

The Effect of Alginate Inclusion on the Extrusion Behaviour of Soya

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SUMMARY

The effect of the addition of a range of polysaccharides on the extrusion behaviour of soya grits has been investigated. Guar gum, locust bean gum, sodium carboxymethyl cellulose, pectin and carrageenan had little effect when incorporated in the feed at the 1% level. The addition of alginates and low viscosity hydroxypropyl and hydroxyethyl celluloses resulted in a significant reduction in extruder torque and product temperature.

The alginate effect was investigated in detail and was observed both for moderate temperature ($\sim 120^{\circ}\text{C}$) and high temperature ($\sim 180^{\circ}\text{C}$) extrusion. In the latter case an expanded textured product was produced and alginate addition resulted in a reduction in expansion ratio. High mannuronate alginates had the greatest influence on extrusion behaviour and there was evidence to suggest that very low molecular weight samples of the polysaccharide did not function in the same way as materials of moderate or high molecular weights. Pressure measurements at the die confirmed that the effect of alginate on extruder torque and product temperature was due to a lowering of the viscosity of the soya melt. The molecular origin of this effect still needs to be understood.

1. INTRODUCTION

In a previous publication (Smith *et al.*, 1982) we have reported that the addition of sodium alginate has an effect on the extrusion behaviour of

soya grits. This observation was unexpected for two reasons. It was apparent that the reduction in extruder torque and product temperature that was observed on alginate addition could be explained by a *reduction* in the viscosity of the soya melt. In conventional uses of polysaccharides, their addition always results in a viscosity increase. Secondly, this preliminary work seemed to show that alginate functioned in a way that was different to other anionic polysaccharides such as sodium pectate and sodium carboxymethyl cellulose.

The objective of the work described in this paper was to confirm and consolidate our original observation and determine how the functionality of alginate depends on the chemical composition of the polysaccharide. Measurements were made with a laboratory extruder under conditions of high temperature and moderate temperature to give both an expanded/texturised and a non-expanded product. While this paper was in preparation Boison *et al.* (1983) have also reported the effects of added alginate as well as methyl cellulose on the extrusion behaviour of soya grits.

2. EXPERIMENTAL

2.1 Materials

2.1.1 Soya grits

Defatted soya grits were obtained from McAuley Edwards Ltd. Two different types were used (400 BS and 400 B). The protein dispersibility index quoted by the suppliers was 68–76% and 25% respectively. The moisture content as determined by oven drying at 105°C for 8 h was generally in the range 7–12%.

2.1.2 Polysaccharides

2.1.2.1 Alginates. A range of sodium alginates (alginates A–H) prepared from different weed types were kindly donated by Kelco/AIL International Ltd. A further sample of alginate (alginate I) was purchased from BDH Ltd. A sample of alginic acid obtained from Sigma Inc. and a propylene glycol alginate with a reported degree of esterification of 70–75% obtained from Kelco/AIL International Ltd were also studied. The latter was described as a medium viscosity material prepared from an alginate containing a high proportion of mannuronate residues.

2.1.2.2 Other polysaccharides. A range of cellulose derivatives were supplied by Hercules Inc. These included a high and low viscosity sodium carboxymethyl cellulose both with reported degrees of substitution of 0.7 (CMC 7HF and CMC 7LFD), a high and low viscosity hydroxypropyl cellulose (Klucel H and Klucel L) and a high and low viscosity hydroxyethyl cellulose (Natrosol 250H and Natrosol LR).

A high methoxyl pectin (rapid set pectin 6025) and a low methoxyl pectin (LMP 2100) were supplied by H.P. Bulmers Ltd.

Guar gum (Supercol U), locust bean gum and carrageenan (Genugel WG) were supplied by Henkel Ltd, Sigma Inc and Hercules Inc, respectively. All polysaccharides were used without any further purification.

2.2 Methods

2.2.1 Characterisation of sodium alginates

2.2.1.1 Mannuronate/guluronate (M/G) ratio. The M/G ratios of the sodium alginates used were determined by the infrared (i.r.) method of Mackie (1971) and by proton magnetic resonance (p.m.r.) spectroscopy of the residue following acid hydrolysis as described by Penman & Sanderson (1972).

