

## Ferrite-Loaded Membranes of Microfibrillar Bacterial Cellulose Prepared by in Situ Precipitation

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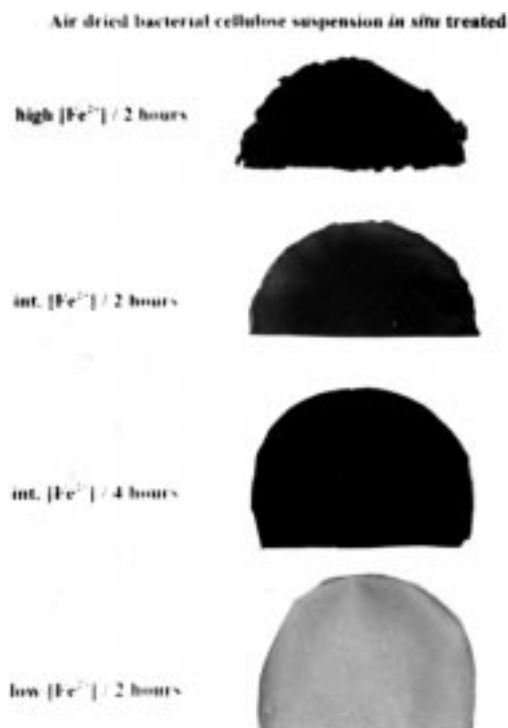
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In previous communications, the in situ synthesis of ferrites inside a swollen cellulose matrix has been reported.<sup>1–3</sup> Bacterial cellulose (BC) and Lyocell gel membranes have provided macroscopically homogeneous substrates for this application. However, the uneven penetrability intrinsic to the membrane makes the laboratory preparation of a uniform nanocomposite extremely difficult. Paper fabrication technology would seem to be a better approach for obtaining a magnetic nanocomposite membrane if the cellulose microfibril can be made a nucleating surface for the in situ synthesized ferrites. Thus microfibrils with attached ferrites would be drained on a screen to form a web with uniformly distributed ferrites.

Bacterial cellulose composed of microfibrils can be biosynthesized in a stirred tank,<sup>4,5</sup> and subsequent purification and beating provide a slurry. For such a microfibrillar suspension, the ferrite synthesis reagents flow homogeneously throughout the reactor, and the chemical reaction conditions control the ferrite size. The suspension was used in this study to explore the conjugation of nanosized ferrites and microfibril surfaces within a magnetic membrane. This development has applications in special papers for reprographic or security printing.

Bacterial cellulose obtained from *Acetobacter xylinum*, prepared in a stirred culture and subsequently purified, was provided by Monsanto (Nutrasweet-Kelco Division, San Diego, CA) under the name Cellulon. The “as-received” material was a fibrous paste made of 1 mm diameter loose pellet aggregates of BC microfibrils in about 85% water by weight. The paste can be homogenized by treatment with a vigorous ultrasound dispersing apparatus, but this procedure was not used in these experiments.

BC suspensions were gently dispersed in distilled water (DW), the cellulose content being set to 0.5% of



**Figure 1.** Photograph of in situ processed membranes; treatment from top to bottom: in high  $[\text{Fe}^{2+}]$  (1.0 mol/L) for 2 h; in intermediate  $[\text{Fe}^{2+}]$  (0.1 mol/L) for 2 h; in intermediate  $[\text{Fe}^{2+}]$  (0.1 mol/L) for 4 h; in low  $[\text{Fe}^{2+}]$  (0.01 mol/L) for 2 h.

the dry weight. After bubbling  $\text{N}_2$  gas through the suspension for 15 min to remove dissolved oxygen, crystals of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were added to bring the initial  $\text{Fe}^{2+}$  concentration ( $[\text{Fe}^{2+}]_{\text{init}}$ ) to 0.01, 0.1, and 1.0 mol/L. After 2–4 h of aging, the sample was centrifuged for a few minutes and redispersed into a solution of NaOH (concentration, 0.1 mol/L). Two hours later, the suspension was oxidized for 2 h in atmospheric air at 80 °C. The sample was then centrifuged, dispersed into DW, and centrifuged a second time, to be finally dispersed in absolute ethanol.

Part of the suspension was poured on a paper filter and dried in an oven at 70 °C. The dried sample was a tough fine sheet easily detached from the filter paper.

