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Swelling and dissolution mechanism of regenerated cellulosic fibers in aqueous alkaline solution containing ferric–tartaric acid complex—Part II: Modal fibers

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ABSTRACT

Morphological changes of modal fibers swollen in FeTNa (Fe–tartaric acid–NaOH complex solution) were investigated by means of microscopy. FeTNa solutions had a constant molar ratio of 1:3.28 for Fe:tartaric acid. In FeTNa solutions, Fe and free NaOH concentration were in the range of 0.15–0.55 and 0.4–5 M, respectively. Fiber diameter measurements following 2 min of swelling and swelling rate of modal fiber up to 60 min were studied. Depending on Fe and free NaOH concentrations in FeTNa solutions and fiber swelling time; limited swelling, swelling, disintegration, dramatic swelling and dissolution of modal fibers were observed. Lyocell fibers showed the same morphological changes but mainly in different FeTNa solutions. In addition, uneven swelling was observed for lyocell fibers in selected FeTNa solutions. Morphological changes of viscose fibers were different than that of lyocell and modal fibers, which was attributed to its inhomogeneous (skin-core) fiber structure compared to homogeneous fiber structure of lyocell and modal fibers.

1. Introduction

Strong swelling agents such as NaOH, KOH, liquid ammonia are mainly used in the textile pre-treatment of cellulosic fibers in order to improve their shrinkage properties, dimensional stability, crease recovery, dyeability and handle. Alkaline aqueous solution of Fe–tartaric acid complex is also a strong swelling agent and does not show higher risks of hazards than most commonly used NaOH solutions. Hence modification of cellulosic fiber with FeTNa can offer new applications.

Swelling and dissolution studies of cellulosic fibers have been carried out by means of microscopy to observe the morphological changes of fibers progressively. Various solutions such as copper–oxide–ammonia (Rockstroh, 1960), Marshall solvent (Mares, 1956), sulfuric acid (Hearle, 1960), Cadoxen (cadmium amine complex) and FeTNa (Jayme & Neuschäffer, 1957) have been used for this purpose. Compared to other aqueous metal-complex solvents, FeTNa solution has more advantages to be used in the swelling–dissolution studies and viscosimetric analyses of cellulosic fibers owing to being more insensitive to oxidation by air and being odorless. (Jayme & Bergmann, 1956). No waste water problem is expected with regards to the used Fe in metal-complex solutions, while the presence of Cu, Cd and Ni causes environmental problems.

Mainly two methods to dissolve cellulose were used for the preparation of FeTNa solutions namely Valtasaari and Jayme methods. Both Valtasaari and Jayme methods use 1:3:13 molar ratio for Fe:sodium tartrate dihydrate:NaOH in FeTNa solutions, but the former one requires 0.3 M Fe in the presence of 1.5 M free NaOH, while the latter method requires 0.5 M Fe in the presence of 2 M free NaOH (Jayme & Bergmann, 1957; Valtasaari, 1957). The dissolution time of various types of modal fibers such as Super CSSR Typ B, Super Cordenka, Glanzstoff RT were investigated in FeTNa solution which was prepared according to Valtasaari method (Wünsch & Hoffrichter, 1962).

An important commercial way to produce cellulosic fibers, films, non-woven fabrics is the viscose method (Cross et al., 1892). Modal fibers are produced via viscose method by the addition of modifiers to viscose dope and coagulation bath (Cox, 1950). Cellulose is dissolved in *N*-methylmorpholine-*N*-oxide (NMMO) to produce lyocell fibers, which have better mechanical properties than that of viscose type fibers (Liu, Shao, & Hu, 2001; Woodings, 1995). Lyocell fibers have circular cross-section, while viscose and modal fibers have multi-lobal cross-section (Krässig, Schurz, Steadmann, Schliefer, & Albrecht, 1986). Lyocell fibers have nanopores in the bulk of the fiber and a very porous skin layer observed by transmission electron microscopy (TEM). Viscose and modal fibers have

