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Fibres for wound dressings based on mixed carbohydrate polymer fibres

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Abstract

Polysaccharide-based dressings have increasingly become viable alternatives to somewhat incompatible and often problematic cotton or viscose gauzes traditionally used for wound dressings. Abundant availability of alginates and their relative ease of reversible solubility in particular have been instrumental in their development into fibres and lately their application as vehicles for delivering drugs. This paper reports on the spinning efficiency of various alginate types (i.e. differing mannuronic/guluronic acid ratios) in a laboratory-based extrusion system and explores the effect of proportional inclusion of a second polysaccharide compound, an arabinoxylan named branan ferulate, on tensile properties of the resulting fibres. It was shown that in the chemical assessment of the fibres, that arabinose content, one of the branan ferulate component monosaccharides, could be used as a means of estimating the branan ferulate content of the fibre. Utilising such an analytical approach has enabled the branan ferulate contents of the fibres to be assessed. Accordingly there need be little anxiety over branan ferulate losses during the production of branan ferulate/alginate fibres by the wet spinning production method.

Keywords: Branan ferulate; Alginate fibre; Wind up speed

1. Introduction

1.1. Wound healing alginates

The concept of wound or rupture in otherwise delicate skin and underlying tissues is neither technical nor alien to man. Wounds and injuries today can result from a range of potential hazards including fire, natural disasters, transport accidents, diseases, operations, cosmetic surgery, sports, self-inflicted injuries and so on. High expectations of recovery and highly efficient reparation demands with minimal discomfort to the patients have in the last decade, in particular, led to some novel and daring wound management practices. New fibrous and wound dressing media have been developed to encourage wound occlusion, exudate transport and drug dispensation on demand with much reduced distress to the patient (Kennedy, Knill, & Thorley, 2001; Kennedy, Paterson, Knill, & Lloyd, 1996; Lloyd, Kennedy, Methacanon, Paterson, & Knill, 1998). In this paper, for one such system, where different alginate types are used, the efficiency of alginate fibres is examined to evaluate their ability to carry a second polysaccharide polymer, which is already marketed as a hydrogel wound dressing (Sterigel®) for the treatment of necrotic and sloughy wounds particularly venous and arterial leg ulcers and pressure sores. The significance of using branan ferulate, an arabinoxylan, as the second polysaccharide, is a consequence of its gel-forming capabilities currently being harnessed in Sterigel® which is a wound healing formulation containing cross-linked branan ferulate.

1.2. Alginate fibres

Consistency in texture and characteristic viscosity in marine algae or seaweed has been known as far back as 1883 and several early patents were granted for their extraction, for the physio-chemical properties and industrial applications of their macromolecular products. Discovery of alginic acid in itself later on and its treatment with alkaline bases led to a variety of products which have become used as stabilisers, thickening agents, sizing and jelling compounds in a range of industries. Between 1912 and 1940, a number of German, Japanese and British patents on the extrusion of alginates into insoluble fibres were published by Hongu and Phillips (1990), Mauersberger

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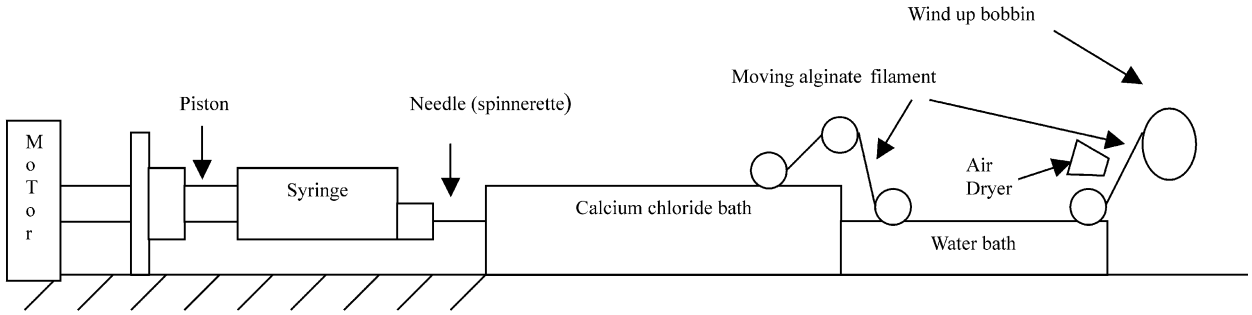


Sketch 1:. The Mini-extruder.