Infrared spectra were obtained from films of alginic acid prepared by immersing glass plates, coated with solutions of sodium alginate (0.5–1.0%) in 0.5 M HCl. The M/G ratio was determined from the ratio of the areas of the peaks at 808 and 787 cm^{-1} as described by Mackie (1971).

As a preliminary to the p.m.r. measurements, samples were partially hydrolysed by boiling (for 5 h under reflux) dispersions of alginic acid in 0.3 M HCl. The alginic acid dispersion was prepared by adding 19.5 ml 3.0 M HCl to 179 ml 0.21% sodium alginate. The alginate concentration used was a factor of 10 lower than that employed by Penman & Sanderson (1972). This was because with some samples using their conditions, it was found that a gel formed on HCl addition which was difficult to hydrolyse. The proportion of homopolymeric blocks to alternating regions was determined from the ratio of the amount of material in the precipitate to that in the soluble (hydrolysable) fraction. Concentrations were measured by the phenol sulphuric acid method (Dubois *et al.*, 1956). Deuterated samples of the residue following hydrolysis were examined on a Bruker WM250 nuclear magnetic

resonance (n.m.r.) spectrometer using ethanol as an internal standard. Spectra were recorded at ambient temperature at a sweep width of 2.5 kHz. The ratio of mannuronate blocks to guluronate blocks was determined from the areas of the peaks assigned to guluronic acid H-1 and mannuronic acid H-5 as described by Penman & Sanderson (1972).

2.2.1.2 Intrinsic viscosity. The intrinsic viscosity of sodium alginate in 0.1 M NaCl was measured at 25.0°C using a Deer Rheometer fitted with concentric cylinder geometry. Newtonian behaviour was confirmed and the intrinsic viscosity was generally obtained from a plot of the reduced viscosity against concentration as indicated by the Huggins equation. In some cases intrinsic viscosity was obtained from the relative viscosity of a 0.3% solution using the relationship reported by Haug & Smidsrod (1962).

2.2.2 Heat degradation of alginate

Degraded samples of sodium alginate were obtained by autoclaving solutions of alginate sample A in a steam retort at 120°C. 300–400 ml 2.5% solutions in distilled water were autoclaved in cans for an operator's process time of 5, 20, 40 and 60 min. A further solution to which a small quantity of 0.1 M HCl had been added was also autoclaved for 60 min. The solution was then freeze-dried and ground prior to extrusion studies.

2.2.3 Extrusion

A Brabender laboratory extruder (Model DN) was employed. Two types of experiment were carried out. Soya was extruded at relatively low temperatures and moisture contents to give an unexpanded product. This will be termed system 1. A higher moisture content feed was extruded at higher temperatures to give an expanded textured material. This will be called system 2.

In both cases the extruder feed material was prepared in the same way. Dry soya grits were mixed with the polysaccharide in a Kenwood Chef mixer. The amount of water needed to give the desired final moisture content was added. (This was calculated from the original moisture content of the grits.) After mixing to ensure an even water distribution the feed material was stored at 4°C overnight in a polythene bag.

2.2.3.1 System 1. The conditions used to produce the unexpanded product were similar to those described by Jasberg *et al.* (1982). A 2:1 compression ratio screw was used and the extruder was fitted with a round die of length 40 mm and diameter 3 mm. The screw speed was 250 rpm and the two barrel sections and die were maintained at temperatures of 120°C. The torque required to drive the extruder and the product temperature at the end of the screw were continuously monitored. In some cases the pressure immediately behind the die was also determined. All three signals were interfaced with a BBC micro-computer and averaged over a 10 s period. The data presented relates to steady state conditions. The feed moisture content was 30%.*

2.2.3.2 System 2. In this case the conditions were similar to those described by Frazier *et al.* (1980). The screw compression ratio was 4:1. The temperatures of the feed and compression sections of the barrel were 150°C and 200°C respectively and the die was maintained at a temperature of 150°C. The screw speed was 250 rpm and the feed moisture content was 38%. The round die employed had a diameter of 4 mm and a length of 25 mm. As before, torque and product temperature at the end of the screw were continually monitored. An expanded product was produced and the expansion ratio was calculated from:

$$\text{Expansion ratio} = \frac{\text{Diameter of extrudate}}{\text{Diameter of die}}$$

The extrudate diameter was measured with a micrometer at ten different points.