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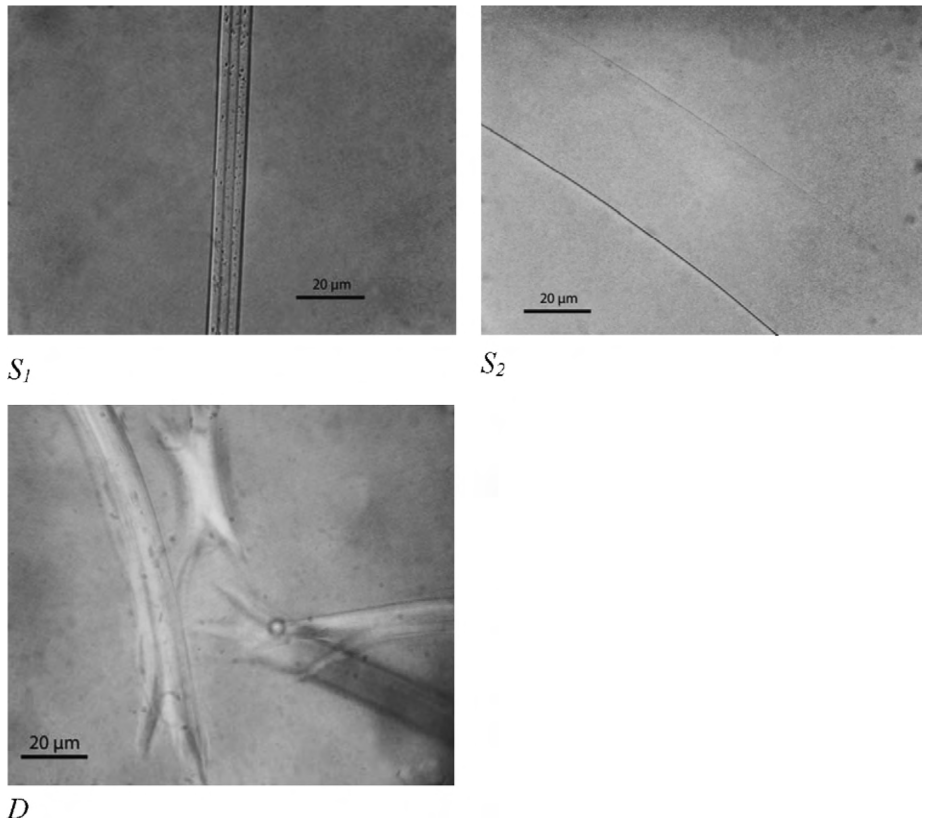

Fig. 1. Morphology of modal fiber during FeTNa treatments; S_1, refers to limited swelling (fiber was swollen in FeTNa solution containing 0.50 M Fe in the presence of 2.5 M free NaOH), S_2 denotes to swelling (fiber was swollen in FeTNa solution containing 0.3 M Fe in the presence of 2.5 M free NaOH), D symbolizes disintegration (fiber was swollen in FeTNa solution containing 0.3 M Fe in the presence of 0.8 M free NaOH).

a very wide pore size distribution from nanometer to micrometer size (Abu-Rous, Ingolic, & Schuster, 2006). The fibrillation tendency of fibers, which occurs due to the high orientation of fibrils, increases in this order: modal < viscose < lyocell (Lenz, Schurz, & Wrentschur, 1993; Sisson, 1960).

Depending on concentrations of Fe, tartaric acid and free NaOH in FeTNa solutions, various FeTNa solutions can be obtained to study the swelling–dissolution mechanism of cellulosic fibers. With this aim, we studied the structural changes of lyocell (Vu-Manh, Öztürk, & Bechtold, 2010) and viscose (Vu-Manh, Öztürk, & Bechtold, in press) fibers *during* FeTNa (Fe:tartaric acid:NaOH molar ratio as 1:3.28:11.84) treatments. The current study presents the structural changes, fiber diameter measurements and swelling rate of modal fibers *during* FeTNa treatments, while comparison to that of lyocell and viscose fibers were also given.

2. Experimental procedure

2.1. Materials

Modal staple fibers (1.3 dtex titer and 38 mm length) without spin finishing were provided from Lenzing AG. Analytical grade sodium hydroxide NaOH (>98%) from Fluka; iron (III) chloride-6 hydrate ($FeCl_3.6H_2O$) (>99%) from Riedel-de Haen AG; tartaric acid ($C_4H_6O_6$) (>99.5%) from Merck and research grade sorbitol ($C_6H_{14}O_6$) from Serva-Feinbiochemica GmbH & Co. were used.

