Magnetic cellulose fibres and paper: preparation, processing and properties*

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Magnetic cellulose fibres can be prepared either by 'lumen loading' or by *in situ* synthesis of ferrites. By using the lumen-loading technology, commercially available magnetic pigments can be introduced into the lumens of softwood fibres from which magnetic paper may be prepared. Lumen-loaded fibres act as magnetic dipoles allowing manipulation of fibre orientation in papermaking. *In situ* synthesis of iron oxide particles is performed through oxidation of ferrous hydroxide precipitated with caustic from the ferrous ion-exchanged form of sodium carboxymethyl cellulose fibres. The latter are characterized by conductometric titration to determine the number of functional groups available for the *in situ* chemistry. Superparamagnetically responsive fibres have smaller and less-coloured pigments which are only magnetic in the presence of a field.

(Keywords: lumen-loading; magnetic fibres; ferrites; conductometry; cellulose; carboxymethyl cellulose; superparamagnetism)

INTRODUCTION

Maghemite (γ-Fe_2O_3) and magnetite (Fe_3O_4) are the most widely used magnetic pigments in the production of magnetic recording and information storage media. A common application for maghemite is the encoding of information on subway tickets in the form of a thin magnetic strip coated on the cardboard stock. Since paper is an integral part of the information transfer system with established technology for low cost fabrication of communication papers, magnetic cellulose fibres offer a new potential for information storage. By using the lumen-loading technology[1,2], commercially available magnetic pigments can be introduced into the lumen of softwood fibres (tracheid cells) from which magnetic paper may be prepared.

Lumen loading of pulp fibres with commercial ferrites makes the cellulose fibres themselves magnetically responsive. After lumen loading, the adsorption of cationic polyethylenimine on the magnetic pigments and unbleached kraft fibres produces a better retention of pigments. Magnetic multi-ply papers have been made using the centrifugal principle of the 'dynamic sheet former' (DSF)[3]. Laminate papers, where the brown-coloured lumen-loaded kraft pulp is covered with a bleached fibre layer, have been produced. These sheets have bulk magnetic properties comparable to commercial information storage and identification media but with optical properties in the range of communication papers[4]. Magnetic fibres are specialities which allow exploration of new concepts in papermaking, information storage, security paper, paper handling, paper sensing, and reprographic applications such as magnetographic printing as well as speciality uses such as electromagnetic shielding.

Magnetic fibres may also be obtained by synthesizing ferrites *in situ*[5–7] using suitable natural cellulose fibres possessing appropriate functional groups or chemically modified cellulose fibres. Such fibres include carboxymethylated cellulose fibres, sulphated cellulose fibres and sulphonated wood fibres. Likewise, man-made continuous fibres of natural polymers (including polysaccharides such as chitosan and alginate) have functional groups which lend themselves to this process. *In situ* synthesis of iron oxide particles was performed via careful oxidation of ferrous hydroxide precipitated with caustic from the ferrous ion-exchanged form of the matrix[6–8]. This chemistry yielded magnetic fibres containing small ferrite (Fe_3O_4) particles of about 10 nm in size. The process could be practised with a wide range of natural biopolymers such as polysaccharides and lignocellulosics with amino, carboxyl and sulphonic acid groups. A possible application for superparamagnetic responsive fibres is in biotechnology such as magnetic separations of specific biologically active molecules from mixtures thereof (e.g. antibody separations). The cellulosic surface lends itself to attachment of suitable antigens for this purpose.

This study describes the conductometric titration of carboxymethylated cellulose fibres to characterize the functional groups for the *in situ* synthesis of ferrites. Also, exploratory magnetic 'lumen-loaded' fibre orientation in papermaking operations is reported.

EXPERIMENTAL

Papermaking and testing

A laboratory papermaking system including a Noram centrifugal sheet former (Noram Quality Control and

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Research Equipment Ltd, Pointe-Claire, Canada), a pulp supply, a wet press and a stationary dryer were used to produce multi-ply sheets. Lumen-loaded pulp[1,2] was diluted to $\sim 3\,g\,l^{-1}$ in the internal tank of the DSF. A commercial bleached kraft pulp was disintegrated (5 min using hot water) in a British disintegrator and diluted to $\sim 3\,g\,l^{-1}$ in the external tank of the pulp supply system. The pulp was then delivered from the nozzle (no. SS2504) to the wire (Unaform 2-ply U-64438 Noram 84 × 60) after forming the 'water wall'. The nozzle angle was fixed at 15° and the distance from the wire at 20 mm.