3. RESULTS

3.1 System 1

The effect of added polysaccharides on the extrusion behaviour of soya grits (400 BS) is illustrated in Fig. 1. This displays the change in extruder torque, product temperature at the end of the screw and pressure behind the die compared with a soya control. The mean values for these three

* Moisture contents are expressed as (g H₂O/g dry solids) × 100.

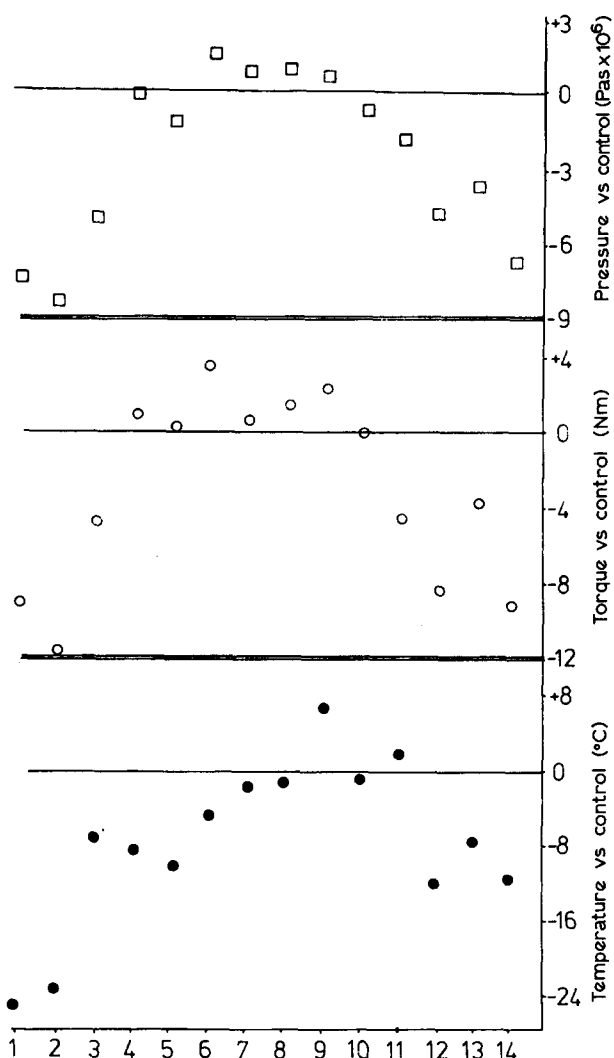


Fig. 1. The change in torque, pressure behind the extruder die and product temperatures on inclusion of various polysaccharides at the 1% level in a soya grit (400 BS) feed. Included polysaccharides from left to right: 1, sodium alginate (sample A); 2, alginic acid; 3, propylene glycol alginate; 4, high methoxyl pectin; 5, low methoxyl pectin; 6, carageenan; 7, guar gum; 8, locust bean gum; 9, c.m.c. (high viscosity); 10, c.m.c. (low viscosity); 11, hydroxyethyl cellulose (high viscosity); 12, hydroxyethyl cellulose (low viscosity); 13, hydroxypropyl cellulose (high viscosity); 14, hydroxypropyl cellulose (low viscosity). (Further details are given in the text.)

parameters for soya alone were 30.3 N m, 132.0°C and 2.27×10^7 Pa s respectively. It is clear from the results in Fig. 1 that there is a very good correlation between the pressure and torque drop ($r = 0.95$). Both pressure and torque are also correlated with product temperature, $r = 0.83$ and $r = 0.75$ respectively. Two classes of polysaccharide have a large effect on the extrusion behaviour of soya grits: alginates and the cellulose ethers.