2.2. Methods

2.2.1. Preparation of FeTNa solution

FeTNa solutions with a molar ratio of $FeCl_3{\cdot}6H_2O$:tartaric acid:NaOH as 1:3.28:11.84 were prepared. The concentration of Fe ion varied from 0.15 to 0.55 M. In addition, 0.4, 0.8, 1.25, 2.5 and 5 M free NaOH were added. The procedure was explained in literature (Vu-Manh et al., 2010, in press).

2.2.2. Fiber diameter measurements

The fibers were swollen in the solution for approximately 2 min. The diameter of swollen fiber was measured by Reichert projection microscope with a magnification of 500×. Fiber diameters above 130 µm could not be measured by this method. Swelling rate of modal fibers was found out by measuring fiber diameter after its swelling in varying times: 5, 10, 15, 20, 25, 30, 45, 60 min. 10 fibers were counted and mean value was taken for measurement.

'S_d' refers to 'dramatic swelling' showing the fiber diameter above ca. 130 µm, '*D*' refers to the disintegration of the fiber structure and the sign '*X*' refers to the dissolution of the fiber for which the fiber diameter could not be measured.

3. Results and discussion

3.1. Morphological changes of modal fibers during FeTNa treatment

During FeTNa treatment of modal fibers, five different structural changes of fibers were observed:

(a) limited swelling, i.e. uniform swelling at a low degree comparable to that of in water (Fig. 1: S_1),
(b) swelling (Fig. 1: S_2),
(c) disintegration (Fig. 1: *D*),
(d) dramatic swelling (S_d), i.e. excess of fiber diameter (above 130 µm),
(e) dissolution (*X*).

Table 1
The differences between lyocell, viscose and modal fibers in terms of fiber properties.

Fiber properties	Differences between lyocell, viscose and modal fibers
APV	By ISEC modal < lyocell < viscose
DP	Viscose < modal < lyocell
Crystallinity	Viscose < modal < lyocell
Pore size[a]	Lyocell < viscose ~ modal
Fiber cross-section[b]	Lyocell (circular), viscose and modal (multi-lobal)

ISEC: inverse size exclusion chromatography.
[a] Abu-Rous et al. (2006).
[b] Krässig et al. (1986).

Table 2
The comparison between fiber properties of lyocell, viscose and modal fibers affecting their swelling/dissolution rate.

	Lyocell	Viscose	Modal
Fiber structure (skin-core/homogeneous)	+	–	–
Cross-section (multi-lobal/circular)	–	+	+
Crystallinity	–	+	*
DP	–	+	*
Pore size	–	+	+
APV	*	+	–

+ supports swelling/dissolution; – retards swelling/dissolution; * have an average effect between 'supporting' and 'retarding' on swelling/dissolution rate. (The magnitude of signs are as following + > * > –. More the number of + for a given fiber, higher the swelling/dissolution rate of that fiber.)

The morphological changes of lyocell (Vu-Manh et al., 2010) and modal fibers *during* FeTNa treatments were found to be limited swelling, swelling, disintegration, dramatic swelling, dissolution, while lyocell fibers showed also uneven swelling in selected FeTNa solutions. Viscose fibers showed limited swelling, swelling, splitting and dissolution *during* FeTNa treatment (Vu-Manh et al., in press).

Swelling of cellulosic fibers in aqueous solutions occurs firstly in the easily accessible regions (amorphous regions, pores) of cellulose. Depending on solvent quality, swelling can occur in the crystalline regions of cellulose also. Physical structure of cellulosic fiber loosens by swelling. By dissolution, the inter- and intramolecular hydrogen bonds of long range order of cellulose are destroyed to form cellulose macromolecules in solution (Klemm, Philipp, Heinze, Heinze, & Wagenknecht, 1998).