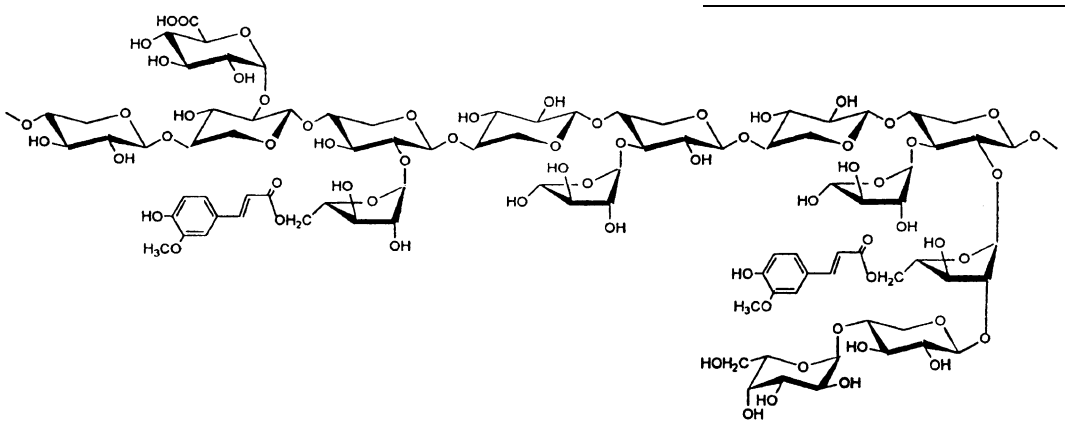
(1947) and Park (1978) and others (Miraftab, Qiao, Kennedy, Anand, & Collyer, 2001).

Seaweed alginate and hence the insoluble fibre of calcium alginate is essentially a copolymer made up of two monomeric acids, D-mannuronic (M) and L-guluronic (G) acids. The relative proportion of the M and G monomers in fibre form in part determines fibre ultimate strength and moisture absorbency. High M unit content is usually related to greater uptake of moisture and hence gives a weaker fibre. Calcium alginate fibres with various proportions of M and G are commercially available (Hongu & Phillips, 1990; Park, 1978; Qin, Agboh, Wang, & Gilding, 1997).

The fibre formation process is simple in operation and is essentially based on exchange of sodium ions (Na^{+}) present in the soluble sodium alginate 'dope' and calcium ions (Ca^{+2}) present in the coagulating calcium chloride bath. The calcium alginate fibre emerging from the coagulation bath is then washed, drawn and dried before being wound up.

1.3. Branan ferulate

Branan ferulate is a polysaccharide or carbohydrate polymer extracted from corn bran. It is composed of L-arabinose, D-galactose, D-glucose, D-glucuronic acid and D-xylose monomer units. Its general chemical structure as described by (Kennedy, Methacanon, & Lloyd, 1999; Kennedy, Methacanon, Lloyd, Paterson, & Knill, 1997) and (USP, 1997) is shown below.



In cross-linked gel form, branan ferulate is currently manufactured by SSL International plc and commercially marketed as Sterigel®. The preparation has special texture, water affinity and water dissolution properties. It is water 'soluble' and its inclusion in alginate fibres would provide instantaneous as well as localised dispensation within the moist wound environment. A laboratory-based extrusion unit has been specifically built and progressively developed for the purpose of developing fibres based on alginate and branan ferulate.