The limited data we have suggests that it is the low viscosity cellulose ethers which have a greater effect than the high viscosity material. In view of the hydrophobic substituent groups on these cellulose derivatives and their associated thermal gelation properties, it is perhaps not surprising that they should show some functionality in an extrusion system.

The results for alginate essentially confirm our preliminary observations with an expanded system (Smith *et al.*, 1982), although we did not find a large reduction in throughput on alginate addition. The flow rate for the feed containing 1% alginate sample A was 1.66 ml s^{-1} compared with 1.70 ml s^{-1} for soya alone.

It appears from the data in Fig. 1 that the extrusion effect is not related to the water solubility of the polysaccharide since it is observed to about the same extent with insoluble alginic acid as with a soluble sodium alginate. Since the propylene glycol derivative was a medium viscosity material prepared from an alginate of similar weed origin to alginate A, it seems likely that esterification reduces the functionality of the alginate in soya extrusion.

In order to determine if there was a relationship between alginate structure and effect on extrusion the mannuronate/gulonate (M/G) ratio and intrinsic viscosity of a range of sodium alginates were determined. The results are shown Table 1. The M/G ratio obtained from i.r. and p.m.r. determinations correlate well, but the i.r. values are significantly higher. One possible reason for this is the assumption of a 1:1 M/G ratio for the 'alternating' region when calculating the overall M/G ratio from the p.m.r. data. It has recently been shown that this region is not strictly alternating and where its composition has been determined a slightly higher content of mannuronate residues compared to guluronate residues has been found (Boyd & Turvey, 1978; Grasdalen *et al.*, 1981). Another limitation of the p.m.r. method is that it relies on a prehydrolysis step. Haug *et al.* (1974) have pointed out that although procedures involving hydrolysis provide a valid comparison between

TABLE 1
Characterisation of Alginates

Sample	Mannuronate/guluronate ratio		Intrinsic viscosity (100 ml g ⁻¹)
	Determined by i.r.	Determined by p.m.r.	
A	1.7	1.4	7.3
B	0.7	0.55	8.7
C	0.8	0.4	4.9
D	0.7	0.5	2.5
E	2.0	1.4	4.9
F	2.1	1.5	3.9
G	1.3	1.0	3.0
H	2.0	—	0.9
I	0.7	0.5	2.5

different alginates, in view of the complicated hydrolysis kinetics, absolute values should be treated with some caution. Since in this work we were concerned with a relationship between M/G ratio and extrusion properties and, hence, interested in relative rather than absolute values of M/G ratio, the reason for this discrepancy was not explored further.

Figure 2 displays the relationship between torque, pressure and temperature relative to a soya control and the M/G ratio of the sodium alginate as determined by i.r. It is apparent that with one exception, high mannuronate alginates have a larger effect on extrusion behaviour than high guluronate alginates. The exception is alginate sample H, although the M/G ratio for this sample was not determined by p.m.r.; since it was prepared from a blend of alginates extracted from *Ascophyllum*, *Durvillea* and *Ecklonia* spp. a high M/G ratio would be expected as is confirmed by the i.r. results.

Alginate H has a low intrinsic viscosity and therefore a molecular weight which is much lower than the other samples. It therefore seems possible that the relationship between M/G ratio and extrusion behaviour breaks down at very low molecular weights. Some evidence in support of this comes from studies on heat degraded alginate sample A. In this case, measurements were made on soya grits with a lower protein