There are different parameters affecting the swelling and dissolution mechanism, kinetics and the solubility of cellulosic fibers in a given solution. The *kinetics* (rate) of swelling and dissolution depend on the

- fiber structure (cellulose structure with skin-core swells/dissolves slower than uniform/homogeneous structured cellulose, round cross-sectioned cellulose structure swells/dissolves slower than multi-lobal cross-sectioned cellulose structure)
- crystallinity index (crystalline parts of cellulose structure swell/dissolve slower than its amorphous parts)
- degree of polymerization (DP) (cellulose structure with higher DP swells/dissolves slower than that of with smaller DP)
- pore size (cellulose structure with smaller pore size swells/dissolves slower than that with bigger sized pores)
- accessible pore volume (APV) (cellulose structure with smaller APV swells/dissolves slower than that of with bigger APV)
- solution type
- temperature (lower temperature increases swelling and dissolution due to entropy effects)
- cellulose concentration in solution (higher the concentration, slower the kinetics of the reaction due to viscosity increase).

Taking these parameters (Table 1) into account with the *same magnitude* for different regenerated cellulosic fibers, the rate of swelling and dissolution of them can be expected as following: viscose > modal > lyocell (Table 2).

In order to compare the dissolution *rate* of lyocell, viscose and modal fibers, the total number of FeTNa solutions which dissolve the fiber within a given time has been counted (Vu-Manh et al., 2010, in press). As can be seen from Fig. 2, lyocell fibers dissolve in a higher number FeTNa solutions at a given time compared to modal and viscose fibers. Hence the dissolution rate of fibers is found as following: lyocell > modal > viscose which is different from the theoretical expectation, i.e. viscose > modal > lyocell (Table 2). This demonstrates the major rate determining factor for dissolution rate of fibers in FeTNa solutions is the access of swelling agent into the fiber structure. Thus viscose fiber with its distinct skin-core character exhibits retarded swelling behaviour. Lyocell fibers having fibrillar structure and nanopores is found to be dissolving earlier than other fibers.

The key parameters for swelling and dissolution *mechanism* are the morphology of fiber and solvent quality. For example, ballooning of cotton, wood, other plant fibers and some cellulose derivatives was observed due to the presence of primary and secondary walls. Regenerated cellulosic fibers do not show ballooning since they do not have these type of walls (LeMoigne & Navard, 2010; LeMoigne, Bikard, & Navard, 2010).

The *homogeneous* fiber structure of lyocell and modal fibers is most probably responsible for their *similar* morphological changes in FeTNa solutions. Lyocell fibers, which have more pronounced fibrillar structure than modal fibers, showed uneven swelling due to uneven distribution of swelling agent in the fiber. Viscose fibers, which have *inhomogeneous* (skin-core) structure, could show splitting of fibrils in selected FeTNa solutions.

The *solubility* of cellulose in solutions depends on solvent quality, temperature of the solution and DP of cellulose. For example, solubility of cellulose in NaOH/urea solution increases by decreasing the temperature to ca. $-12\,^{\circ}C$ (Qi, Chang, & Zhang, 2008). The maximum limit of DP of cellulose that 9% NaOH, 6% NaOH/4% urea solution, 6% NaOH/5% thiourea solution and 7% NaOH/12% urea solution can dissolve is DP 200, DP 425, DP 500 and DP 700, respectively (Zhou & Zhang, 2000; Isogai & Atalla, 1998).

3.2. Fiber diameter measurements

Fiber diameter of modal fibers after swelling ca. 2 min in FeTNa solutions containing 0.4, 0.8, 1.25, 2.5 and 5 M free NaOH in the presence of 0.15–0.55 M Fe was shown in Fig. 3.

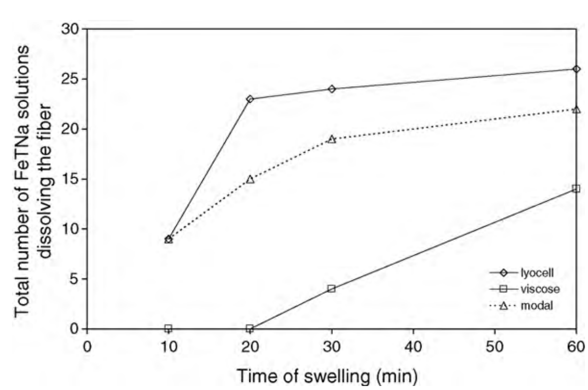

Fig. 2. Total number of FeTNa solutions dissolving lyocell, viscose and modal fibers after a given time of swelling.