2. Experimental

2.1. Extrusion system and materials

A mini-extruder based on wet extrusion principles has been designed and built in the laboratory. The extrusion unit, as shown in Sketch 1, consists of a surgical syringe and needle, fibre coagulation and water baths, glass guide rollers, and a motorised take up system. A stepper motor geared to the piston inside the syringe controls the dope delivery rate.

The forward movement of the piston pushes the alginate solution through the needle and into the coagulating bath of calcium chloride of known concentration where sodium/calcium ion exchanges take place and a single continues calcium alginate filament is generated. The filament is subsequently guided into and through

Table 1
Details of experimental polymers

Polymers	Company	Manufactures Name and Type
Alginates	Pronova Biopolymer Company	Protanal LF 10/60 (SLP 2975) 65–75% G
	Snap Natural & Alginate Products Ltd	FG (076998)
		EMP (076898)
		LVP (076798)
	NutraSweet Kelco Company	Manucol DH (1039)
		Manucol DM (1040)
		Manucol GHB (1012)
		Manucol DMB (1018)
Corn bran polysaccharide	SSL International	Branan ferulate

the water bath and air blow-dried prior to winding up on a rotating bobbin. The details of the various carbohydrate polymers used in this work as shown in Table 1.

A range of filaments was initially produced from each of these alginates and the influence of the following variables on ultimate fibre properties were determined: dope delivery rate; sodium alginate dope concentration; calcium chloride bath concentration; needle gauge size; and wind up speed.

Each alginate was then extruded with a maximum loading of branan ferulate, i.e. 75% w/w under identified optimum conditions and their tensile properties compared in both dry and wet states. The best performing alginate, i.e. Manucol DH, with respect to relative consistency in strength and extensibility, was subsequently selected for further investigations, Figs. 1 and 2.

Having eliminated all other alginate types, the Manucol DH fibres were further assessed for the effect of wind up

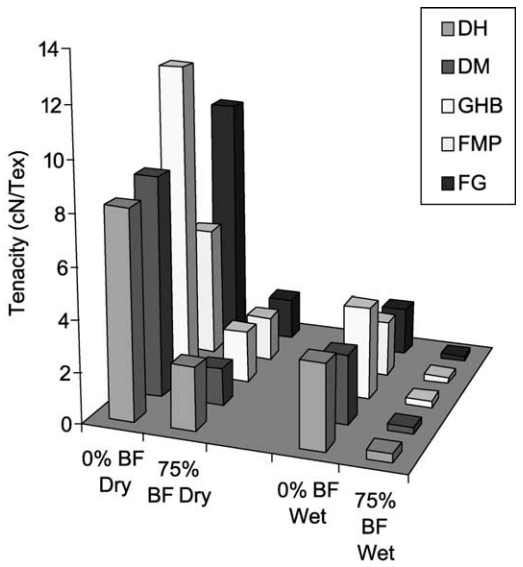


Fig. 1. Comparative tenacity values for various alginate fibres with and without 75% branan ferulate loading.

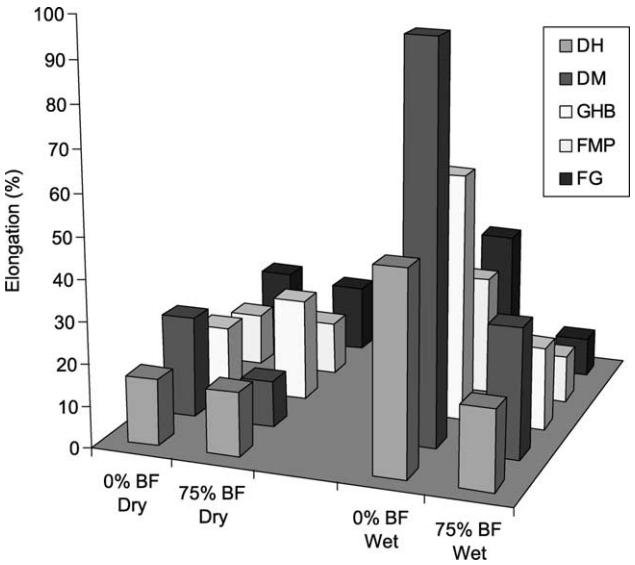


Fig. 2. Comparative elongation values for various alginate fibres with and without 75% branan ferulate loading.

speed on their ultimate tensile properties when containing branan ferulate between zero and 50% w/w. Optical microscopy was later used to examine the filaments in both cross and longitudinal sections.

