Manufacture and Physical Properties of Alginate Fiber Papers as an Analysis Model of Cellulosic Fiber Papers

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Synopsis

The staple fibers of Ca alginate or alginic acid were found to have interfiber self-bonding, which allowed us to make papers composed of fibers with homogeneous fiber diameter and fiber length without binders. The analysis of the effect of the molecular weight (MW) and fiber diameter on physical properties of the sheets showed that strength factors, except zero span breaking length and tear index, increased with increase of MW of alginic acid up to 6 $\times$ 10^5 dalton. The folding endurance was the most sensitive to MW, requiring a MW of 5 $\times$ 10^5 dalton or higher to reach the level of 10 folds. The breaking length of alginate fiber papers ranged from 2.0 to 3.5 km and was higher than that of the corresponding free acid fiber sheets. Investigation of the effect of fiber length indicated that the folding endurance increased almost linearly with increase in fiber length but that the breaking length and tear index were maximum at a fiber length of 3.0 mm, suggesting that these factors were mainly influenced by sheet formation. The paper formability of the metallic salts of alginate fiber was as follows: Ca^{2+} > Ba^{2+} > Al^{3+} > > Fe^{3+}. The admixture of acidic polysaccharides, such as pectin and κ -carrageenan with Na alginate, also made it possible to spin continuous yarn. Papers obtained from the admixed fibers had higher bulk density and Young's modulus by 1.5–1.8 times and were very transparent, just like glassine paper. X-ray microanalysis showed that the Ca alginate fiber had no skin-core structure, homogeneously distributing Ca^{2+} in whole fiber.

INTRODUCTION

Sodium alginate, a water-soluble block linear polymer comprised of α-(1,4)-L-guluronate and β-(1,4)-D-mannuronate, is well known to have spinnability.[1-7] Several trials were made to produce nonwoven from continuous alginate filament binders, such as Na alginate.[8-14] The nonwovens thus obtained were weak in strength for practical applications. Two patents[15,16] suggesting the application possibilities of Ca alginate fiber to papermaking have been published to date but did not provide methods for producing paper with good formation because of the application of Na alginate binder[15] and crushing the gel fiber by beating.[16]

Based on the authors' finding that the wet fiber web had interfiber self-bonding properties when slender fibers with suitable fiber length were homogeneously dispersed in water without beating, papermaking with the fiber has succeeded in yielding paper with good formation very similar to that of cellulosic paper. Considering that regenerated cellulosic fibers, such

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as rayon fiber, generally lose interfiber self-bonding ability, with a few exceptions, such as rayon with a large hollow structure,[17] this fiber paper was supposed to offer a model for analysis of physical constitution and roles of hemicelluloses in paper. The present paper reports the manufacture and fundamental physical properties of papers made from staple fibers comprised of alginic acid, a mixture of the acid with other uronic acids, or their water-insoluble metallic salts without binders.

EXPERIMENTAL

Materials

Sodium alginate with different polymerization degrees, graded IL-2, I-1, I-3, H, and IS, was available from Kimitsu Kagaku Co., Ltd., Chiba Prefecture, Japan. The molecular weights were determined by intrinsic viscosity measurement in 0.1 *M* NaCl using the formula reported by Smidsrd.[18,19] Citrus pectin and κ -carrageenan were obtained from Wakô Pharmaceutical Co., Ltd., Osaka, Japan, and Fushimi Pharmaceutical Co., Ltd., Marugame, Japan, respectively.

Apparatus

A wet spinneret for rayon designed and constructed by Tôhô Rayon Co., Ltd., was applied by attaching two kinds of nozzles with 1000 holes 0.10 and 0.055 mm in diameter. The Ca alginate fiber spun through the latter nozzle was measured at 0.6 denier (air-dried).

Production of Staple Fibers

Aqueous dopes (3–5 wt%) of Na alginate or its mixture with citrus pectin or κ -carrageenan, the weight ratio of which was 3:1, were filtered through a pressurized filter holder KST-293-01 manufactured by Tôyô Kagaku Co., Ltd. using Tôyô Roshi's filter paper No. 60. The filtered dopes were extruded through the wet spinneret into a coagulating solution of 5.0 wt% metallic chloride (Ca^{2+}, Ba^{2+}, Al^{3+}, or Fe^{3+}) at a spinning rate of 13.8 ml/ml, followed by stretching 1.2–1.6 times.