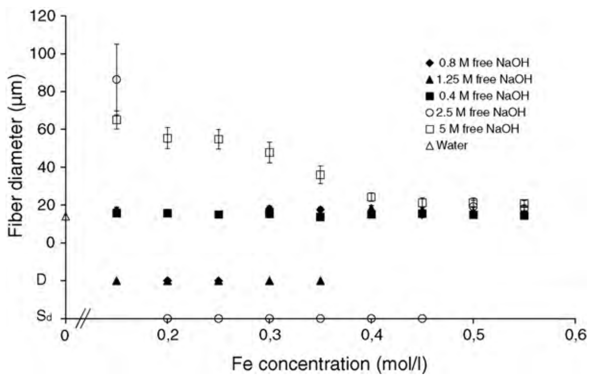

Fig. 3. The relation between fiber diameter of modal fibers (swollen ca. 2 min) and Fe concentration of FeTNa solutions in the presence of varying free NaOH concentration (*D*: disintegration, S_d: dramatic swelling).

0.4 M free NaOH containing FeTNa solutions led to limited swelling. Disintegration and limited swelling occurred in FeTNa solutions (0.8–1.25 M free NaOH) containing 0.15–0.45 and 0.50–0.55 M Fe, respectively. When free NaOH concentration of FeTNa solution was 2.5 M, dramatic swelling (0.15–0.45 M Fe in FeTNa solution) and limited swelling (0.50–0.55 M Fe in FeTNa solution) were observed. 5 M free NaOH containing solutions led to swelling, which decreased with the increase of Fe concentration in FeTNa solution.

Table 3 shows the morphological changes of ca. 2 min swollen lyocell, viscose, modal fibers in FeTNa solutions containing various free NaOH and Fe concentrations. FeTNa solutions containing 2.5 M free NaOH caused different morphological changes for lyocell and modal fibers. In the other FeTNa solutions, similar behavior of these fibers was observed. FeTNa solutions containing 0.8–2.5 M free NaOH led to different morphological changes for viscose fibers compared to lyocell and modal fibers. The effect of FeTNa solutions containing 0.4 and 5 M free NaOH on morphological changes of lyocell, viscose and modal fibers is found to be the same, i.e. limited swelling and swelling are observed, respectively. The main parameters causing *similar* morphological changes for *different* cellulosic fibers in FeTNa solutions after ca. 2 min swelling are as following:

Table 3
Morphological changes of ca. 2 min swollen lyocell, viscose, modal fibers in FeTNa solutions containing various free NaOH and Fe concentrations.

Free NaOH conc. (M) in FeTNa solution	Lyocell[a]	Viscose[b]	Modal
0.4	Limited swelling (0.15–0.55 M Fe)	Limited swelling (0.15–0.55 M Fe)	Limited swelling (0.15–0.55 M Fe)
0.8	Disintegration (0.15–0.45 M Fe) Limited swelling (0.50–0.55 M Fe)	Limited swelling (0.15–0.55 M Fe)	Disintegration (0.15–0.45 M Fe) Limited swelling (0.50–0.55 M Fe)
1.25	Disintegration (0.15–0.45 M Fe) Limited swelling (0.50–0.55 M Fe)	Splitting (0.15–0.25 M Fe) Swelling (>0.30 M Fe)	Disintegration (0.15–0.45 M Fe) Limited swelling (0.50–0.55 M Fe)
2.5	Dissolution (0.15–0.55 M Fe)	Swelling (0.15–0.55 M Fe)	Dramatic swelling (0.15–0.45 M Fe) Limited swelling (0.50–0.55 M Fe)
5	Swelling (0.15–0.55 M Fe)	Swelling (0.15–0.55 M Fe)	Swelling (0.15–0.55 M Fe)

[a] Vu-Manh et al. (2010).
[b] Vu-Manh et al. (in press).

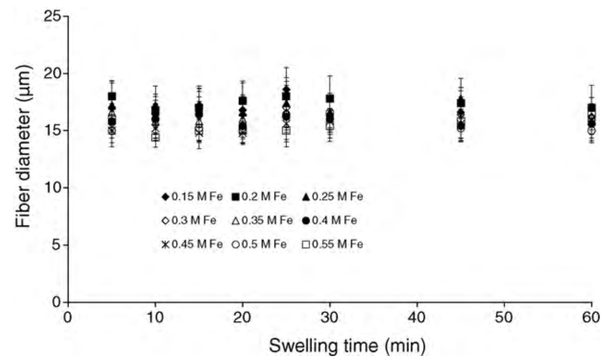

Fig. 4. Swelling rate of modal fibers in FeTNa solutions containing 0.4 M free NaOH concentration in the presence of varying Fe concentration.