A 1 cm<sup>2</sup> portion of the dried sample was mounted on a glass slide by means of double-sided tape. X-ray diffraction patterns were obtained on a powder diffractometer in reflection using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). A crystallite size ( $D$ ) was estimated from the half-height broadening (HHB) of the one or two most intense peaks (at diffraction angle  $2\theta$ ) using the Sherrer–Debye expression

$$\text{HHB} = 54\lambda/D \cos(2\theta/2)$$

The size derived is in the orthogonal direction to the plane addressed by the selected diffraction angle.

A drop of each ethanol suspension of in situ product was deposited and allowed to dry on a carbon-coated copper grid. A Philips CM 200 transmission electron microscope (TEM) operated at 200 kV was used for

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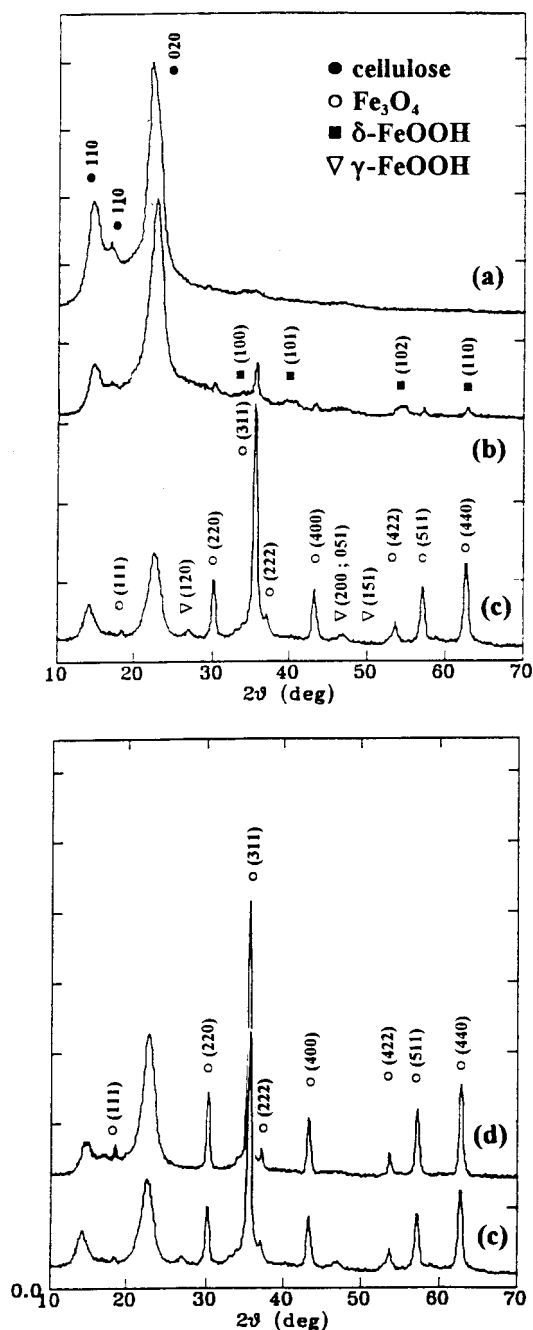
(1) Raymond, L.; Revol, J.-F.; Ryan, D. H.; Marchessault, R. H. *Chem. Mater.* **1994**, *6*, 149.

(2) Raymond, L.; Revol, J.-F.; Ryan, D. H.; Marchessault, R. H. *Polymer* **1995**, *36*, 5035.

(3) Sourty, E.; Ryan, D. H.; Marchessault, R. H. *Cellulose* **1998**, *5*, 5.

(4) *CELLULON Technical Bulletin*, Monsanto Performance Materials, 8225, Aero Drive, San Diego, CA.

(5) Watanabe, K.; Yamanaka, S. *Proceedings of the International Symposium on Fibre Science and Technology*, Yokohama, Japan, 1994, p 445.