The A1 alginate was too weak to give continuous yarn.

The wound continuous yarns were dehydrated the centrifugation and then cut using a guillotine cutter manufactured by Onouchi Seisakusho Co., Ltd., Kyoto, Japan. The fiber lengths prepared were 1.5, 3.0, and 5.0 mm. Fibers with fiber length greater than 5.0 mm were not well dispersed in water. Fibers of alginic acid or its mixture of acidic polysaccharides were prepared by soaking the corresponding Ca salt fibers in 18% HCl for 20 min at room temperature, followed by water washing.

Papermaking

As the short-cut fibers contained a small amount of clots and bundles, they were defiberized by a disintegrator with a capacity of 10 L at a consistency of approximately 2.5–6.0% for 10–30 min and then were screened through a 6/1000 in. mesh flat screen. The screen-passed fibers were collected using a 250-mesh cloth sieve. Sheets were hand-made according to

Japan Industrial Standards P 8209. As the wet webs had high shrinkage, they were air-dried by fixing them together with filter paper upon dry rings under tension with a cover of filter paper. The basic weight of the papers thus obtained ranged usually from 70 to 80 g/m^2 but were sometimes around 100 g/m^2.

Analysis of Physical Properties

Strength index was calculated according to Cunningham et al.[20] Young's moduli were measured by sonic sheet tester SST-200 manufactured by Nomura Shoji Co., Ltd., Tokyo, Japan.

RESULTS AND DISCUSSION

Spinnability and Dispersibility

The spinnability of Na alginate dope was not affected by MW within the range $1.8–7.8 \times 10^5$ dalton but was largely dependent on coagulating metallic salts: $CaCl_2$ and $BaCl_2$ yielded smoothly continuous yarns though $FeCl_3$ afforded a somewhat continuous yarn with frequent repair of cutting during the stretching operation. The Fe^{3+} alginate fiber permitted papermaking only when it was made within a week because it became very fragile with lapse of time. In the dispersing operation for papermaking, the Ca^{2+} alginate fiber had a noticeable tendency to cohere when compared with the corresponding free acid fiber. In papermaking the alginic acid fiber was often observed to stick to the wire net too fast to peel off. This was due to salt formation on reaction of the metallic ion on the wire.

Interfiber Self-bonding

Regenerated cellulosic fibers, such as rayon, have usually far less interfiber self-bonding than natural cellulosic pulps, and in general require binders to make rayon paper.[21] Exceptional self-bonding rayon fiber, like Avisco RD-101,[21,22] has a large hollow constitution with a large bonding area. An attempt was made to spin carboxymethylcellulose in a similar manner to alginate spinning, but no yarn was obtained. The fibers of alginic acid and its water-insoluble metallic salts were found to have interfiber self-bonding properties even if they had small contacting area, just like a slender round fiber. This indicates that paper could be made from 100% alginic acid or its water-insoluble salts without the necessity of working binders, such as Na alginate and PVA, or fibrillation. Moreover, the fiber showed a clear x-ray diffraction pattern similar to that of cellulose, calculating that the distance along the fiber axis was 8.7 instead of 10.3 Å for cellulose.[23] These data implied that papers from fibers with given diameter and fiber length of alginic acid or its water-insoluble salt salts provided models for the analysis of physical properties concerning with natural pulp paper.

Effects of Molecular Weight and Fiber Diameter

Fixing at a fiber length of 3.0 mm, four types of the paper were prepared: Ca alginate fibers spun through 0.1 and 0.055 mm hole diameter and the corresponding alginic acid fibers. The strength characteristics as well as

other physical properties were analyzed as a function of MW. The bulk density of sheets made of the fibers gradually increased with an increase in MW and lessening fiber diameter, ranging from 0.4 to 0.8 g/cm^3. The sheets from Ca alginate were higher in density than those of the corresponding free acid fibers. The results are illustrated in Fig. 1. In comparison with self-bonded rayon paper (density, 0.55 g/cm^3),[22] the alginate fibers gave higher bulk density in a higher MW region. Breaking length was comparatively small in the smaller MW range but rapidly increased over a MW of 5.0×10^5 dalton (Fig. 2). This indicated that higher tensile strength required higher MW. The sheets composed of the fibers 0.10 mm in diameter were higher than those of 0.055-mm fibers, regardless of the Ca salt, and free acid types. Moreover, the Ca salt fiber sheets were higher in tensile strength than the free acid fiber, which showed that the anionic surface provided larger interfiber bonding. The zero span breaking length, an index of single fiber strength, of the four types was not much influenced by MW and ranged from 4.4 to 5.6 km. The ratio of zero span breaking length to breaking length was in the range 1.5–3.8, except the free acid fiber, which was 0.055 mm in diameter and had a ratio of 5.2. The results are summarized in Fig. 3.

