell} and the concentration of sulfuric acids as the coagulant C_{H2SO4}. It was found that at constant polymer concentration (8 wt %) the membrane prepared by using 5 wt % aqueous sulfuric acid exhibits a higher water flux, far smaller swelling anisotropy parameter L_t, and larger porosity P_r with a thinner skin structure, and these parameters were proven with a lower $(1\bar{1}0)$ crystal plane orientation coefficient $f_{\|(1\bar{1}0)}$ compared with those for the membranes obtained by aqueous sulfuric acid with more than 10 wt %. In the case of a constant coagulant concentration (10 wt %), the membrane prepared by using the polymer solution with 5 wt % shows far greater P_r with practically no distinct skin structure; hence, a higher flux. The drastic changes in the morphology and structural parameters as functions of C_{Cell} and C_{H2SO4} were found to correlate with the abrupt changes in material transportation (copper

ion and water) from the polymer solution to aqueous coagulants as functions of C_{Cell} and C_{H2SO4}.

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