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Fibrillation tendency of cellulosic fibers—part 3. Effects of alkali pretreatment of lyocell fiber

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Abstract

The influences of pretreatments with different alkalis on the fibrillation tendency of lyocell fiber were investigated. The fibril number (FN_{pre}) decreased after pretreatment in aqueous sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions at concentrations between 3.0 and 7.0 mol/l, and minimized at 5.0 mol/l. The water retention value of the fiber after the pretreatment (WRV_{pre}) in NaOH and KOH at the concentration where the FN_{pre} was minimized was 0.66 cm^3/g. Contrarily, the FN_{pre} with trimethylammonium hydroxide (TMAH) increases with increasing the concentration and weight loss. Analysis using scanning electron microscope suggested the uniform reorganization of the macrofibrils of the lyocell fiber treated with 5.0 mol/l of NaOH solution while the pretreatment in TMAH and LiOH led to the uneven reorganization, resulting in the acceleration of fibrillation. The results indicate that the fibrillation of lyocell fiber is retarded when the fiber structure is uniformly reorganized without the high loss of cellulose component.
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Keywords: Alkali pretreatment; Alkaline retention value; Fibrillation; Lyocell; Scanning electron microscope; Weight loss; Water retention value

1. Introduction

Lyocell fibers, which is a regenerated cellulose manufactured by means of *N*-methyl morpholine-*N*-oxide dissolution followed by coagulation, are eco-friendly products and are used widely in apparel and other fashion for their great comfort to wear.

In the swollen state lyocell has an extensive fibrillation tendency owing to linear high crystalline fibrillar morphology (Nemec, 1994; Rohrer, Retzl, & Firgo, 2001). The fibrillation tendency of lyocell enables this fiber to be used in specific finishing effects such as peach skin, silk touch and soft denim. On the other hand, the fibrillations induce, e.g. rope marking defect in hank finishing, graying of dyed fabrics and a change of handle of clothes, that spoils garments features (Rohrer et al., 2001). Efforts to control the fibrillation tendency of lyocell fibers by dyeing with reactive dyestuffs or treating fabrics with crosslinking agents are undergone (Nechwatal, Nicolai, & Mieck, 1996; Nicolai, Nechwatal, & Mieck, 1998).

An aqueous alkaline solution especially sodium hydroxide is widely used for cellulosic materials to improve their mechanical and chemical properties such as tensile strength, dimensional stability, dyeability and reactivity (Freytag & Donze, 1983). Other alkali solutions and solvent, e.g. aqueous tetraalkylammonium and liquid ammonium have also gained industrial interest owing to recent decrease in their price. The effects of these alkaline solutions on structure, morphology, and reactivity of cellulose polymer have been studied (Colom & Carrillo, 2002; Tanczos et al., 2000; Toth, Borsa, Reicher, et al., 2003; Toth, Borsa, & Takacs, 2003; Vickers, Briggs, Ibbett, Payne, & Smith, 2001). However, effect of the alkaline solution on the fibrillation tendency of the cellulosic fibers has been less investigated.

We have investigated fibrillation tendency of various cellulosic fibers in different types of aqueous alkalis and ethanol solutions at different concentrations (Zhang, Okubayashi, & Bechtold, in press). The fibrillation tendencies were related to two different fibrillation

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resistances, i.e. fibrillation stability to alkalis indicated by $CPF_{conc.}$ and fibrillation sensitivity to alkalis indicated by I_i. The $CPF_{conc.}$ is an extrapolated concentration of the solvent where the fibrillation begins and the I_i is an increase of fibril number to the change of the solvent concentration. Untreated lyocell fiber showed the lowest $CPF_{conc.}$ meaning lowest fibrillation stability and highest I_i meaning highest fibrillation sensitivity to alkalis, resulting in highest fibrillation tendency.

In the present study, the effects of the pretreatment with alkaline solutions on the fibrillation tendency of the lyocell fiber are discussed.

2. Experimental

A staple fiber of lyocell was supplied by Lenzing AG in Austria and used for the experiments. The titer of the fiber was 1.3 dtex and the length was 38 mm. Analytical grade of trimethylammonium hydroxide (TMAH; aqueous 25% sol.), lithium hydroxide (LiOH; >99%) sodium hydroxide (NaOH; >98%), potassium hydroxide (KOH; >99%) and other chemicals were purchased from Fluka.

