

Calcium Alginate Gel Fibers: Influence of Alginate Source and Gel Structure on Fiber Strength

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SYNOPSIS

The low-deformation extension modulus was measured for Ca–alginate gel fibers prepared from alginates of different compositions and molecular weights. The modulus showed an increase with increasing molecular weight for alginates of the same composition and sequence parameters. Fibers prepared with an inhomogeneous polymer concentration profile showed higher moduli than did fibers with a homogeneous polymer concentration profile. The higher modulus observed for fibers prepared from an alginate with low Ca²⁺ affinity is tentatively explained as resulting from a higher degree of polymer chain alignment. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Alginates are a family of linear copolymers of β -D-mannuronate (M) and α -L-guluronate (G) with widely varying monomer composition and sequence. The alginates are well known for their gelling and viscosifying properties,^{1,2} and they are also used for fiber spinning by extruding a sodium alginate solution into a calcium chloride spinning bath.

Alginate fibers have several commercial or potential areas for use in such diverse areas as in pharmacy as wound dressings,^{3–6} in food technology,⁷ for paper production,^{8–10} in the textile industry,^{6,11,12} and for immobilization purposes.¹³ Despite the diversity in the use of alginate fibers, not much is found in the literature regarding the physical properties of such fibers in relation to the chemistry of the material used. Alginates, which often are regarded as a defined polymer, are, in reality, a family of biopolymers rather than one polymer with defined physical and chemical properties.^{1,2} The physical and chemical properties of alginates depend on both the monomeric composition and sequence of the polymer, which vary greatly depending on the source of

the alginate.^{2,14} In this work, we show that some physical properties of such fibers are strongly dependent on the type and, thus, on the chemistry of the alginate used for fiber production.

EXPERIMENTAL

Four commercial *Laminaria hyperborea* alginates (denoted LF 5/60, LF 10/60, SF a, and HF a) and one *Ascophyllum nodosum* alginate (LV M) were provided by Pronova Biopolymers, Drammen, Norway. One alginate (W-1) was obtained from Wako Pharmaceutical Co., Osaka, Japan. The composition and sequence parameters, given as the molar fraction of guluronate and mannuronate residues (F_G and F_M), the diad frequencies (F_{GG} , F_{MM} , and F_{GM} [$\approx F_{MG}$]), the G-centered triad frequencies (F_{GGG} , F_{MGM} , and F_{GGM}) and the average number of consecutive guluronate residues in the G-blocks ($N_{G>1}$) were determined from the ¹H-NMR spectra recorded at 92°C on a Bruker 500 WM spectrometer.^{15,16} The molecular weight of the alginate samples was determined from intrinsic viscosity measurements using the Mark–Houwink–Sakurada equation.^{17,18} The intrinsic viscosity was measured in 0.1M NaCl in aqueous solution in a Micro-Ubbelohde viscometer, Schott-Geräte. The composition and molecular weight parameters are given in Table I.

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Table I Sequence Parameters and Intrinsic Viscosities of Alginates

Alginate	F_G	F_{GG}	F_{GM}	F_{GGG}	F_{GGM}	F_{MGM}	$N_{G>1}$	$[\eta]$	M_v (g/mol)
LF 5/60	0.70	0.59	0.10	0.54	0.05	0.05	13.1	3.0	100,000
LF 10/60	0.69	0.57	0.12	0.52	0.05	0.07	13.2	7.2	210,000
SF a	0.67	0.55	0.12	0.51	0.05	0.07	13.0	11.0	310,000
HF a	0.70	0.59	0.11	0.55	0.04	0.06	14.9	13.8	380,000
LV M	0.39	0.23	0.16	0.17	0.07	0.09	4.5	7.4	280,000
W-1								7.2	270,000

Alginate gels, when prepared by diffusing gelling ions into a Na-alginate solution, show a concentration inhomogeneity as illustrated in Figure 1. This concentration inhomogeneity can be controlled by a careful selection of alginate molecular weight, concentration of gelling ions in the gelling bath, and concentration of nongelling ions in the alginate solution and in the gelling bath.^{19,20} Fibers with a homogeneous alginate concentration profile were made by extruding a 3% Na-alginate/0.2M NaCl solution through syringes with a diameter of 0.5 mm into a bath of 0.1M CaCl₂/0.2M NaCl and winding them onto a drum with a diameter of 20 cm. Fibers with an inhomogeneous concentration profile were made from a 3% Na-alginate solution extruded into 0.1M CaCl₂. The flow rate was approximately 0.5 mL/min. In one experiment, the drum speed was varied while keeping the flow rate constant.