Standard Brookfield viscometer was used to determine dope viscosity under room condition using a RV6 spindle and result expressed in centipose. All tensile measurements were conducted on Statimat tensiometer with a gauge length of 250 mm and cross-head speed of 100 mm^{-1} throughout the work. 'Dry' fibres were conditioned at 20 °C and 65% R.H. for 24 h prior to tensile testing.

2.2. Analysis of fibres for branan ferulate, etc. contents

The moisture content of the standards and branan ferulate was measured using the Metler–Toledo Halogen Moisture Analyser. The standard drying programme at 80 °C was used. The moisture content of the fibres was measured using an Adberhalden dryer because the sample quantities were typically 50 mg which is too small a quantity to give accurate results using the Metler–Toledo Halogen Moisture Analyser. Samples were placed in the Adberhalden dryer with P_2O_5 under vacuum, using methanol as the refluxing solvent. After 48 h they were re-weighed, and the results recorded.

The samples were weighed into vials. The samples were hydrolysed in duplicate along with pure branan ferulate. Two millimolar Trifluoroacetic acid (1 ml), (TFA) solution was added to each vial. The samples were crimp-sealed and placed on a Grant QBT4 heating block at 121 °C for the required time. The samples were removed from the heating block when required, and the sealed containers were rapidly cooled in cold water. At this point there was no un-dissolved material in the solutions. The samples were rotary evaporated at 45 °C, to remove the TFA. Two additional washes of distilled water (1 ml) were used to ensure TFA removal.

Distilled water (1 ml) was added to the residue. The container was agitated on the whirl-mixer to ensure any products were re-solvated. The samples were then analysed by HPLC, using a Waters 625 LC non-metallic system fitted with a Waters 464 PAD/gold electrode, and a Carbopack PA10 analytical column. Fibres were also ashed and analysed for sodium and calcium using atomic absorption spectroscopy.

3. Results

The investigations revealed that the delivery rate of 1.35 ml min^{-1} produced a steady flow of polymer and allowed sufficient time for coagulation to occur. Alginate dope concentration of 5% w/v gave viscosities in the range of 2.48×10^3–8.3×10^3 cp which extruded well and led to uniform and consistent filaments with good fibre properties. The calcium chloride concentration of 5% w/v was the lowest concentration investigated and provided adequate coagulation so long as the bath containing the solution was no shorter than 1 m in length. Needles of various gauge sizes (20–27 equivalent to cross-sectional areas of 0.125–0.384 mm^2) were used. The finer needles caused intermittent breakage in the spun filaments and the coarsest needle yielded a dope sheet that failed to convert fully in terms of enabling efficient sodium/calcium ion exchange to occur thus drastically affecting fibre strength. The intermediate gauge size of 25 or 0.196 mm^2 produced the best results. Filament wind up speeds in excess of 20 m min^{-1} influenced both the tenacity and breaking extension values of the fibres. These will be referred to again at a later stage.

All the types of alginates mixed adequately with branan ferulate and showed no apparent difference in terms of initial solubility between the types. However, the DM and GHB types prepared under similar conditions were much more viscous and did not spin as easily as the FMP, FG and the DH types. Tensile testing at zero and 75% branan ferulate loading (Fig. 1) under dry state showed a dramatic reduction in fibre tenacities of all alginates types at 75% branan ferulate content, as expected. The reduction in fibre strength was even higher when the fibres were tested wet. The tenacity values for Manucol DH, at 75% loading showed marginally higher values than the other contending alginates when tested wet or dry.