The number of nozzle sweeps was adjusted to give a predetermined basis weight for each layer. The jet speed and the peripheral drum speed were kept constant at 690 and $1100\,m\,min^{-1}$, respectively, to obtain preferential fibre orientation in the machine direction. The wet sheets, having a solids content of about 13 wt%, were pressed with two passes at 700 kPa in between two new blotters in each pass on the laboratory press giving a sheet of about 40% solids. The sheets were then dried in between the blotters to about 5% moisture in a laboratory drier under canvas tension and tested in accordance with the standard methods of the Technical Section of the Canadian Pulp and Paper Association.

Ultrasonic technique

The in-plane elastic properties are determined by measuring the velocity of ultrasound (60 kHz) in paper using a robot-based instrument developed by the Institute of Paper Chemistry[9]. The engineering elastic constants are calculated according to[10,11]:

$$E_x = E_{MD} = \rho V_{Lx}^2 (1 - u_{xy}u_{yx}) = C_{11}(1 - u_{xy}u_{yx})$$

$$E_y = E_{CD} = \rho V_{Ly}^2 (1 - u_{xy}u_{yx}) = C_{22}(1 - u_{xy}u_{yx})$$

$$R_{xy} = C_{11}/C_{22}$$

$$G_{xy} = a(E_x E_y)^{1/2}$$

where E_x, E_y = sonic Young's moduli corresponding to the machine and cross-machine direction respectively (GPa), ρ = apparent density of paper ($g\,cm^{-3}$), V_{Lx} = bulk longitudinal velocity in the x direction ($mm\,\mu s^{-1}$), u_{xy} = Poisson's ratio (ratio of the lateral contraction in the x direction to the axial extension in the y direction when the material is stressed uniaxially in the y direction), C_{ij} = elastic stiffness coefficients, R_{xy} = machine direction– cross direction (MD–CD) stiffness ratio or anisotropy ratio, G_{xy} = shear modulus in the xy plane and $a^{-1} = 2[1 + (u_{xy}u_{yx})^{1/2}]$.

Conductometric titration

A sample of sodium *O*-(carboxymethyl)cellulose (Na-CMC) known as CLD-2 (The Buckeye Cellulose Corp., USA), was used in the form of lap pulp. Approximately 2.5 g of the moist fibres were acidified by three 30 min repetitive agitations in a 0.1 M HCl solution for the 'normal' procedure. The sample was washed three times for 15 min with deionized water to remove excess HCl. The filtered product was then transferred to a three-neck flask containing 450 ml 0.001 M NaCl and 5 ml 0.1 M HCl. The 0.1 M NaOH titrant was added in fixed volume increments (0.5 ml) at 5 min intervals. A 'direct' conductometric titration was also performed on the Na–CMC sample. The fibres were immersed in 0.001 M NaCl solution containing 5 ml 0.1 M NaOH and titrated with 0.1 M HCl in the same volume increments as in the normal procedure. In both procedures, it was found desirable to minimize swelling by adding ethanol prior to the titration.

A digital titration burette (Metrohm 665 Dosimat) and a conductivity meter (Metrohm 600) all interfaced to an AT-286 personal computer via an A/D converter were used for the automated titrations. Conductivity was measured with a sleeveless immersion cell with built-in temperature probe. The computer controlled the titration parameters such as volume and rate of titrant addition using a program developed by the Pulp and Paper Research Institute of Canada (Paprican). The tip of the burette and the electrode were immersed in the fibre suspension under a N_2 atmosphere maintained by continuous bubbling. Slow stirring was maintained during the titrations. Volume-corrected specific conductance as a function of the volume of titrant was recorded throughout the titration. The equivalence points were determined from the intersection of the linear segments of the plot. The difference between the two intersection points corresponds to the volume of base required to neutralize the carboxylic acid groups, in the case of the 'normal' procedure, and to the volume of acid needed to protonate these groups, for the 'direct' titration. The number of functional groups available for the *in situ* chemistry was calculated in equivalents per kilogram:

$$[COOH] = \frac{VM}{W}\,(eq\,kg^{-1})$$

where V = volume of the titrant (ml), M = molarity of the titrant and W = dry weight of the material following the titration (g).