The elongation of fiber sheets was within the range 0.6–2.7%, increasing with increase of MW up to 6×10^5 dalton and then decreasing (Fig. 4). The Ca alginate fiber sheets always had higher values than the corresponding free acid fiber sheets. In comparing fiber diameter, the sheets of thick fibers showed higher elongation. The tear indices of the sheets from the alginic acid and Ca alginate fibers ranged from 5 to 8 mN • m^2/g and were almost independent of MW, fineness, and Ca salt or free acid. Compared with those of seld-bonding rayon sheets,[22] the values were ranked approximately from one-half to one-third. The burst indices of the sheets ranged from 0.03 to 2.7 kPa•m^2/g. They increased with increase in MW up to 6×10^5 dalton and then decreased. The Ca alginate fiber sheets had higher values than the free acid sheets. The greater fineness reflected the higher index. Therefore, the sheet from alginic acid fiber of 0.055 mm fiber diameter was generally very low in this index, as shown in Fig. 5. The folding endurance of the fiber sheets was found to be greatly influenced by MW,

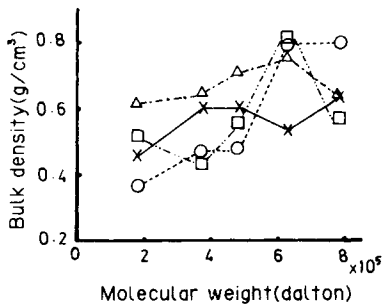


Fig. 1. Dependence of bulk density on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers: (X—X) Ca alginate fiber with diameter 0.10 mm; (○ · · ·○) alginic acid fiber with diameter 0.10 mm; (△– · –△) Ca alginate fiber with diameter 0.055 mm; (□– · · □) alginic acid fiber with diameter 0.055 mm.

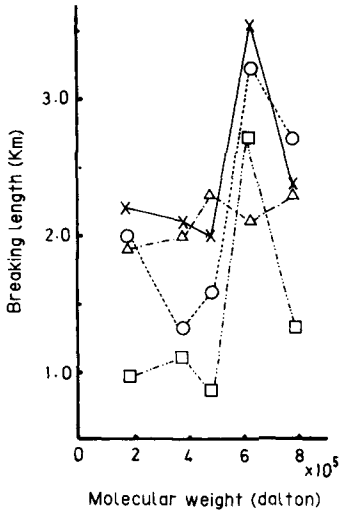


Fig. 2. Dependence of breaking length on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.

as given in Fig. 6. The sheets from the fiber with MW 4×10^5 dalton or less gave fewer than 10 folds, but the values reached the level of several tens of folds when the MW was over 5×10^5 dalton. It was higher with the Ca alginate and greater fineness. The aforementioned strength items were collated with strength index,[20] and the dependence of MW upon strength index is summarized in Fig. 7. The index increased with increase in MW up to 6×10^5 dalton. The selection of Ca alginate and greater fineness gave higher values. The Young's moduli of the sheets from Ca alginate and free acid fibers of 0.10 mm fiber diameter were measured as a function of MW. As illustrated in Fig. 8, the modulus had a tendency to increase with increase in MW. The values were not much influenced by the form of alginic acid, ranging from $1.0–5.0 \times 10^{10}$ dyn/cm^2. Concisely summarizing the relationship of strength properties with MW, most

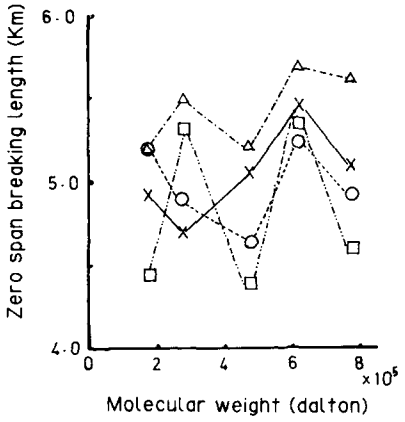


Fig. 3. Dependence of zero span breaking length on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.