- 0.4 M free NaOH concentration causes limited interfibrillar swelling (swelling comparable to that of in pure water) irrelevant to the fiber type (Vu-Manh et al., 2010)
- 5 M free NaOH concentration causes total accessibility of crystalline and amorphous regions of cellulosic fibers irrelevant to the fiber type (Öztürk, Okubayashi, & Bechtold, 2006; Vu-Manh et al., 2010)
- Lyocell and modal fibers, which have homogeneous fiber structure showed similar morphology in FeTNa solutions, while viscose fibers having inhomogeneous fiber structure (skin-core) showed different ones.

3.3. Effects of Fe concentration in FeTNa solutions on the swelling rate of modal fibers

Figs. 4–7 shows the swelling rate of modal fibers in FeTNa solutions containing 0.4, 0.8, 1.25 and 5 M free NaOH, respectively. After 5 min of swelling, modal fibers were dissolved in FeTNa solutions containing 2.5 M free NaOH, hence swelling rate studies for these solutions could not be conducted.

Independent of Fe concentration in FeTNa solution and swelling time, limited swelling occurred when free NaOH concentration of the solution was 0.4 M (Fig. 4). In conclusion, this solution did not swell the fiber more than pure water can do.

FeTNa solutions containing 0.8 M free NaOH in the presence of 0.15–0.35 M Fe caused disintegration after ca. 5 min of swelling and dissolution after 30 min of swelling (Fig. 5). As the Fe concentration of FeTNa solution increased up to 0.25 M, the time to disintegrate and dissolve was comparable. Further increase in Fe concentration of the solution to 0.30 and 0.35 M led to a delay in disintegration and dissolution of modal fibers. When the Fe concentration of FeTNa solution was 0.40–0.55 M, limited swelling was observed.

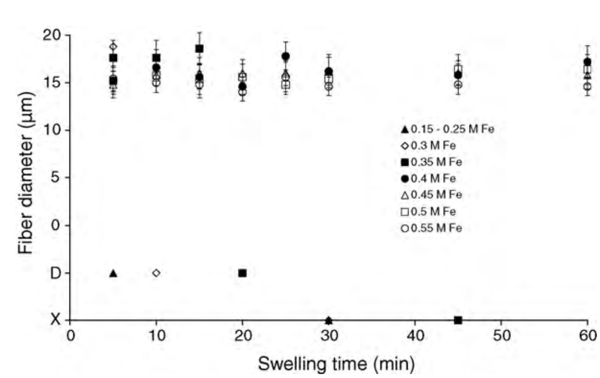

Fig. 5. Swelling rate of modal fibers in FeTNa solution containing 0.8 M free NaOH concentration in the presence of varying Fe concentration (*D*: disintegration, *X*: dissolution).

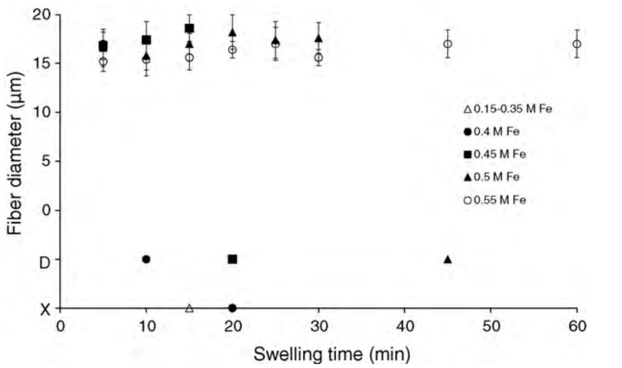

Fig. 6. Swelling rate of modal fibers in FeTNa solution containing 1.25 M free NaOH concentration in the presence of varying Fe concentration (*D*: disintegration, *X*: dissolution).