Fiber strength was measured by stretching 13 cm-long wet gel fibers at 2 cm/min in a Toyo Baldwin Tensilon UTM-III-500, and the initial tangent of the stress-strain diagram was calculated. The cross-

sectional areas of the fibers were measured by microscopy. These data permitted the calculation of the extension modulus of the gel fibers. The relative deformation speed of 0.154 min⁻¹ should give not more than 5% error in the modulus at a zero deformation rate.^{21,22} This error is negligible compared to other factors like variation in cross-sectional area and uncertainty in determining the initial tangent of the stress-strain diagram.

RESULTS AND DISCUSSION

A summary of the results is given in Tables II and III. Figure 2 gives the moduli of *L. hyperborea* alginates of different molecular weights. The modulus of these alginate fibers increases in the whole range of intrinsic viscosities. This is contrary to the behavior of alginate gel cylinders or beads formed by diffusing Ca²⁺ ions into a solution of Na-alginate. For cylindrical and spherical gels prepared this way, the modulus increases with increasing molecular

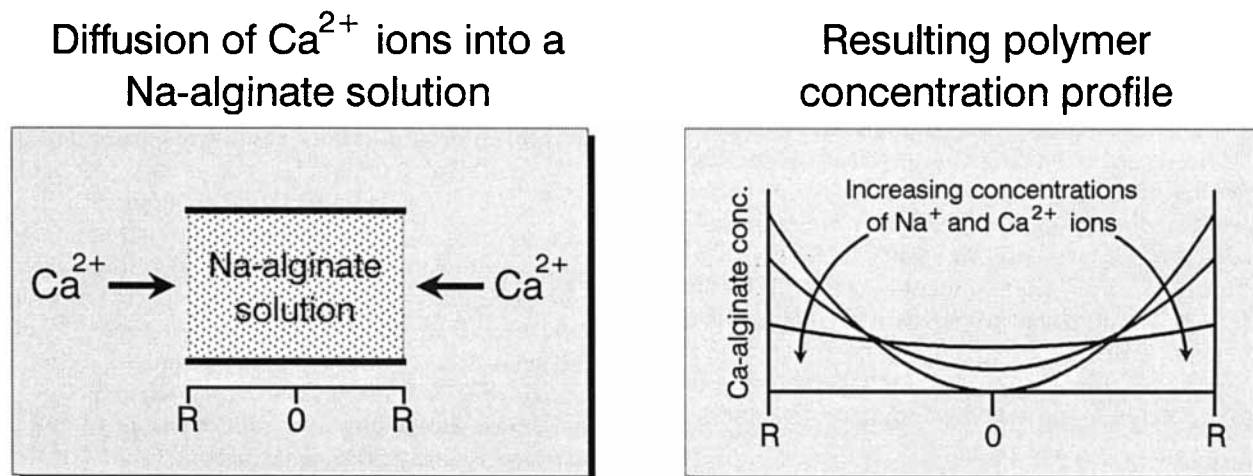


Figure 1 Gel concentration profiles for Ca-alginate gel cylinders prepared by diffusing Ca²⁺ ions into a Na-alginate solution.¹⁹

weight up to a molecular weight of approximately 300,000 g/mol.^{22,23} The difference between fibers and other types of alginate gels may be due to the flow orientation of molecules. Such orientation is preferred in the spinning of fibers and are vital for obtaining a high modulus along the fiber axis. This phenomenon is illustrated in Figure 3, which indicates that the modulus of alginate fibers seem to increase with increasing spinning speed at a constant flow rate. The increased spinning speed would also counteract "die swell," something that is reported to have a negative effect on molecular chain orientation in alginate gels obtained by the flow-gelation method.²⁴

As seen from Figure 2 and Table II, inhomogeneous alginate fibers have considerably higher moduli than those of homogeneous fibers. The modulus of alginate gels is proportional to the square of the alginate gel concentration,²² as should be expected for a gel formed by bimolecular association of chains. The modulus (E) of an alginate gel fiber averaged over the cross-sectional area may, thus, be given by

$$\bar{E} = \frac{1}{\pi R^2} \int_0^R k \cdot [c(r)]^2 dA$$

$$= \frac{2k}{R^2} \int_0^R [c(r)]^2 \cdot r dr \quad (1)$$

where

$$c_{av} = \frac{1}{\pi R^2} \int_0^R c(r) \cdot r dr \quad (2)$$

and R is the cross-sectional radius of the fiber; A , the cross-sectional area of the fiber; k , a constant; $c(r)$, the polymer concentration at the distance r from the center of the cross section; and c_{av} , the average polymer concentration of the gel.