Fibre elongation behaved differently by showing an increase in overall elongation when tested wet, with and without branan ferulate. Manucol DM under wet condition showed the biggest increase in elongation at 75% branan ferulate loading (Fig. 2)

Acknowledging that fibre tenacity plays a greater role in determining the functional ability of fibres than does elongation, Manucol DH alginate type was selected for further detailed study. Its better water solubility also influenced the choice.

Filaments containing increasing proportions of branan ferulate were subsequently produced using the Manucol DH at different wind up speeds and the resulting fibres were tensile tested in dry state. Figs. 3–5 show the effect of branan ferulate content and wind up speed on breaking load, tenacity and breaking elongation, respectively.

These figures show that an increase in wind up speeds, irrespective of branan ferulate content, generally reduces breaking load, tenacity and breaking elongation. A blend of up to 10% w/w branan ferulate marginally improves or at least maintains tensile properties equivalent to those free from branan ferulate. Further increases in branan ferulate content gradually reduce the magnitude of these parameters and at 50% w/w branan ferulate content the fibres become

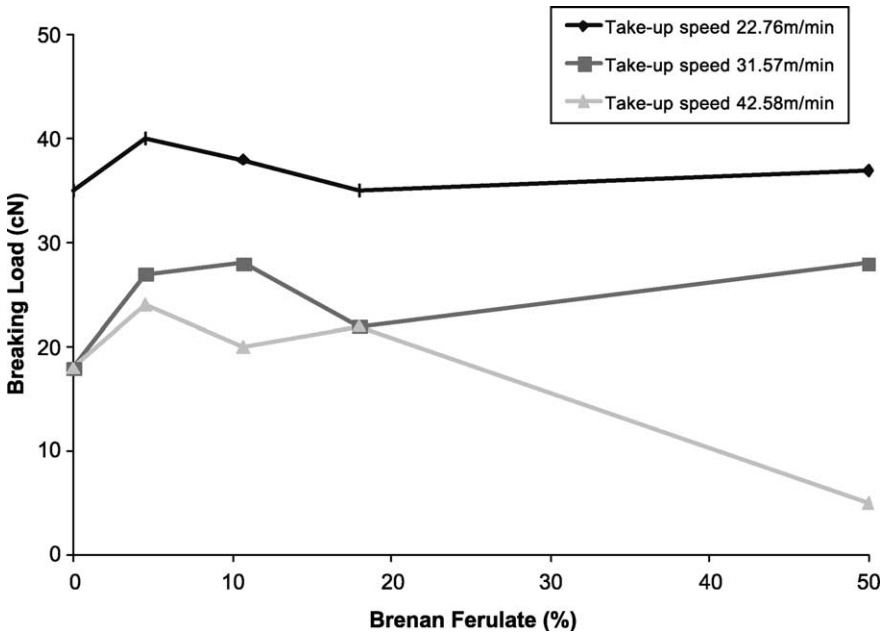


Fig. 3. Effect of branan ferulate content and wound up speed on breaking load of alginate DH fibres.