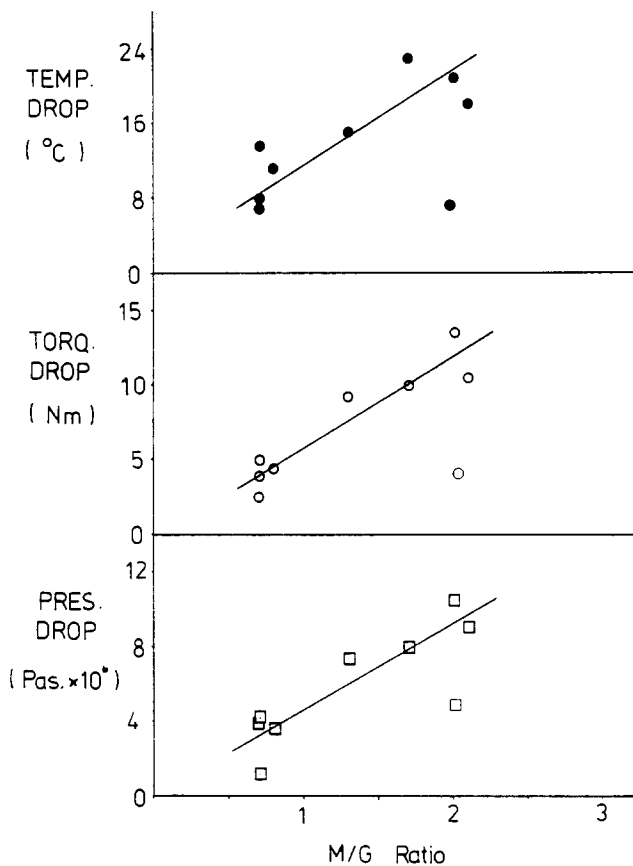


Fig. 2. The effect of mannuronate/guluronate ratio of included sodium alginate (1% w/w) on extruder torque, pressure and product temperature. The three parameters are expressed relative to a soya grit control containing no sodium alginate. Feed moisture content was 30% w/w; extruder heaters for feed, compression and die sections were set at 120°C. Screw speed was 250 rpm, Off-line point is data for sodium alginate (sample H).

dispersibility index (400B). With this material alginate also had a clear effect on the extrusion behaviour. This is illustrated by Fig. 3 which shows the effect of included alginate A concentration on torque, product temperature and pressure. If the results for 1% inclusion are compared with the data in Fig. 1, it is apparent that the temperature

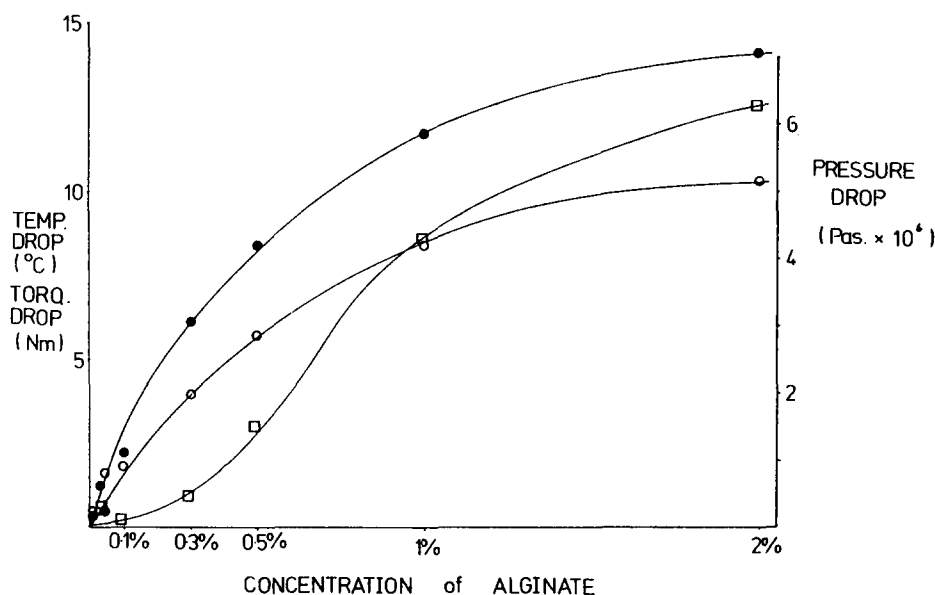


Fig. 3. Effect of concentration of included sodium alginate (sample A) on extrusion parameters. In this case soya grits were low protein dispersibility material (400B). (□) Pressure; (○) torque; (●) temperature. (Other details are given in the text and in caption to Fig. 2.)