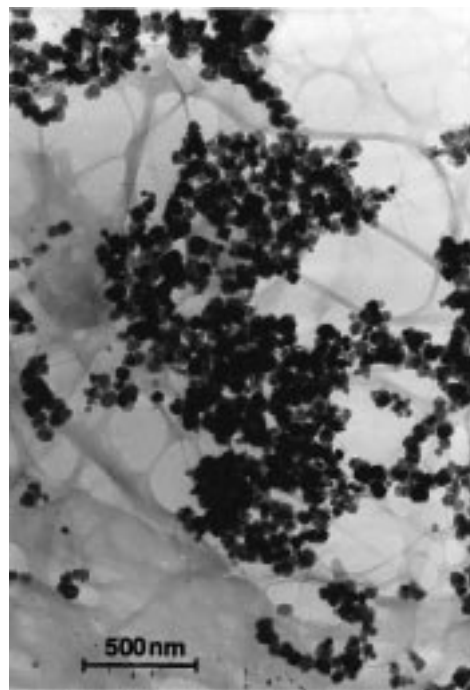


**Figure 2.** XRD powder pattern demonstrating the "aging" effect for in situ treated samples. The spectra correspond to the following conditions: (a) treated for 2 h in  $[\text{Fe}^{2+}] = 0.01$  mol/L; (b) treated for 2 h in  $[\text{Fe}^{2+}] = 0.1$  mol/L; (c) treated for 2 h in  $[\text{Fe}^{2+}] = 1.0$  mol/L; (d) treated for 4 h in  $[\text{Fe}^{2+}] = 0.1$  mol/L.

imaging by diffraction contrast and for selected area (SA) diffraction.

The magnetic properties of the in situ treated materials after air-drying were examined by vibrating sample magnetometry (VMS). Approximately 20 mg of the dried membrane was rolled and vibrated perpendicular to a magnetic field of up to 1.5 T. The response of the material was plotted as a function of the applied field to yield a magnetization curve.

The membrane colors shown in Figure 1 correspond to varying mixtures of  $\text{Fe}_3\text{O}_4$  (black/dark brown) and  $\text{FeOOH}$  (yellow/rusty). Solutions after oxidation were strongly alkaline ( $\text{pH} > 12$ ), except for treatment with



**Figure 3.** Transmission electron micrograph of a bacterial cellulose suspension treated for 4 h in ferrous chloride ( $[\text{Fe}^{2+}] = 0.1$  mol/L), deposited, and dried on a grid.

the highest  $[\text{Fe}^{2+}]_{\text{limit}}$  (1.0 mol/L), the pH being then slightly acid ( $\text{pH} \sim 5-6$ ).

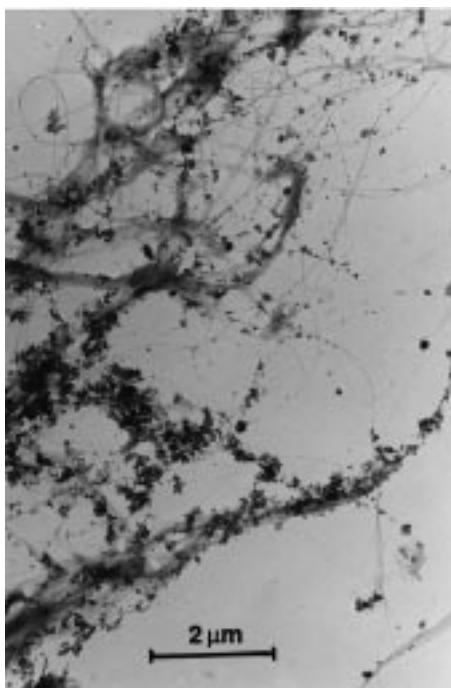
Three characteristic peaks are systematically present at low angles in all diffractometer traces (Figure 2), including the one for a nontreated (blank) cellulose membrane (not presented). These peaks are attributed to the presence of crystalline cellulose I, corresponding from lower to higher  $2\theta$  to the (110), ( $1\bar{1}0$ ), and (020) reflections.<sup>6</sup> The peak of highest intensity, corresponding to  $2\theta \sim 22.81$ , was chosen as a reference for the intensity ( $I_{\text{ref}}$ ) of all diffraction peaks.

Peaks associated with the presence of magnetite can be distinguished for samples treated with  $[\text{Fe}^{2+}]_{\text{limit}}$  above 0.1 mol/L. The most intense peaks related to magnetite were measured for the sample treated with the highest  $[\text{Fe}^{2+}]_{\text{limit}}$  (1.0 mol/L),  $I(440)/I_{\text{ref}} \sim 0.9$ , and for the sample aged for 4 h in ferrous chloride,  $I(440)/I_{\text{ref}} \sim 0.7$ . The crystallite sizes calculated from the HHB were respectively  $\sim 20$  and 50 nm perpendicular to the 440 crystallographic plane.