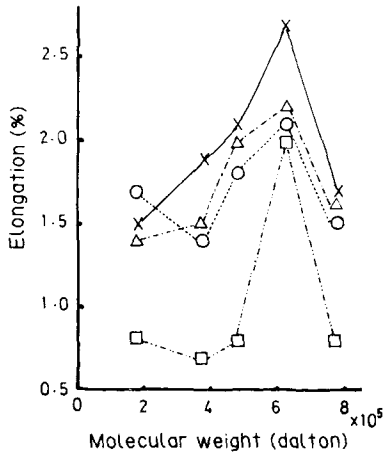


Fig. 4. *Dependence of elongation on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.*

strength factors, except zero span breaking length and tear index, increased with increase in MW up to approximately 6×10^5 dalton. Among the strength items, the folding endurance was the most sensitive.

Effect of Fiber Length

The fiber length was limited within the range from 1.0 to 5.0 mm because fibers longer than 5.0 mm were promoted to aggregate. The dependence of fiber length upon strength properties was determined using sheets from Ca alginate fibers with fiber diameters of 0.055 mm and MW of 6.3×10^5 dalton. The results are summarized in Fig. 9. It was found that the burst

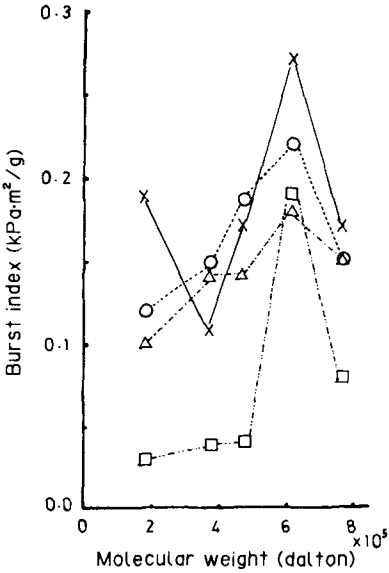


Fig. 5. *Dependence of burst index on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.*

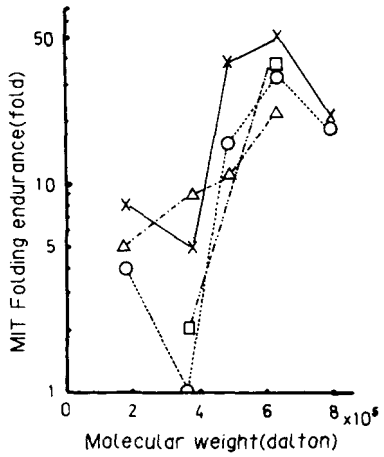


Fig. 6. Dependence of MIT folding endurance on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.

index and elongation were not very much affected by fiber length. The folding endurance increased almost linearly with increase in fiber length. These results coincide with Clark's measurement[24] that the folding endurance is strongly influenced by fiber length. The breaking length and the tear index unexpectedly reached a maximum at a fiber length of 3.0 mm. Combined with the fact that the formation was best at this fiber length (data not shown), it could safely be said that these factors in the alginate fiber sheets were mainly determined by formation. This is because the breaking length and tear index in rayon paper increase with fiber length at a given content of PVA binder.[25] In comparison with cellulosic fiber sheets, alginate fiber sheets have much lower scattering coefficients (80–170 cm^2/g) and absorption coefficients (5–10 cm^2/g). Both coefficients were plotted against fiber length, and the results are illustrated in Fig. 10. The scattering coefficient increased with increase in fiber length because the optical non-bonding area became larger. On the other hand, the absorption coefficient decreased with increase in fiber length. The Ca alginate fiber

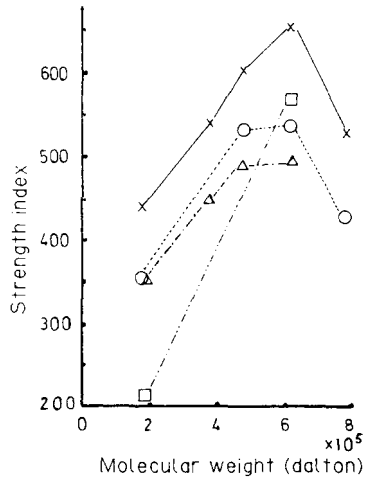


Fig. 7. Dependence of strength index on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notation in Fig. 1.