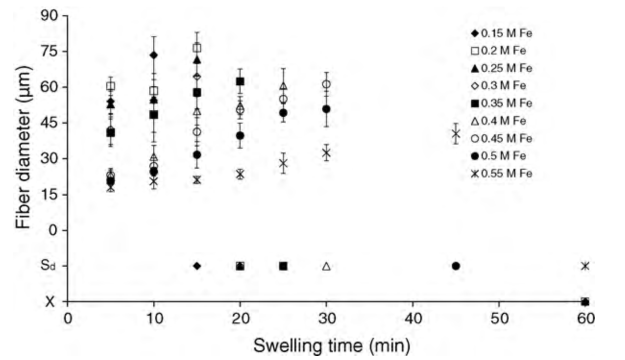

Fig. 7. Swelling rate of modal fibers in FeTNa solution containing 5 M free NaOH concentration in the presence of varying Fe concentration (S_d: dramatic swelling, *X*: dissolution).

FeTNa solutions containing 1.25 M free NaOH (Fig. 6) in the presence of 0.15–0.35 M Fe and 0.40 M Fe dissolved modal fibers in 15 and 20 min, respectively, while 0.45 and 0.50 M Fe containing FeTNa solutions disintegrated modal fibers in 20 and 45 min, respectively. Limited swelling of fibers occurred before either disintegration or dissolution took place.

5 M free NaOH containing FeTNa solutions (Fig. 7) swelled modal fibers to higher degrees (max ca. 75 µm) compared to other FeTNa solutions can do. As the Fe concentration of FeTNa solution increased from 0.15 to 0.55 M, the time to disintegrate the fiber increased from 15 min to 60 min. For example, 0.40 M Fe containing FeTNa solution caused S_d in 30 min, while 0.50 M Fe containing solution caused it in 45 min. Dissolution occurred in FeTNa solutions containing 0.15–0.20 M Fe after 60 min of swelling.

As a result, swelling rate studies of modal fibers showed that an increase in Fe concentration of FeTNa solution led to a delay of time in the morphological change of the fiber. This is due to the association of ions with the increase of Fe concentration in FeTNa solution, increasing the viscosity and decreasing the conductivity of the solution. The high interaction between ions causes less interaction between FeTNa solution and cellulose, hence less swelling (Vu-Manh et al., 2010).

Free alkali concentrations in FeTNa solutions up to 2 M ease the dissolution of cellulose due to the reduction in the intermolecular forces between cellulose chains which assist dissolution (Achwal, Narayan, & Purao, 1967). Current study showed that modal fibers dissolve in FeTNa solutions containing free NaOH concentration ca. 0.8–5 M depending on swelling time and Fe concentration of FeTNa solution. Free NaOH concentration of FeTNa solutions to dissolve viscose and lyocell fibers was 1.25–5 and 0.8–2.5 M, respectively (Vu-Manh et al., 2010, in press).

3.4. Morphological changes of modal fibers depending on Fe and free NaOH concentration for different periods of swelling

Fig. 8 shows the morphological changes of modal fibers depending on swelling time from 10 to 60 min. Dramatic swelling (S_d) occurred after 20 min of swelling (Fig. 8b) of fibers in FeTNa solutions containing 5 M free NaOH. The S_d region grew to the right side (to higher Fe concentrations of FeTNa solution) after