The lyocell fiber was treated with alkali as follows; 0.5 g fibers was immersed in the aqueous alkaline solution at certain concentration for 2 h at room temperature. After the solution was filtrated through a sintered glass filter (G4), the fiber was washed with hot water at 60 °C for 5 min, neutralized with an acetate buffer containing 0.1 mol/l of acetic acid and 0.1 mol/l of sodium acetate (pH 5.0). The fiber was then washed with water sufficiently until the pH value of the solution indicated 7.0 and dried in an oven at 60 °C for 1 h.

Fibrillation was induced by a method using metal balls with tumbling in water or alkaline solutions (Zhang, Okubayashi, & Bechtold, in press). Degree of the fibrillation was assessed as the fibril numbers counted using an optical microscope. Alkaline retention values (ARV) of the untreated fibers, water retention values of the untreated fiber (WRV) and of the fiber pretreated in the alkaline solution (WRV_{pre}) were also measured by a centrifugal method according to the literatures (Zhang, Okubayashi, & Bechtold, in press).

Weight loss of the fiber during the pretreatment with alkali was determined. 0.5 g of fibers was conditioned at 65% relative humidity and 20 °C for 24 h and weighed (W_1). The fiber was treated with the aqueous alkaline solution at certain concentrations by the same method for the pretreatment of the fiber with alkalis. After the fiber was dried at 105 °C for 2 h, the fiber was conditioned at 65% relative humidity and 20 °C for 24 h again and weighed (W_2). The weight loss (WL) was calculated from Eq. (1)

$$\mathrm{WL}(\%_{\mathrm{w/w}}) = 100(W_1 - W_2)/W_1 \tag{1}$$

Images of the fiber cross sections were obtained using a scanning electron microscope (SEM; HITACHI S-2600H). The sample fiber after the pretreatment without fibrillation test was frozen in liquid nitrogen and broken apart by bending with hands.

3. Results and discussion

3.1. Fibrillation of untreated lyocell fiber in alkaline solution

Fig. 1 shows the relation between number of fibrils (FN) that was induced in the different alkaline solutions and the concentration of the alkaline solutions. The fibril number increases with increasing the alkaline concentration for all alkalis. The degree of increase is larger in the order of TMAH > LiOH > NaOH > KOH. This result is attributed to the large size and non-polar part of TMAH being able to penetrate into the non-polar part of the lyocell fiber (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998).

The alkaline retention values of untreated lyocell fiber are plotted against the alkaline concentration in Fig. 2. The ARVs of the untreated fiber in LiOH, NaOH and KOH solutions increase up to 5.7, 4.8 and 2.4 cm^3/g at the alkali concentrations of 3.0, 3.0 and 7.0 mol/l. After the curves show the peaks of the ARV, the ARVs decrease with increasing the alkali concentrations. These increase and decrease of ARV against the alkali concentrations agree with those reported by Bredereck et al. (Bredereck, Stefani, Beringer, & Schulz, 2003). The ARV in TMAH intensively increases at the low concentration and slightly increases with increase in the concentration up to 2.5 mol/l. No peak of the ARV appears in the graph in the range of the concentration used in this work. The FN is larger in the order of TMAH > LiOH > NaOH > KOH at 2.0 mol/l of the alkali concentration (Fig. 1) whereas the ARV is larger in the order of LiOH > NaOH > TMAH > KOH. The fibrillation is induced

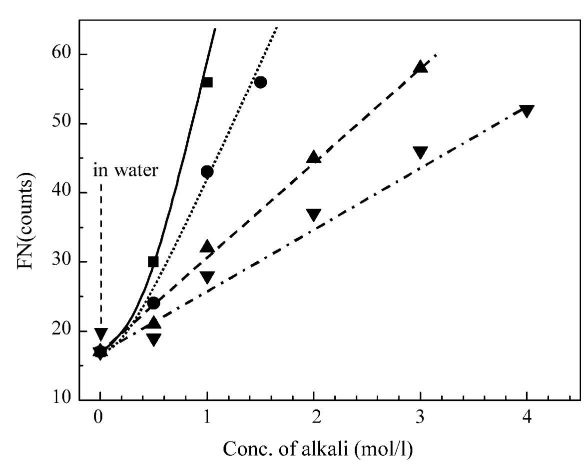

Fig. 1. Plots of fibril number of untreated lyocell fiber against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