RESULTS AND DISCUSSION

Magnetic multi-ply paper loaded with magnetite

The DSF is a centrifugal laboratory sheet former based on the formette dynamique developed by the Centre Technique de l'Industrie des Papiers, Cartons et Cellulose, Grenoble, France. The operating conditions of the DSF can be set to reproduce the fibre orientation of a Fourdrinier machine through the entire MD–CD plane as well as fines distribution in the z-direction of the sheet[12].

The pulp supply system allows the formation of laminates for up to four different stocks. *Figures 1* and *2* show optical and scanning electron micrographs of lumen-loaded fibres with Fe_3O_4. These micrographs show particles of variable shape located mainly in the lumen of the fibres.

The use of bleached kraft (BK) pulp in surface lamination improves both brightness and sheet formation. *Figure 3* shows polar plots for the square of the ultrasonic velocity for oriented magnetic DSF sheets compared with a BK randomly oriented handsheet. This figure shows that, at the same jet/wire speed ratio and degree of restraint during drying, the lumen-loaded spruce fibres tend to align in the MD more easily than the shorter and finer BK fibres. Furthermore, all our plots of the multilayers fall in between the 100% BK and 100% lumen-loaded unbleached kraft pulp (UBK) of black spruce.

At similar dewatering conditions, which in this case were similar wet pressing pressures, the BK fibre network presents more fibre-to-fibre contacts per fibre (i.e. an increase in the bonded area per fibre) and therefore has

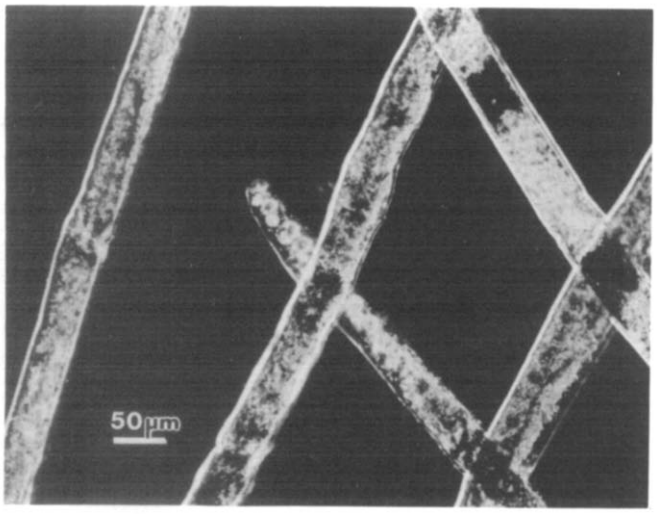


Figure 1 Dark field optical micrograph of unbleached black spruce kraft pulp lumen-loaded fibres with 15.5 wt% Fe_3O_4

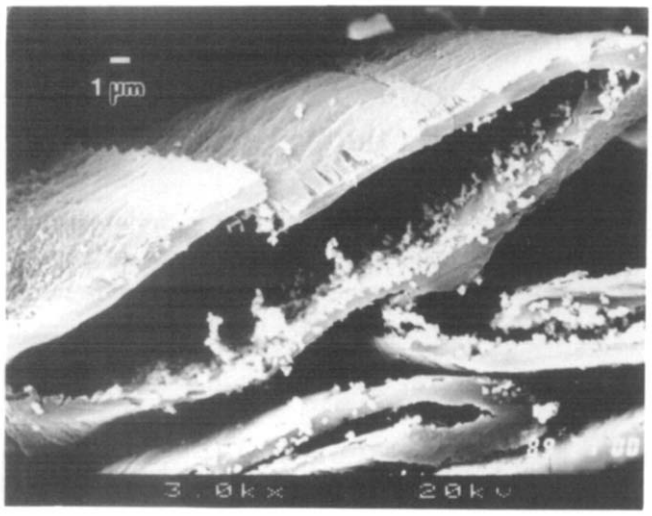


Figure 2 Scanning electron micrograph of a cross-section of a chemithermomechanical pulp fibre lumen loaded with 14 wt% Fe_3O_4

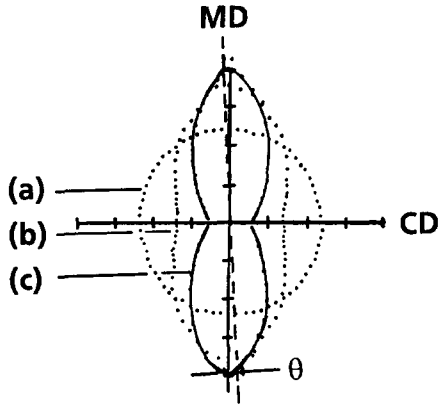


Figure 3 Typical polar plots for the square of the ultrasonic velocity for: (a) bleached kraft (BK) randomly oriented handsheet; (b) oriented BK DSF sheet; (c) oriented unbleached kraft lumen-loaded DSF sheet. θ represents the deviation of the mean angle with the machine direction (MD). CD is the cross direction. Graphic scale: 1 $mm^2 \mu s^{-2} div^{-1}$

higher elastic modulus than the lumen-loaded UBK, as shown in *Table 1*.