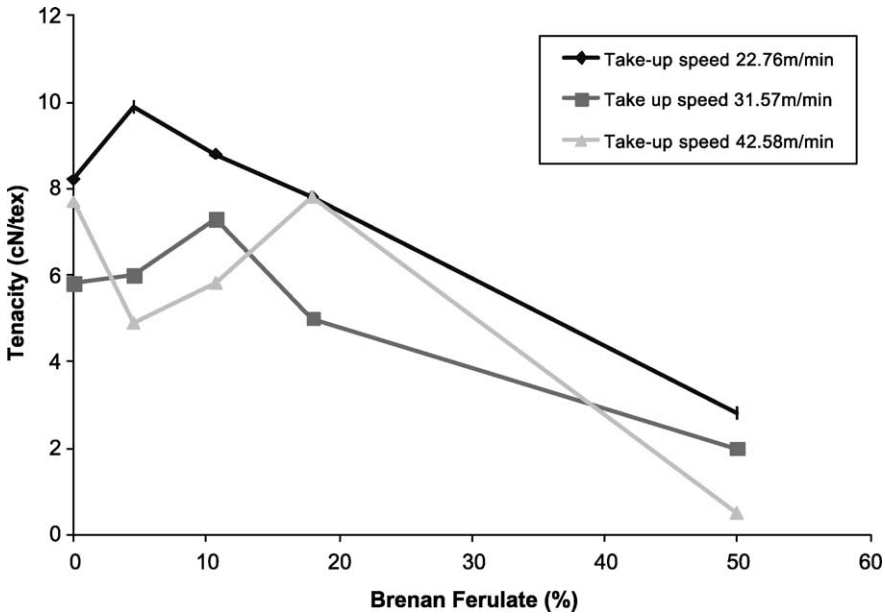


Fig. 4. Effect of branan ferulate and wound up speed on tenacity values of alginate DH fibres.

increasingly sticky causing fibre/fibre and fibre/bobbin adhesion. A branan ferulate content of $>50\%$ increases spinning dope viscosity and reduces extrusion efficiency. However, under these circumstances fibres are still extrudable but, as may be expected, display a marked drop in tensile properties and substantial stickiness. A wind up speed of 22.76 m min^{-1} produces optimum tenacity and elongation for all combinations of alginate/branan ferulate content.

In order to assess the inclusion of branan ferulate into the fibre it was necessary to hydrolyse the fibre to release as monosaccharides the fibre components. The initial aims were to (a) find a monosaccharide released by hydrolysis from the branan ferulate that could be used as a marker and facilitate the determination of the branan ferulate content, and (b) find the hydrolysis time that would produce a high yield of the chosen monosaccharide. During hydrolysis the monosaccharide monomers within the polysaccharide became free monosaccharides. Each monosaccharide molecule gains the molecular weight of water in the process. Where quantification is undertaken this is usually back calculated and the water weight subtracted, and

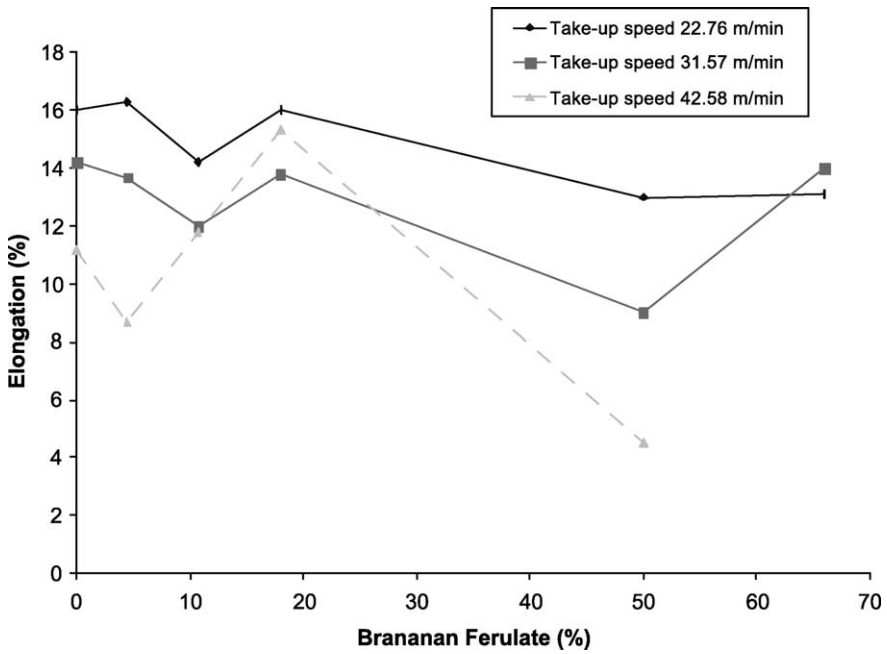


Fig. 5. Effect of branan ferulate and wound up speed on elongation of alginate DH fibres.