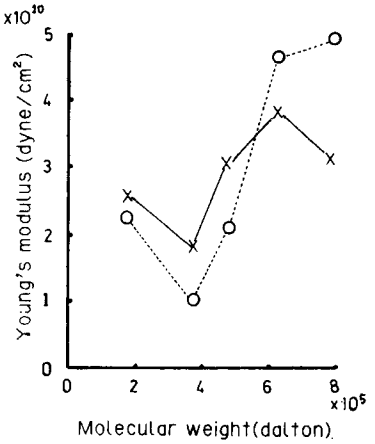


Fig. 8. Dependence of Young's modulus on molecular weight of alginate in papers made from Ca alginate and alginic acid fibers. See notations in Fig. 1.

sheets had a lower scattering coefficient but a higher absorption coefficient than the corresponding free acid fiber sheets.

Effect of Metallic Ions

Sheets were hand-made from Al^{3+}, Ba^{2+}, and Fe^{3+} alginate fibers in addition to Ca^{2+} alginate fibers. The fibers were composed to have a fiber length of 3.0 mm. The results are summarized in Table I. The Al^{3+} alginate fiber was so weak that it did not give continuous yarn during spinning. The sheet from this fiber was also weak. The Ba^{2+} alginate yielded comparatively superior continuous yarn under wet conditions but gave very rigid and brittle sheets. The Fe^{3+} alginate fiber yielded a fragile sheet with very small interfiber bonding, although the fiber itself was easily spun. From the viewpoint of papermaking, the order of metallic ions as coagulants was

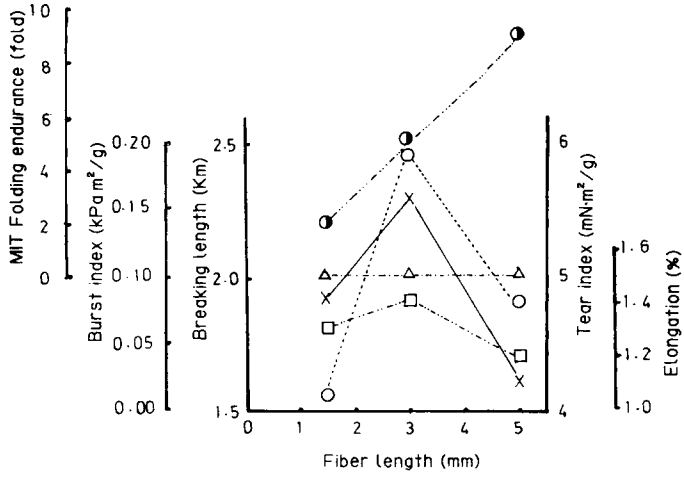


Fig. 9. Dependence of strength properties on fiber length in papers made from Ca alginate and alginic acid fibers. The fibers with diameter 0.055 mm had a MW of 1.8×10^5 dalton: (x—x) breaking length; (△–·–·–△) burst index; (○· · ·○) tear index; (□–· — · □) elongation; (◐– · · · –◐) MIT folding endurance.

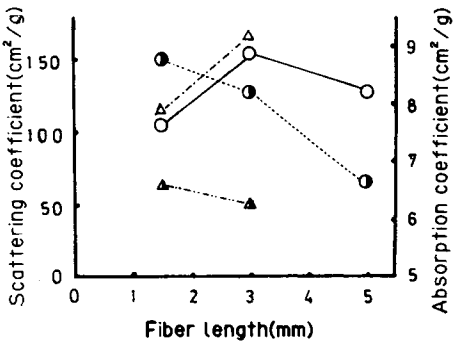


Fig. 10. Dependence of optical properties on fiber length in papers made from Ca alginate and alginic acid (MW; 1.8 × 10^5 dalton) fibers: (○—○) Scattering coefficient of paper made from Ca alginate fibers with diameter 0.10 mm; (△–·–·–△) Scattering coefficient of paper made from Ca alginate fibers with diameter 0.055 mm; (◐– · · · –◐) absorption coefficient of paper made from alginic acid fiber with diameter 0.10 mm; (△– · · –△) absorption coefficient of paper made from alginic acid fiber with diameter 0.055 mm.