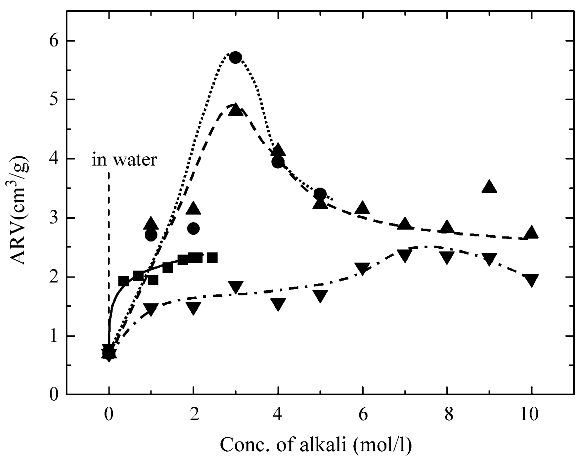

Fig. 2. Plots of alkaline retention value of untreated lyocell fiber against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

not only by the higher swelling but also the penetration of organic alkali TMAH into the non-polar part of the lyocell fiber (Klemm et al., 1998).

3.2. Fibrillation of lyocell fiber pretreated with alkaline solution in water—effect of ARV and WRV_{pre}

The influence of the alkaline concentration for the pretreatment of the lyocell on the fibril number (FN_{pre}) was investigated. The results are shown in Fig. 3. The lyocell fiber was treated with an alkali at a given concentration and then the fibrillation was induced in water by the method using metal balls with tumbling. The FN_{pre} at 0 mol/l of alkaline concentration is the fibril number of the lyocell treated with water. As the fiber was treated with TMAH and LiOH, the fibril number increases with increasing the alkaline concentration. The FN_{pre} of the lyocell treated with NaOH decreases, increases and decreases to seven counts continuously with increasing the alkaline concentration to 5.0 mol/l. Further, the FN_{pre} increases again and reaches

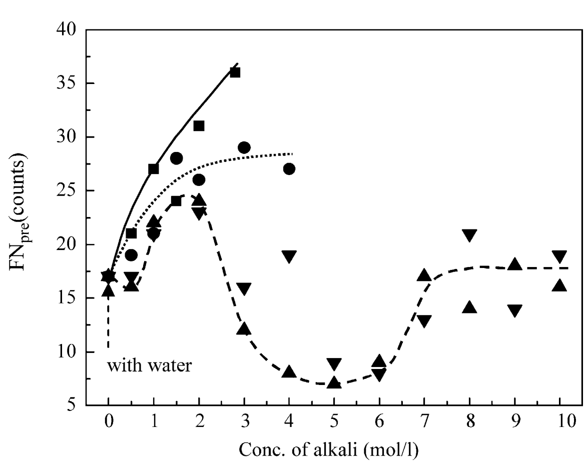

Fig. 3. Plots of fibril number of lyocell fiber pretreated in alkaline solution against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

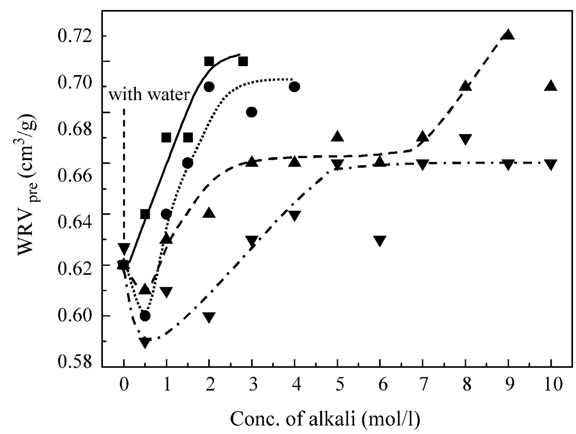

Fig. 4. Plots of water retention value of lyocell fiber pretreated in alkaline solution against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

the constant value at 7.0 mol/l. The curve of the FN_{pre} with KOH is comparable to that with NaOH.