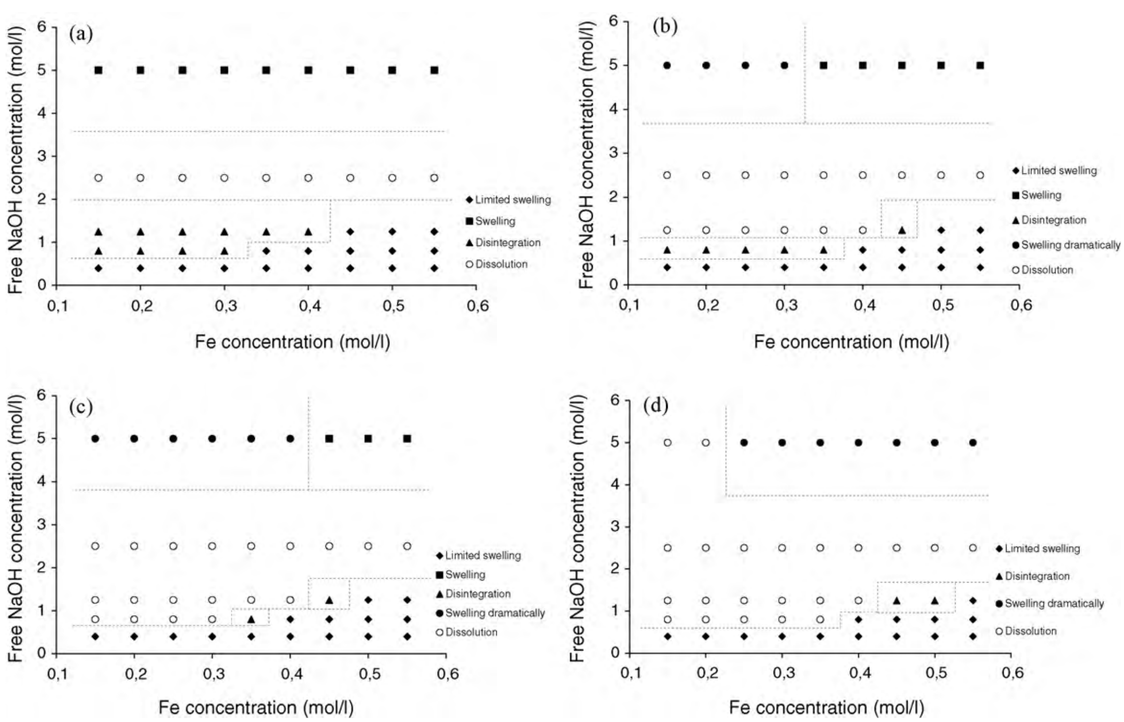

Fig. 8. Swelling–dissolution diagram of modal fibers after (a) 10, (b) 20, (c) 30, and (d) 60 min of swelling in FeTNa solutions containing varying Fe and free NaOH concentration.

30 min of swelling (Fig. 8c). Disintegration region grew also to the right side after 20 min of swelling of fibers (Fig. 8b). Dissolution region grew to the down side (to lower concentrations of free NaOH of FeTNa solution) as the time for swelling increased up to 30 min. For example, swelling from 10 min (Fig. 8a) to 20 min (Fig. 8b) and then to 30 min (Fig. 8c) led the dissolution region to grow from 2.5 to 1.25 M and then to 0.8 M free NaOH of FeTNa solutions.

As a result, Fig. 8 shows that either the dramatic swelling (S_d) or the disintegration is the previous step of the dissolution of modal fibers. The progress from disintegration to dissolution of modal fibers takes place when free NaOH is 0.8–1.25 M and the progress from S_d to dissolution occurs when free NaOH concentration is 5 M in FeTNa solutions.

The dissolving of modal fibers started after ca. 3 min of swelling in FeTNa solution prepared according to Valtasaari method (Hoffrichter, 1963). When this solution was diluted, mushroom like swelling from the end of modal fibers occurred (Baudisch, Maron, & Gröbe, 1967; Hoffrichter, 1963).

4. Conclusions

Depending on Fe and free NaOH concentration in FeTNa solution and swelling time, five morphological changes on modal fibers were observed which were limited swelling, swelling, disintegration, dramatic swelling and dissolution.

0.4 M free NaOH containing FeTNa solutions caused limited swelling for modal fibers which is an indication of less interaction between cellulose and complex ions. 0.8–1.25 M free NaOH containing FeTNa solutions can cause limited swelling, disintegration and dissolution while 5 M free NaOH containing FeTNa solutions can lead to swelling, dramatic swelling and dissolution depending on Fe concentration of the solution and swelling time. 2.5 M NaOH containing FeTNa solutions dissolved modal fibers after 20 min of swelling.

Among fiber properties (fiber structure, crystallinity index, DP, pore size, APV), the access of swelling agent into the *fiber structure* was mentioned to be the major factor governing the swelling and dissolution *rate* of fibers in FeTNa solutions. Swelling and dissolution *mechanism* of fibers in FeTNa solutions was attributed to the *homogeneity* of the fiber structure.

Current study suggests the possible usage of FeTNa solutions as both solvent and treatment solution for modal fibers. In order to get various fiber morphology types such as swelling, disintegration, dramatic swelling, dissolution on modal fibers, Fe and free NaOH concentration in FeTNa solutions and the fiber swelling time should be varied.

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