lowering effect in particular is not as large for the lower protein dispersibility index material. Although this may be explained by the different soya used, we believe it is also possible that it is due to wear resulting in an increase in the clearance between the screw and barrel, since the data reported in Fig. 3 and Table 2 were obtained at a later date than the other work described in this paper. Our experience has been that the magnitude of the torque drop occurring on alginate addition is less effected by wear than the temperature drop. Data in support of this is presented later for the expanded system (Table 3). Table 2 displays the torque, temperature and pressure drop observed when heat degraded alginate A was included in the 400B grits at a level of 0.5%. At the highest levels of alginate heat treatment extrusion was not possible. The torque rose substantially and the extruder blocked.

TABLE 2
Effect of Heat Degradation of Alginate Sample A on Intrinsic Viscosity and Functionality in Extrusion

<i>Treatment</i>	<i>Intrinsic viscosity (100 ml g⁻¹)</i>	<i>Decrease in extruder torque and product temperature compared with soya alone (alginate incorporated in feed at 0.5% level)</i>	
		<i>Torque decrease (N m)</i>	<i>Temperature decrease (°C)</i>
None	7.3	5.7	8.4
Material dissolved freeze dried and ground (no heat treatment)	7.4	6.6	6.4
Autoclaved at 120°C for 5 min	2.4	5.4	4.9
Autoclaved at 120°C for 20 min	1.2	3.5	3.5
Autoclaved at 120°C for 40 min	0.6	-2.5	-1.7
Autoclaved at 120°C for 60 min	0.4	Extruder blocked	
Autoclaved at 120°C for 60 min after HCl addition	0.3	Extruder blocked	

TABLE 3
Effect of Wear on Extrusion Behaviour of Soya Grits With and Without Alginate

	<i>New barrel and screw</i>		<i>Worn barrel and screw</i>	
	<i>Soya</i>	<i>Soya + 1% alginate A</i>	<i>Soya</i>	<i>Soya + 1% alginate A</i>
Temperature at screw end (°C)	182	170	173	170
Torque (N m)	24	19	20.5	15.2
Flow rate (cm ³ s ⁻¹)	1.80	1.75	1.55	1.55
Expansion ratio	2.04	1.3	2.09	1.8

3.2 System 2

The inclusion of alginate also had an effect on the extrusion behaviour of soya grits (400 BS) at higher temperatures. Figures 4, 5 and 6 show that not only was there a significant lowering of the torque and the temperature of the product compared with the values for the soya control of 24 N m and 182°C, but there was also a significant drop in expansion ratio on alginate addition. The observation that the effect was far greater for alginate sample A compared with alginate sample B is consistent with the relationship between functionality in extrusion and M/G ratio found for the unexpanded system.