The WRV of the lyocell fiber treated with alkalis was measured and plotted against the alkaline concentration in Fig. 4. The WRV_{pre} with TMAH and LiOH increase up to approximately 0.70 cm^3/g with increasing the concentration of alkaline solution in the range of concentration between 0.5 and 4.0 mol/l. The WRV_{pre} of the fiber treated with NaOH solution increases to 0.66 cm^3/g, the value is unchanged at the concentration between 3.0 and 7.0 mol/l, and then increases again. For the pretreatment with KOH solution the WRV_{pre} increases to 0.66 cm^3/g at the concentration of 5.0 mol/l and the value is constant until the concentration increases to 10.0 mol/l. At the concentration of 5.0 mol/l where the minimal FN_{pre} is obtained the WRV_{pre} with both NaOH and KOH is the equal value of 0.66 cm^3/g though the ARV in NaOH is larger than that in KOH as shown in Fig. 2. The WRV_{pre} with NaOH at the concentration between 3.0 and 7.0 mol/l where the FN_{pre} decreases is unchanged at the value of 0.66 cm^3/g. These results suggest a consecutive structural change of the fibrils in NaOH solution at the concentration between 3.0 and 7.0 mol/l. The change of fibril structure improves the fibrillation tendency of the lyocell fiber.

From the results shown in Figs. 2 and 4 the FN_{pre} is plotted against the WRV_{pre} in Fig. 5. The FN_{pre} with TMAH and LiOH increases with increasing the WRV_{pre}. Considering that the water retention value is related to pore volume of the fiber (Kongdee, Bechtold, Burtscher, & Scheinecker, 2004), the pretreatment with TMAH and LiOH solutions causes larger pore volume, which accelerates the fibrillation. The curves for NaOH and KOH show the same minimal FN_{pre} at the same WRV_{pre} of 0.66 cm^3/g. The fibers pretreated with TMAH and LiOH solutions show no reduction of FN_{pre} at the WRV_{pre} of 0.64 cm^3/g. The effect of the pretreatments with NaOH and KOH is different from those with TMAH and LiOH. The results suggest that no or the lowest fibrillation tendency would be observed on

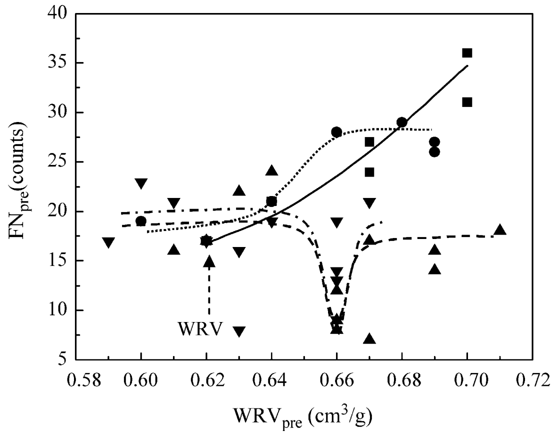

Fig. 5. Plots of fibril number of lyocell fiber pretreated in alkaline solution against water retention value after pretreatment with TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

the fiber which has degree of swelling 0.65–0.66 cm^3/g in water after pretreatment in KOH and NaOH solutions.

3.3. Fibrillation lyocell fiber pretreated with alkaline solution in water—effect of WL

For further discussion of the effect of alkali treatments on the fibrillation tendency, the dependency of the fibrillation on the weight loss of the fiber during the alkaline pretreatment was investigated. The results are given in Fig. 6.

The weight loss of the fiber in TMAH solution remarkably increases from 4.0 to 30$\%_{w/w}$ at the concentration of 2.0 mol/l and then decreased with increasing the concentration. The weight loss in LiOH solution also increases but without any decrease under the condition used in this study. The weight loss in NaOH is approximately the same as that in KOH at each concentration. This similar weight loss of the fiber treated in NaOH and KOH would bring on the similar WRV_{pre} after the pretreatment.

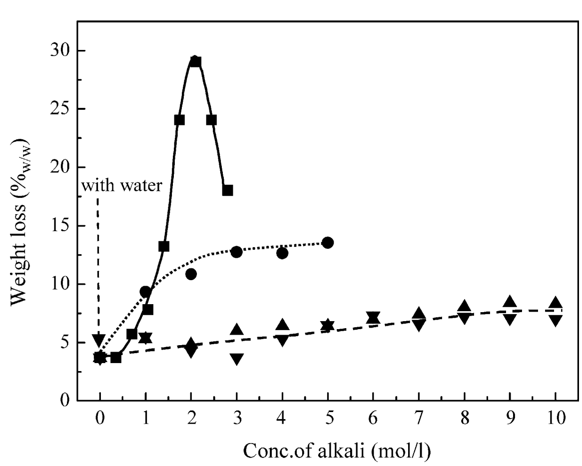

Fig. 6. Plots of weight loss of lyocell fiber in alkaline solution against concentration of TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