The integral can be evaluated numerically by choosing an arbitrary function for $c(r)$, which gives a qualitative agreement with experimental data. This is illustrated in Figure 4, where the function $c = A \cdot r^n + B$ is chosen as $c(r)$ and the parameters A and B are chosen so as to give a constant average concentration. The integral $\int_0^R (A \cdot r^n + B)^2 \cdot r dr$ is then evaluated numerically. It is evident that the parameters B and n are indications of the homogeneity of the gel: $B = 0$ is equivalent to maximum inhomogeneity, whereas $B = c_{av}$ is equivalent to a homogeneous gel. Likewise, $n = 0$ is equivalent to a perfectly homogeneous gel, whereas increasing values for n denotes an increasing inhomogeneity. This shows that the highest gel fiber strength is obtained

Table II Moduli of Ca-Alginate Fibers Made from Different Alginates

Alginate	F_G	$N_{G>1}$	$[\eta]$	Na-Alginate concn, % (w/v)	Ca-Alginate concn, % (w/v)	Extension Modulus, E (N/cm ²)		Extension Modulus at 3% Gel Concentration, $E_{c=3}$ (N/cm ²)	
						Homogeneous	Inhomogeneous	Homogeneous	Inhomogeneous
LF 5/60	0.70	13.1	3.0	3.0	4.0	30 ± 3	145 ± 15	16.9 ± 1.7	82 ± 8
LF 10/60	0.69	13.2	7.2	3.0	4.0	80 ± 9	215 ± 19	45 ± 5	121 ± 11
SF a	0.67	13.0	11.0	3.0	4.0	164 ± 27	338 ± 25	92 ± 15	100 ± 7
HF a	0.70	14.9	13.8	3.0	4.0	186 ± 39	142 ± 12	105 ± 22	
LV M	0.39	4.5	7.4	3.0	5.5	313 ± 32		176 ± 10	
W-1			7.2	3.0		86 ± 5			

Table III Moduli of Ca-Alginate Fibers Made from LF 10/60 Alginate

Spinning Speed (rpm)	Spinning Speed (cm/min)	Modulus (N/cm ²)
2	126	68 ± 9
3	188	71 ± 4
4	251	80 ± 7
7	440	107 ± 9

Dependence of modulus on spinning speed. Gulosonic acid content of alginate (F_G): 0.7; intrinsic viscosity ($[\eta]$): 7.2 dL/g.

by optimizing the concentration inhomogeneity of the fiber.

It can also be seen from Table II that the modulus for a low-G alginate, LV M, is considerably higher than for a high-G alginate of the same intrinsic viscosity, even when correcting for the increased synthesis of low-G alginate gels.²³ For alginate gel cylinders or beads, the modulus increases with increasing guluronate content and also with increasing average guluronate block length.^{22,23} One can only speculate on the reason for the difference between alginate gel fibers and other types of alginate gels in this context. One hypothesis that may provide an explanation is that the weaker chain-chain interactions of the *Ascophyllum* alginate with shorter guluronate blocks allow a better alignment of polymer molecules. This could then give a higher gel strength parallel to the fiber axis. The effect of inhomogeneity is also lower for this alginate, a fact that supports this hypothesis. For a gel with the polymeric molecules perfectly aligned with the fiber

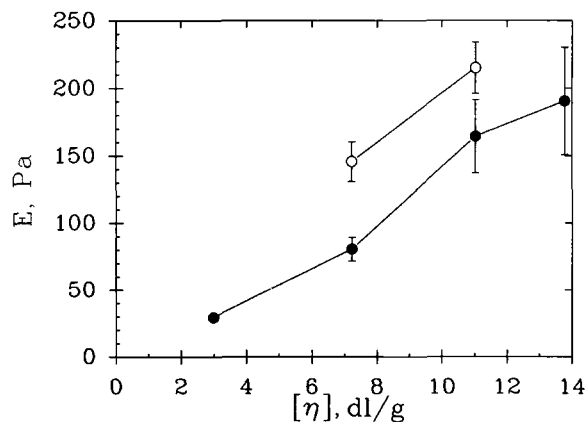


Figure 2 Extension modulus for Ca-alginate gel fibers prepared from 3% (w/v) Na-alginate solutions, $F_G = 0.7$. Dependence on intrinsic viscosity of alginate. (●) Homogeneous fibers; (○) inhomogeneous fibers.