Since coarser fibres have thicker cell walls, and are fewer per gram, black spruce UBK fibres are less flexible and resist collapse; they make a more porous and

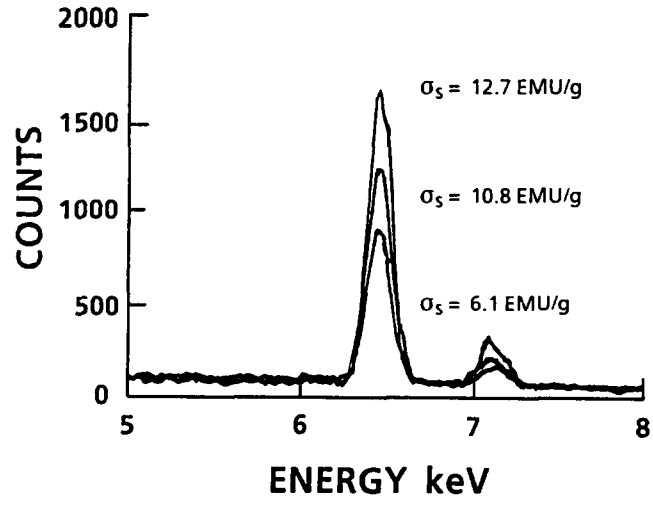


Figure 4 Energy dispersive X-ray spectra of magnetic sheets as a function of the specific magnetization at saturation, σ_s

permeable network. Therefore, it appears that lumen loading does not change the sonic elastic engineering parameters but has a small effect on the elastic moduli (E_x, E_y) as determined by tensile tests. Furthermore, no significant magnetic anisotropy has been observed because ferrites were randomly oriented in the lumen surfaces.

However, the DSF sheets exhibit a substantial decrease in apparent density with an increase in lumen-loaded fibres content. The increase in coarser fibres tends to produce a mat with a higher proportion of uncollapsed fibres, and therefore a sheet with lower Young's modulus and breaking length. The results also show that sheet lamination produces superior stiffness in the MD of lumen-loaded papers as is required in numerous printing processes.

Figure 4 displays the energy dispersive X-ray spectra (EDX, 5–8 keV) of magnetic papers at 300× magnification which is a non-destructive method for ferrite quantification. The number of counts is plotted on a vertical full scale of 2000 as a function of energy. The peak intensity is correlated with the specific magnetization at saturation (σ_s).

Conductometric titration

Conductance is a function of the sum of the conductance of each type of ion present in solution. The titration was carried out in a NaCl solution for the purpose of creating a uniform distribution of ions between the interior of the fibre wall and the external solution. The first descending branch of the conductometric titration curve of the CMC in *Figure 5a* corresponds to the neutralization of the H^+ ions of the 5 ml of HCl added during the 'normal' procedure[13,14]. The curvature at the lower end of the branch is attributed to the initial dissociation of weak carboxylic acid groups. As NaOH is added, the weak acid is progressively neutralized. A plateau region results from the small variation in conductance because of the low level of H^+ in equilibrium with the weak acid as it is being titrated. This region can have a slightly positive slope due to the accumulation of weak acid anions and sodium ions. The third branch of the curve corresponds to the increase in conductance due to an excess of base being added. By comparison, the

Table 1 Sonic elastic engineering parameters for DSF sheets containing 0–100% lumen-loaded fibres with Fe_3O_4 and for standard handsheet. Values in parentheses were determined by tensile tests