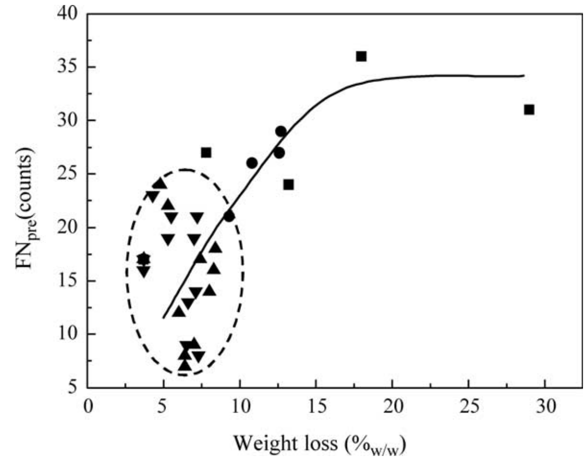

Fig. 7. Plots of fibril number of lyocell fiber pretreated in alkaline solution against weight loss of lyocell fiber treated with TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

As compared to the weight loss in NaOH and KOH, the value in TMAH and LiOH is large. The alkaline solution containing TMAH or LiOH dissolves the cellulose molecules more massively than NaOH and KOH solutions, which enhances the fibrillation.

The FN_{pre} and WRV_{pre} are plotted against the weight loss in Figs. 7 and 8. Both the FN_{pre} and the WRV_{pre} increase up to the weight loss of 15$\%_{w/w}$ and reach at constant value of 35 counts and 0.70 cm^3/g, respectively, regardless of the type of alkalis.

Consequently, the ARV, WRV_{pre} and weight loss of the lyocell fiber treated with alkali increase with increasing the concentration of the alkali except in the FN_{pre}, though the degrees of the increases are different among the alkali. The FN_{pre} of the fiber pretreated with TMAH and LiOH increases with increasing the alkaline concentration. Contrarily, the FN_{pre} is minimized at the concentration of 5.0 mol/l by the pretreatments in NaOH and KOH solutions. The similarities in the relation of

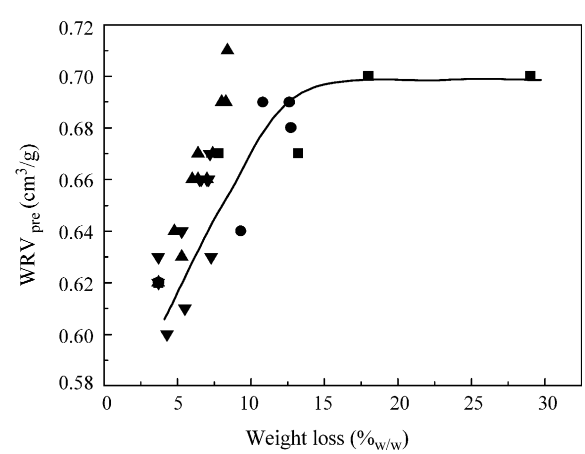

Fig. 8. Plots of water retention value of lyocell fiber pretreated in alkaline solution against weight loss of lyocell fiber treated with TMAH (■), LiOH (●), NaOH (▲) and KOH (▼).