Table 2
Hydrolysis of branan ferulate/alginate with respect to time

Hydrolysis time (minutes)	Mean arabinose as (% w/w)
15	1.79
30	1.73
45	1.73
60	1.70

Table 3
Arabinose content of fibre samples and calculated percentage of branan ferulate

Content of alginate (AL) and franan ferulate (BF)	Arabinose (% w/w[a])	Calculated Branan ferulate content (% w/w)
100 % Branan ferulate	13.44	100
	13.05	100
100% Alginate	0	0
	0	0
90% AL 10% BF	1.09	8.26
	1.13	8.52
90% AL 10% BF	1.19	9.02
	1.21	9.17
75% AL 25% BF	3.12	23.55
	3.08	23.23
70% AL 30% BF	3.72	28.08
	3.69	27.89
60% AL 40% BF	4.72	35.62
	4.70	35.51
55% AL 45% BF	5.46	41.19
	5.59	42.23
50% AL 50% BF	6.26	47.27
	6.15	46.45
30% AL 70% BF	9.05	68.30
	8.81	66.48
25% AL 75% BF	9.48	71.58
	9.64	72.75

[a] Duplicate analyses.

the results reported as percentage dry weight in weight. The initial hydrolysis with respect to time to determine optimum hydrolysis conditions was done using a sample the nominal contents of which were alginate 90% and branan ferulate 10%. This sample was chosen as it had the smallest content of branan ferulate, and would prove that even with this

Table 4
Moisture, ash and ion contents of fibres

Analyses	Alginate/branan ferulate fibres	
	30% Branan ferulate	50% Branan ferulate
Loss on drying at 103 °C (% w/w)	17.5	18.2
Ash after 2 × 450 °C (% w/w)	28.2	26.5
Calcium (% w/w on dry basis)	12.2	13.6
Sodium (% w/w on dry basis)	1.1	1.0

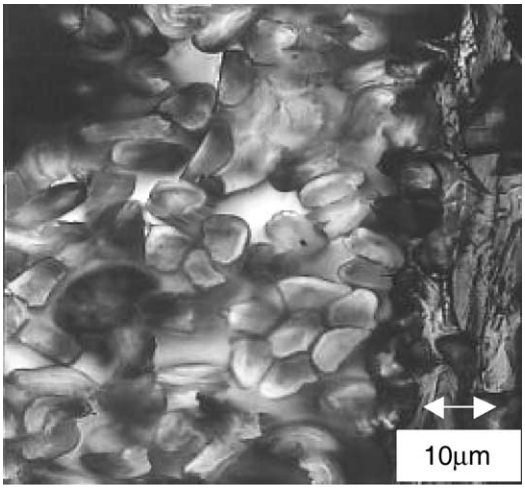


Fig. 6. Cross-section of alginate fibres carrying branan ferulate at low wind up speed.

sufficient amounts of monosaccharide could be obtained for analysis. The chromatogram for the fibre sample showed arabinose, galactose, glucose, xylose, manose and uronic acids. Arabinose could be attributed to the branan ferulate alone, and was maximally released at 15 min hydrolysis (Table 2). The quantity generated by the alginate/BF fibres could be expressed as a percentage of the arabinose in the pure branan ferulate at 15 min.

This procedure was therefore used for analyses of the various fibres produced and the data for such are recorded in Table 3. Other aspects of the composition of two example fibres are shown in Table 4.

The visual appearance of alginate filaments containing increasing proportions of branan ferulate changes from off white to pale yellow and eventually to gold. The cross-sectional shapes of the fibres also change with increasing wind up speeds and drying efficiency (Figs. 6 and 7).