Parameters	100% UBK	100% UBK	100% UBK, lumen-loaded	10% UBK, lumen-loaded, 3 layers	30% UBK, lumen-loaded, 3 layers	40% UBK, lumen-loaded, 2 layers	BK, standard handsheet
V_{Lx}^2 ($mm^2\,\mu s^{-2}$)	17.90	21.50	19.41	18.75	17.69	17.62	12.28
V_{Ly}^2 ($mm^2\,\mu s^{-2}$)	6.68	2.91	2.55	5.66	5.75	4.96	11.70
ρ ($g\,cm^{-3}$)	0.63	0.52	0.58	0.64	0.60	0.54	0.30
B ($g\,m^{-2}$)	63	70	62	72	65	67	40
R_{xy}	2.7	7.5	7.5	3.1	3.1	3.5	1.05
U_{xy}	0.167	0.192	0.188	0.138	0.166	0.145	0.253
U_{yx}	0.434	1.065	1.106	0.434	0.518	0.488	0.267
E_x (GPa)	10.5 (7.2)	8.9 (8.6)	8.9 (7.0)	11.3 (8.5)	9.7 (7.6)	8.8 (6.7)	3.45
E_y (GPa)	3.9 (2.7)	1.2 (1.5)	1.2 (1.2)	3.6 (3.0)	3.1 (2.7)	2.5 (2.2)	3.3
G_{xy} (GPa)	2.5	1.1	1.1	2.5	2.1	1.8	1.3
Breaking length (km)							
MD	(17.6)	(16.3)	(13.3)	(18.2)	(16.7)	(13.2)	–
CD	(4.3)	(2.4)	(2.4)	(4.1)	(3.6)	(3.2)	–
Elongation (%)							
MD	(4.0)	(2.4)	(2.4)	(3.7)	(3.5)	(3.2)	–
CD	(3.4)	(3.4)	(3.2)	(3.7)	(3.0)	(3.0)	–

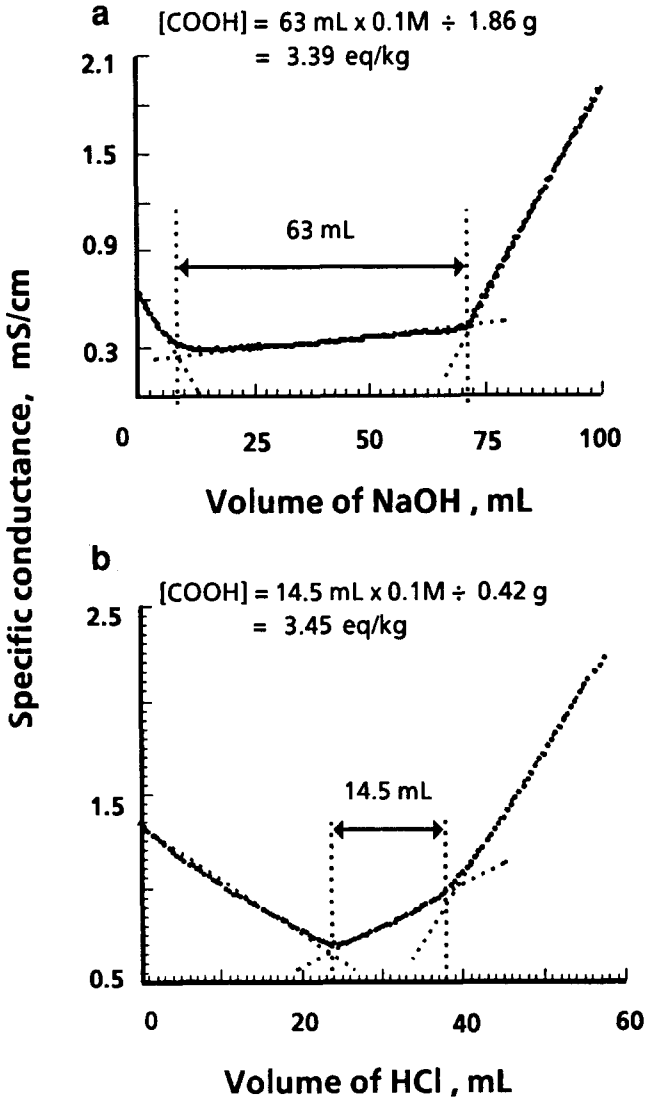
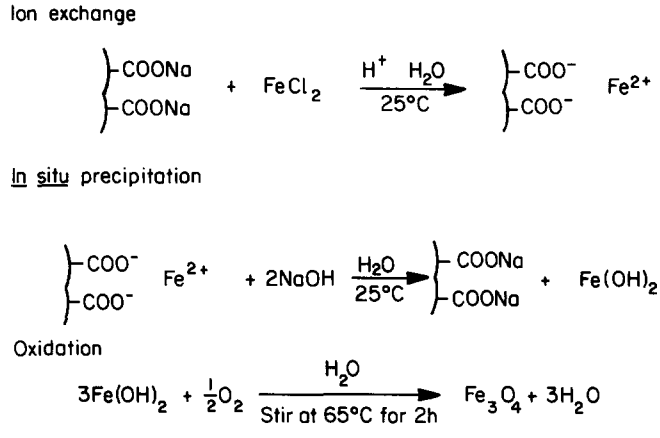