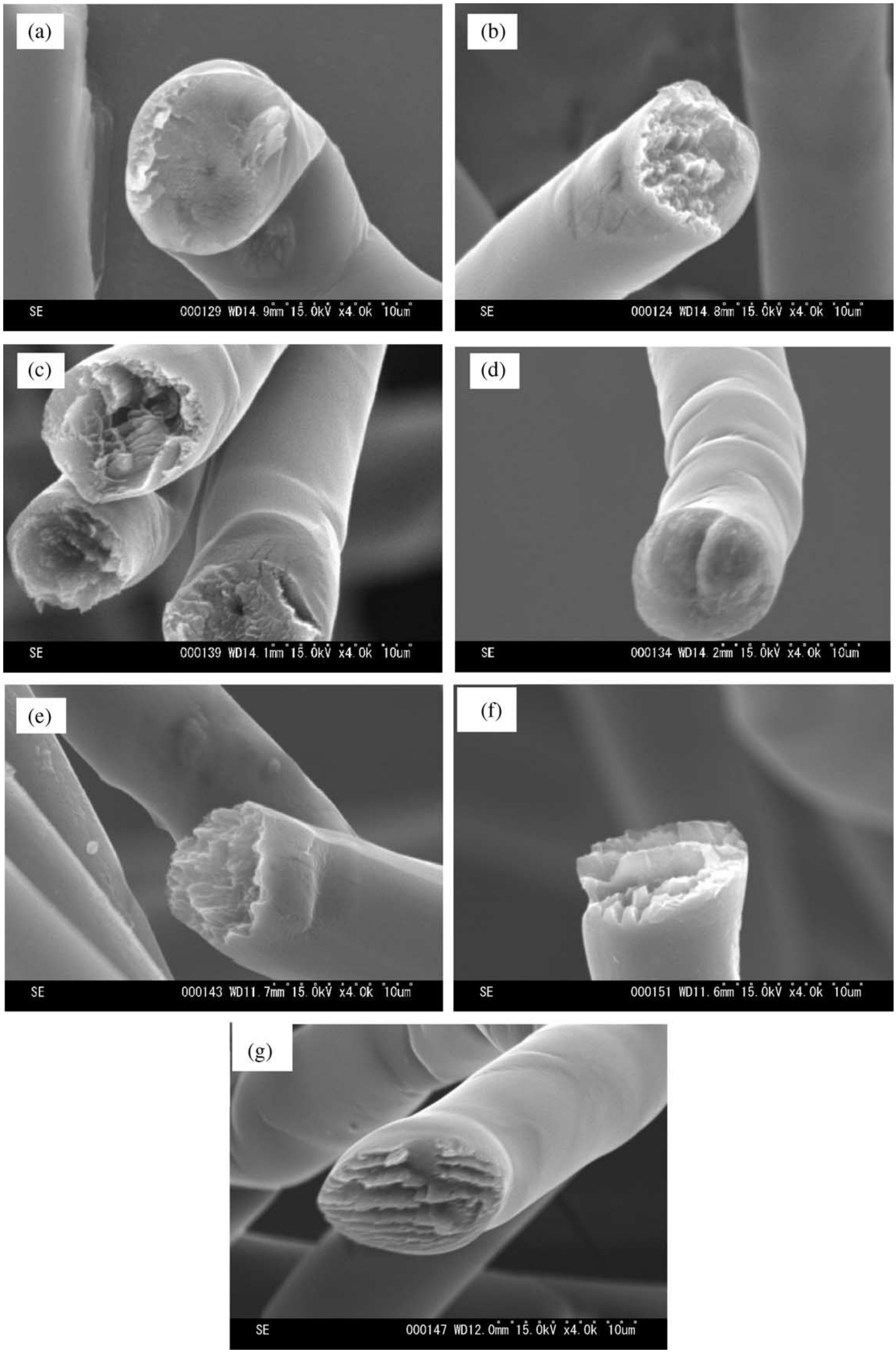

Fig. 9. SEM images of untreated lyocell fiber (a), treated with water (b), 0.5 mol/l of NaOH (c), 5.0 mol/l of NaOH (d), 8.0 mol/l of NaOH (e), 0.5 mol/l of TMAH (f) and 2.1 mol/l of TMAH solution (g).

Table 1
Fibril structure and fibrillation tendency of lyocell fiber after pretreatment with alkali

Code[a]	Alkali	Concentration of alkali (mol/l)	Fiber properties				Fibril structure		
			FN_{pre} (counts)	WRV_{pre} (cm^3/g)	ARV (cm^3/g)	WL ($\%_{w/w}$)	Macrofibril[b] (μm)	Roughness (μm)	Layer of macrofibril
(a)	–	–	21	0.72	–	–	0.2–0.5	0	None
(b)	Water	0.0	17	0.62	0.62	3.7	0.5–1.0	0.2–1.5	Clear
(c)	NaOH	0.5	16	0.61	0.73	4.6	0.2–0.5	0–0.5	Less clear
(d)	NaOH	5.0	7	0.66	1.04	6.4	0.2–0.5	0	None
(e)	NaOH	8.0	14	0.69	1.07	8.0	Unclear	2.0–2.5	Clear
(f)	TMAH	0.5	21	0.64	0.80	4.0	Unclear	2.0–2.5	Clear
(g)	TMAH	2.1	31	0.70	0.89	29.0	Unclear	1.5–2.0	Clear

[a] The codes correspond to those in Fig. 9.
[b] The diameter of the macrofibril or the bundle of macrofibrils.

alkaline concentration, ARV, FN_{pre} and WRV_{pre} between NaOH and KOH solutions as shown in Figs. 3–8 indicate that the mechanism of fibrillation after pretreatments in NaOH and KOH is similar but different from those in TMAH and LiOH.