Ca^{2+} > Ba^{2+} > Al^{3+} >> Fe^{3+}. Trivalent metals gave paper with lower physical properties.

Effect of Addition of acidic polysaccharides

Attempts were made to spin pectin and κ -carrageenan using $CaCl_2$ as a coagulant, but they did not form continuous yarns. With the aid of Na alginate, pectin was used to try to form yarn. Although the mixture was found to have difficulty in forming yarn at a mixing ratio of 1 (pectin) to 2 (Na alginate), the production of continuous yarn was successful at a ratio of 1:3 using $CaCl_2$ aqueous solution as a coagulant. Spinning of the mixed

TABLE I
Physical Properties of Papers Made From Fibers of Various Metallic Salts of Alginic Acid

Fiber diameter (mm) (spinning base)		0.10			0.055	
Molecular weight (dalton)		6.3 × 10^5			3.8 × 10^5	
Alginate salt	Ca^{2+}	Ba^{2+}	Al^{3+}	Fe^{3+}	Ca^{2+}	Ba^{2+}
Bulk density (g/cm^3)	0.54	0.59	0.51	0.32	0.65	0.78
Breaking length[a] (km)	3.6	1.7	1.5	1.6	2.0	1.4
Zero span breaking length (km)	5.4	4.2	2.6	UM[b]	5.5	3.6
Tear index ($mN·m^2/g$)	5.9	4.2	2.6	UM	7.0	5.4
Burst index ($kPa·m^2/g$)	0.27	0.03	0.13	UM	0.14	0.08
MIT folding endurance (folds)	53	UM	UM	UM	9	8
Elongation (%)	2.7	0.8	1.6	1.3	1.5	1.0

[a] Fibers were 3.0 mm long.
[b] Unmeasurable.

TABLE II
Physical Properties of Papers Made From Fibers Composed of Mixtures of Alginate and Acidic Polysaccharides

Components / Properties	Ca Alginate (100)	Ca Alginate-Ca pectate (75:25)	Ca Alginate-κ-Carrageenan (75:25)	Alginic acid (100)	Alginic acid-pectin (75:25)	Alginic acid-κ-Carrageenan (75:25)
Bulk density (g/cm^3)	0.54	0.85	0.98	0.80	0.74	0.85
Breaking length (km)	3.56	4.45	3.89	3.34	6.63	3.98
Zero span breaking length (km)	5.43	6.11	5.71	5.24	6.54	5.23
Tear index ($mN \cdot m^2/g$)	5.9	3.7	3.1	4.4	2.9	2.7
Burst index ($kPa \cdot m^2/g$)	0.27	0.50	0.37	0.22	0.58	0.27
MIT folding endurance (folds)	53	65	49	33	38	30
Elongation (%)	2.7	4.4	2.3	2.1	2.5	2.3
Young's modulus ($\times 10^{10} dyne/cm^2$)	3.86	5.86	6.61	ND[b]	6.52	5.60
Scattering coefficient (cm^2/g)	102	45.7	15.4	ND	ND	ND
Absorption coefficient (cm^2/g)	8.0	7.2	3.2	ND	ND	ND

[a] Fibers were 01.0 mm in diameter and 3.0 mm long.
[b] Not determined.