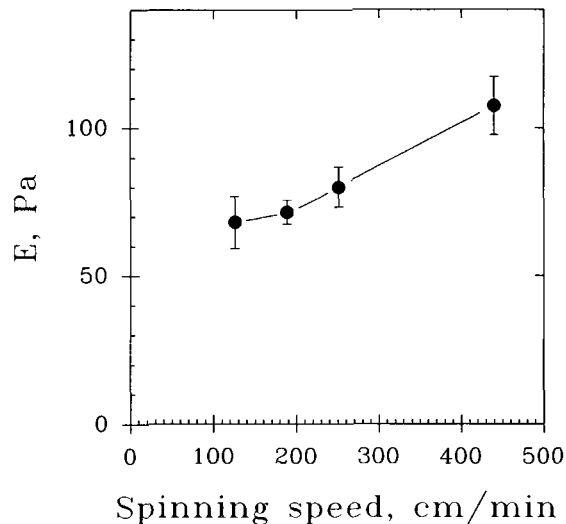


Figure 3 Extension modulus for Ca-alginate gel fibers prepared from 3% (w/v) Na-alginate solution; $F_G = 0.7$; $[\eta] = 7.2$ dL/g. Dependence on spinning speed.

axis, the modulus should be proportional to the number of chains per unit cross-sectional area. Thus, the modulus should be proportional to the polymer concentration in the first power rather than in the second power, as is the case for an isotropic gel. This would lead to the modulus of the gel fibers being independent of the polymer concentration profile.

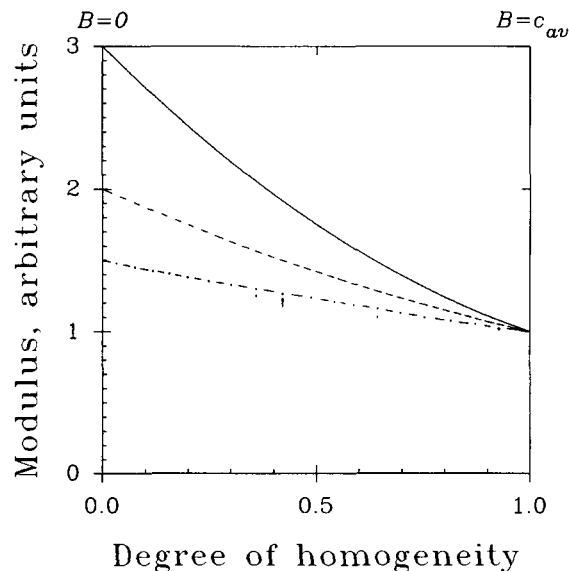


Figure 4 Calculated extension modulus of Ca-alginate gel fibers at various degrees of homogeneity. Calculated using eq. (1) with $c = Ar^n + B$. (—) $n = 2$; (---) $n = 1$; (-·-·-·-) $n = 0.5$ (the magnitude of n is indicative of the degree of inhomogeneity).

CONCLUSION

The low-deformation extension modulus of Ca-alginate gel fibers increases with increasing molecular weight of the alginates. This increase is apparent in a larger molecular weight range than for alginate gel cylinders and beads. Gel fibers with an inhomogeneous concentration profile have a higher modulus than that of gel fibers with a homogeneous concentration profile. This is in accordance with the literature that shows that the modulus of alginate gels is proportional to the square of the polymer concentration. Fibers made from an alginate with a low guluronate content and a lower average guluronate block length have a higher modulus than that of fibers made from alginates with a high guluronate content and high average guluronate block length. There is apparently no difference in the modulus of homogeneous and inhomogeneous fibers made from a low-G alginate. This may be due to a less concentration-dependent modulus because of a better alignment of the polymer molecules.

The preliminary results given in this article suggest that the alginates are interesting molecules for elucidating effects of varying the chemical composition of the polymer, ion-induced chain-chain interactions, and the distribution of polymer over the cross-sectional area of the fibers. Further work is in progress in our laboratory.

The work has been performed during a stay at the Research Institute of Polymers and Textiles, Tsukuba, Japan. Two of the authors (S.T.M. and G.S.B.) gratefully acknowledge the financial support from the Norwegian Research Council for Science and Technology and from Pronova Biopolymers A/S, Drammen, Norway.

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Received June 4, 1993

Accepted August 30, 1993