Ferrites in the form of *small particles* were observed using TEM with a mean size between 10 and 30 nm. These particles are inclined to aggregate into lumps of varying compactness (usually 100–500 nm in size). *Polyhedral particles* (50–100 nm in dimension) are present in samples having the darkest hue. These species (small and polyhedral particles) gave diffraction patterns corresponding to *magnetite*. The sample treated for 4 h in ferrous chloride (Figure 3) contains cubic particles of two homogeneous sizes, the larger particles ( $\sim 70$  nm) being clumped and the smaller ( $\sim 20$  nm) dispersed. The cellulose microfibrils are clearly visible in the background.

Figure 4 shows a treated suspension at lower magnification: the smaller ferrites are closely associated

(6) Marchessault, R. H.; Sundararajan, P. R. In *The Polysaccharides*; Aspinall, G. O., Ed.; Academic Press Inc.: London, 1985; Vol. 2.



**Figure 4.** Transmission electron micrograph showing the localization of the grown ferrites along the cellulose fibrils.

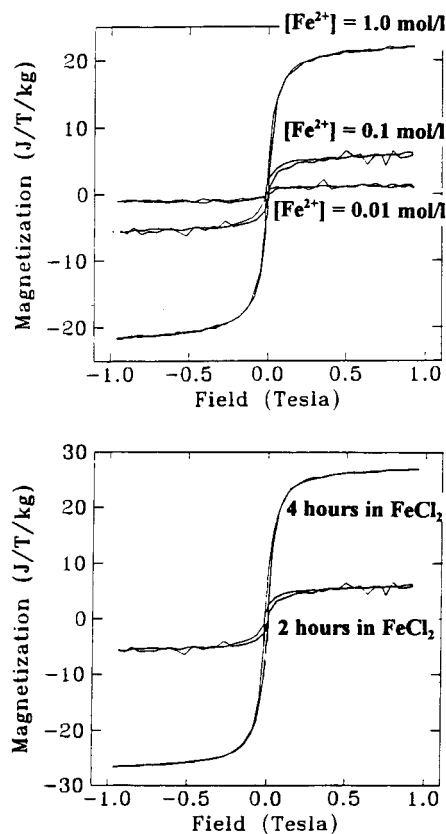
**Table 1. Percent of Iron Measured by Atomic Absorption, the Saturation Magnetization and Coercivity Measured by VSM, Corresponding to Different  $[\text{Fe}^{2+}]$  and Aging Times in Ferrous Chloride in the Course of the in Situ Treatment**

$[\text{Fe}^{2+}]$ , mol/L	aging time, h	iron content, % total weight	$M_s$ , J/(T kg)	$H_c$ , mT
0.1	4	21	28	10
1.0	2	27	22	5
0.1	2	12	7	10
0.01	2	2	2	8

with fibrils, which suggests that they act as nucleation sites for crystal growth.

The magnetization was measured as a function of an applied magnetic field in the range  $|H_{\text{app}}| < 1.5$  T (Figure 5). Increasing the ferrous ion concentration by a factor of 10 ( $[\text{Fe}^{2+}]_{\text{init}} = 0.01, 0.1, 1$  mol/L) leads to a 4-fold increase in the saturation magnetization (Figure 5). Doubling the aging time in  $\text{FeCl}_2$  approximately doubles the iron content and multiplies the saturation magnetization by 4, with no significant effect on the coercivity (Table 1).

Kiyama<sup>7</sup> defines the molar ratio  $R = 2[\text{OH}^-]/[\text{Fe}^{2+}]$ . This ratio has been varied in our experiments by



**Figure 5.** Room-temperature magnetization curves measured by VSM.

changing the ferrous ion concentration. For  $R \sim 20$ ,  $R \sim 2$ , and  $R \sim 0.2$ , the synthesis proceeded respectively through the formation of mixtures of  $\text{Fe}(\text{OH})_2/\text{FeOOH}/\text{Fe}_3\text{O}_4$ ,  $\text{Fe}(\text{OH})_2/\text{Fe}_3\text{O}_4$ , and green rust/ $\text{Fe}_3\text{O}_4/\text{FeOOH}$  in varying proportions. The magnetite preponderance is favored at the lowest  $R$  with the increase of the inherent magnetization saturation. Longer aging times in  $\text{FeCl}_2$  before precipitation by  $\text{NaOH}$  also favored the magnetite preponderance and increased the saturation magnetization, indicating the slow diffusion/adsorption character of the ferrous ions onto the cellulose fibrillar network.

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(7) Kiyama, M. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1646.