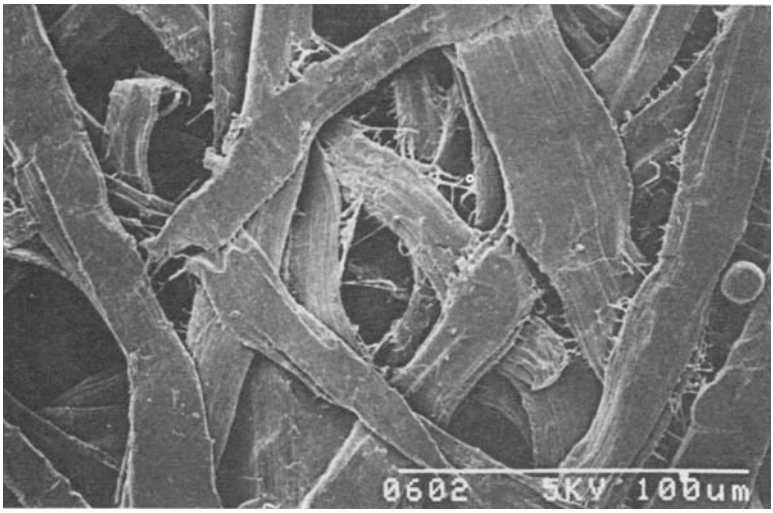
dope (3 wt%) of κ -carrageenan and Na alginate also resulted in a continuous yarn at the same ratio. Quite differentiated from the whole Ca alginate fiber sheet, the papers from the mixture of pectin or κ -carrageenan were found to be dense, filmlike, and high in tensile strength, as shown in Table II. These had distinstive traits: bulk density and Young's modulus were larger by 1.5–1.8 times and the scattering coefficient was extremely lower. This indicated that the optical contact area was small, which made the papers very transparent. The sheets made from mixtures of alginic acid and pectin or alginic acid and κ -carrageenan had the same tendency as the corresponding Ca salt sheets.

Scanning Electron Microphotograph and X-ray Microanalysis

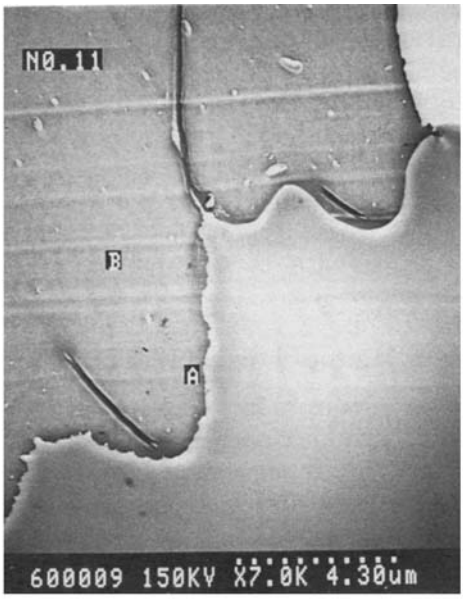
Scanning electron microphotograph showed that the Ca alginate fiber paper was composed of wrinkled and straight fibers and that the fibers adhered firmly to other fibers, suggesting Campbell compression at the fiber-to-fiber crossings (Photo 1). The distribution of Ca^{2+} density throughout the whole fibers was determined by x-ray microanalysis. The results indicated that the metallic ion dispersed homogeneously over all the fibers. A typical example is illustrated in Photo 2. This is quite different from the skin-core structure of rayon.[26]

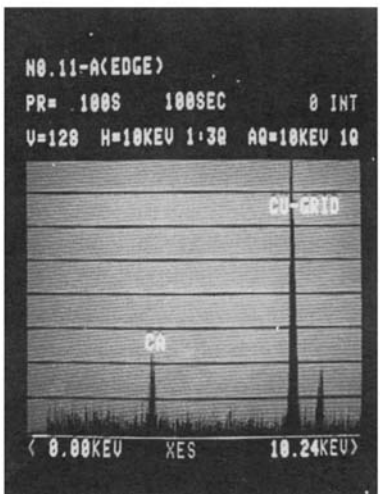
CONCLUSIONS

The fibers of Ca alginate and alginic acid were aligned to have a structure similar to cellulose[23] and were found to have interfiber self-bonding properties, which permitted us to make paper composed of fibers of given diameter and length without the aid of binders. The Ca alginate or alginic acid fiber paper thus obtained had a tendency to shrink greatly during drying but had strengths almost equivalent to those of newsprint grade.



Scanning electron microphotograph of Ca alginate fiber paper in which fiber-to-fiber crossing sections were shown to be enlarged by Campbell compression.





A typical analysis example of Ca density in an edge (A) and an inner part (B) of Ca alginate fiber.

Compared with paper from self-bonding rayon, they had almost the same tensile and burst strengths but smaller tear strength. Analysis of the effect of MW, fiber diameter, and fiber length on physical properties of the sheets could provide some information about their contribution to paper constitution. Finally, these fiber papers from alginate or alginic acid were considered extremely promising in medical uses because of their hemostatic activity.

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