In order to clarify the structural change during alkaline treatments, image analysis was performed using SEM. Fig. 9 gives the images of the cross section of the fiber. The conditions of the alkaline pretreatment used for the fiber shown in Fig. 9, results of FN_{pre}, WRV_{pre}, ARV and weight loss are summarized in Table 1. The diameter of the macrofibrils and the roughness of the cross section were estimated from the SEM images and given also in Table 1. The roughness is mean length of the protuberance of the macrofibrils. The small and uniform macrofibrils are observed in the cross section of untreated fiber. The surface is smooth and no layer of the fibrils is recognized. On the other hand, the large bundles or layers of macrofibrils are clearly observed on the cross section of the fibers treated in water, 8.0 mol/l of NaOH, 0.5 and 2.1 mol/l of TMAH solutions. The fiber pretreated with aqueous solution containing 5.0 mol/l of NaOH shows a smooth cross section without any bundle and layer of macrofibrils. The fiber surface treated with 0.5 mol/l of NaOH is less rough than that treated with water or 8.0 mol/l of NaOH. The less fibrillation was observed on the fiber with the smooth cross section without the bundle or the layers of macrofibrils. The formation of the bundle and the layers of the macrofibrils clearly elevate the fibrillation. These results suggest that the pretreatments with water and alkalis cause the reorganization of the fibril structure and the fibrillation tendency is related to the reorganized microfibril structure. When the macrofibrils are reorganized unequally, the bundles or the layers of the macrofibrils generate and the fiber shows high fibrillation tendency. Contrarily, the fibrillation is retarded if the uniform reorganization of the fibrils is induced by the treatments. In this study, the uniform reorganization of the macrofibrils was obtained by the alkaline treatment with 5.0 mol/l of NaOH and KOH.

4. Conclusions

In the present study, the fibrillation tendency of lyocell fibers pretreated with alkalis was discussed. The dependency of FN_{pre} on the concentration of alkaline solution indicates that the fibrillation is retarded by the pretreatment in NaOH and KOH solutions at the concentration between 3.0 and 7.0 mol/l and minimized especially at 5.0 mol/l. The WRV_{pre} and WL of the lyocell fiber after the pretreatment both in NaOH and in KOH solutions at the concentration of 5.0 mol/l were 0.66 cm^3/l and 7$\%_{w/w}$. The WRV_{pre} and WL were almost unchanged at the concentration between 3.0 and 7.0 mol/l where the fibrillation was inhibited. The results suggest a consecutive structural change of the fibrils in NaOH and KOH solutions in the range of concentration between 3.0 and 7.0 mol/l. The SEM images show the large bundles or layers of the macrofibrils in the cross section of the fiber treated in water and TMAH solution. Contrarily, the fiber treated in 5.0 mol/l of NaOH solution has the smooth cross section with small and uniform macrofibrils.

Taking the results of the FN, FN_{pre}, ARV, WRV_{pre}, WL and SEM analysis into consideration, it is concluded that the fibrillation tendency is declined when the fibril structure is reorganized uniformly, e.g. by the alkaline treatment in 5.0 mol/l of NaOH and KOH solution where the WRV_{pre} is 0.66 cm^3/g. The facts that the fibrillation is not retarded by the pretreatment in TMAH solution which WRV_{pre} are 0.64 cm^3/l, and that the larger amount of the fiber is dissolved in THAH solution though the ARV with TMAH is smaller than those with other alkalis, imply that not only the extent of swelling but also the weight loss of the cellulose molecules are critical indicators to estimate the fibrillation tendency of the lyocell fiber.

Acknowledgements

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Appendix A. Symbols

TMAH	trimethylammonium hydroxide
WRV	water retention value (cm^3/g)
WRV_{pre}	water retention value after pretreatment with alkali (cm^3/g)
ARV	alkaline retention value (cm^3/g)
W_1	weight of fibers before pretreatment with alkali (g)
W_2	weight of fibers after pretreatment with alkali (g)
WL	weight loss ($\%_{w/w}$)
SEM	scanning electron microscope
FN	fibril number in alkaline solution (counts)
FN_{pre}	fibril number after pretreatment with alkali in water (counts)

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