Figure 5 The conductometric titration curves of the CMC fibres: (a) normal procedure; (b) direct titration



Scheme 1

first descending branch of the 'direct' titration curve in *Figure 5b* corresponds to the neutralization of the 5 ml 0.1 M NaOH and the plateau, to the protonation of the weak acid groups. The third branch of the curve is due to the presence of an excess of acid.

The addition of 5 ml of ethanol increases the linearity of the branches, prevents sticking of the fibres to the electrode and facilitates the filtration of the final product. The alcohol inhibits swelling of the bibulous Na-CMC fibres thereby increasing the diffusional exchange rate of ions in the gel.

Scheme 1 outlines the steps involved in the conversion of CMC fibres to magnetic elements.

Magnetic characterization

The magnetic properties of film/paper were demonstrated using a classical vibrating-sample magnetometer instrument (EG&G Princeton Applied Research). *Figure 6* shows the specific magnetization as a function of the applied field for the lumen-loaded and the *in situ* synthesized magnetic papers. The differences in the two magnetization curves reflect two fundamental levels of

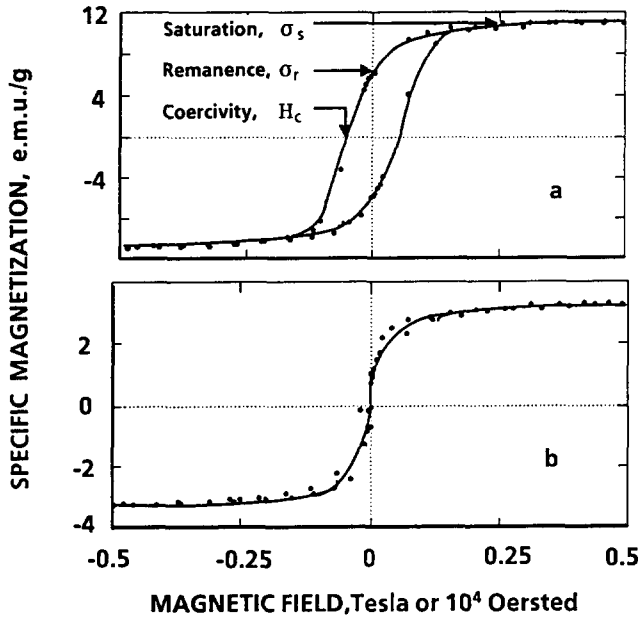


Figure 6 Hysteresis loops of a: (a) ferrimagnetic lumen-loaded fibres with 21 wt% γ-Fe_2O_3; (b) superparamagnetic *in situ* synthesized CMC composite

magnetic properties: ferrimagnetism (*Figure 6a*) and superparamagnetic behaviour[4,15,16] (*Figure 6b*). In the latter case, it is the magnetization curve passing directly through the origin which indicates that these *in situ* synthesized materials are superparamagnetic, that is, they do not display the remanence and coercivity phenomena characteristic of commercial ferrites used in information storage applications. This characteristic is attributed to the small size of the *in situ* synthesized particles, which is also responsible for the relatively light brown colour as compared to commercial synthetic magnetite particles, which are 10–100 times larger and much darker in colour.

CONCLUSIONS

Papers produced from magnetic fibres have elastic properties comparable with similar non-magnetic papers, and the presence of the magnetic particles has little effect on the elastic properties. The lumen-loaded magnetic fibres are found to align in a magnetic field and the anisotropy of the fibres can be manipulated hydrodynamically to yield axially oriented papers. However, these papers do not display magnetic anisotropy. Potential applications for magnetic paper include information storage, security paper uses and new methods of paper handling in copiers. *In situ* synthesis has the potential to provide magnetic effects with smaller and less coloured pigments which are only magnetic in the presence of a field.

Future work will focus on the use of *in situ* magnetic fibres in biotechnological separations. Model systems involving separation of lectin mixtures or enzyme mixtures, some of which are specific for cellulose, will be explored using simple laboratory equipment.

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