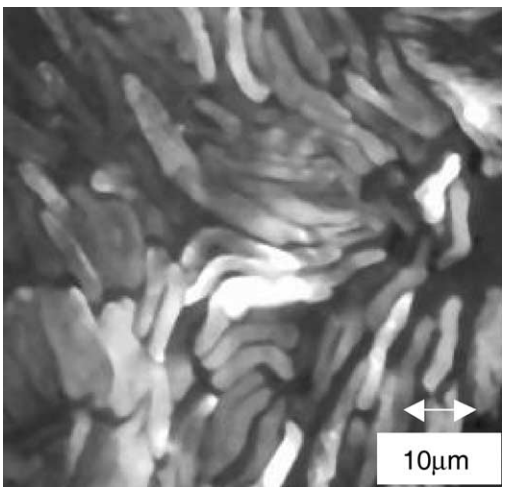


Fig. 7. Cross-section of alginate fibres carrying branan ferulate at maximum wind up speed.

4. Discussion and conclusions

Whilst branan ferulate cannot be spun into fibres in its pure or unaided state, it can easily be blended and carried by an alginate-based fibre as has been demonstrated by this work. The addition of branan ferulate to appropriately selected alginates can be as high as 75% w/w without severely affecting fibrous characteristics. Although all alginate types show a reduction in tenacity and increase in elongation when tested wet, some types show proportionally better retention of these properties when combined with branan ferulate. However, since branan ferulate is inherently sticky, this will gradually be reflected in the resulting fibres with its increasing addition. Depending on the specific method of fabric conversion and area of application, i.e. non-woven, knitted or woven, the branan ferulate content may be adjusted to achieve desired tensile and other mechanical properties. Generally, increase in wind up speed reduces breaking load and tenacity of all alginates irrespective of branan ferulate content. However, larger additions of branan ferulate, i.e. nominally $>20\%$, gradually suppresses these parameters and at the highest branan ferulate concentration show drastic effects. A take-up speed of 22.76 m min^{-1} produces the best results under all conditions and maintains consistent elongation-at-break values under all branan ferulate-loading conditions. However, to address practical applications, optimum formulations should not exceed 18% w/w branan ferulate content to avoid unnecessary adhesion whilst maintaining acceptable tensile and mechanical properties. In addition, cross-sectional dimensions of these fibres are shown to be independent of branan ferulate content. They may be regulated, however, with respect to the type of drying unit employed and spinning conditions adopted.

According to Table 3, the inclusion of branan ferulate into the fibres was nearly the maximum possible. The mean loss of branan ferulate from the fibres was 2.7 % (range 1.3–4.4%). This was encouraging since there was a chance that water soluble branan ferulate could be lost into the spinning and washing baths liquids.. The loss of soluble branan ferulate from the fibres showed no specific trend and it did not increase with branan ferulate concentration. This would suggest that the loss of branan ferulate only occurs from the surface of the precipitating fibre. This surface loss has implications for the fibre production:

- A fibre with a circular section would lose the least amount of branan ferulate.
- Fibre spinning with a smaller gauge needle would increase the loss of branan ferulate.

The two fibres examined show that the calcium contents c.f. sodium contents are: 91–93% Ca, 9–7% Na% w/w or 85–88 Ca% molar basis, 15–12 Na% molar basis. This means that on average approximately one in seven carboxyl groups are sodium substituted rather than calcium. Changes in these ratios could be achieved and may improve fibre properties. Two ways are possible—changes in the cation composition of the fibre spinning bath, and ion exchange on the pre-made fibre. The latter could prove more difficult on account of low permeability of the fibre, but the variations possible may affect the quantities of the fibre produced.

It may be concluded that the mini-extruder, designed and built in the laboratory, has enabled fundamental investigation into alginate fibres containing branan ferulate and has allowed exploration of the range of qualities of these fibres.

Acknowledgements

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