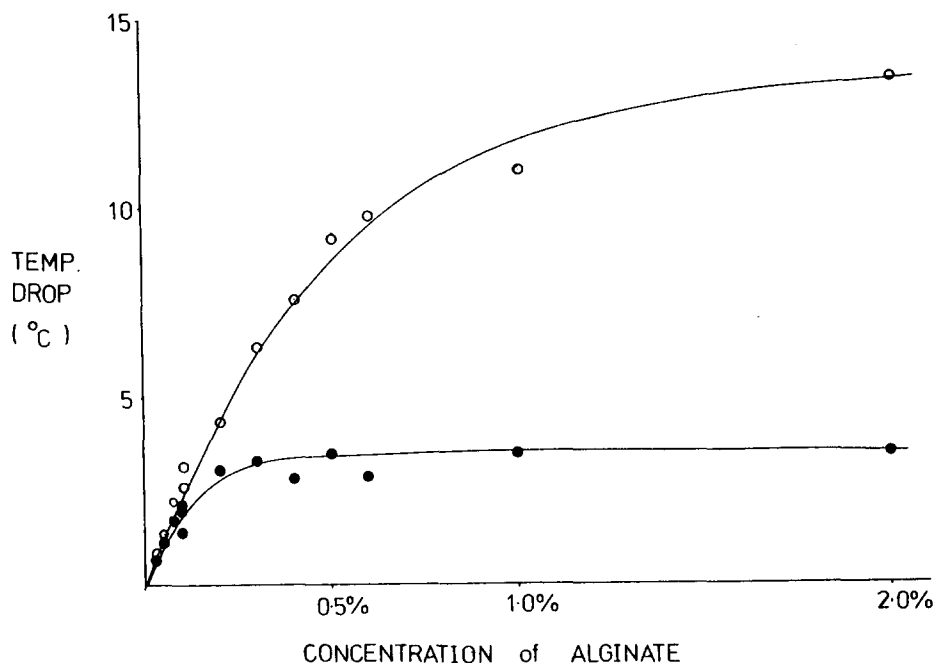


Fig. 4. Effect of concentration of included sodium alginates on product temperature for soya grits (400 BS) extruded at high temperatures. In this case the temperatures of the feed, compression and die sections of the extruder were 150, 200 and 150°C respectively. Screw speed was 250 rpm and feed moisture content was 38% w/w. (○) Sodium alginate (sample A); (●) sodium alginate (sample B).

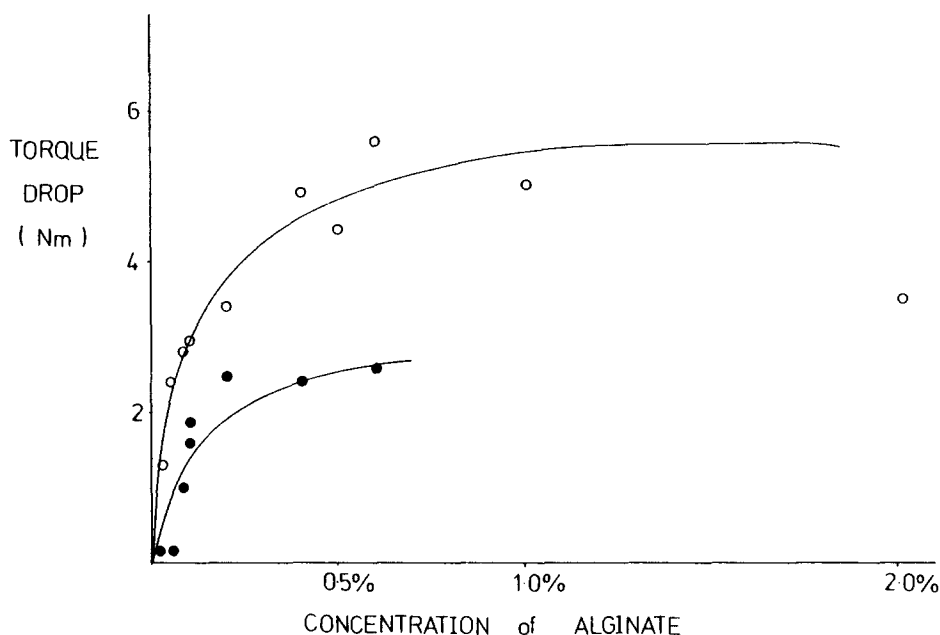


Fig. 5. Effect of concentration of included sodium alginate on extruder torque. (Conditions as described in caption to Fig. 4.)

Extrudate expansion will be partly determined by the temperature of the material prior to emerging from the die. To determine whether the same decrease in expansion ratio would be obtained if this temperature drop was caused by physical means rather than alginate addition, the temperature of a soya control was lowered by reducing the heat input to the second section of the extruder barrel. Figure 7 shows that the change in expansion ratio in this case is much smaller than if the temperature drop is caused by the addition of alginate sample A. Also, reducing the temperature in this way results in an increase in extruder torque compared with the decrease observed on alginate addition.

A factor which makes physical measurements on small extruders more complicated is the effect of screw and barrel wear on performance. As mentioned previously, the majority of data reported in this paper were determined with an extruder fitted with a relatively new barrel and screw. Some measurements were made on the expanded system with an extensively worn extruder, where the clearance between the

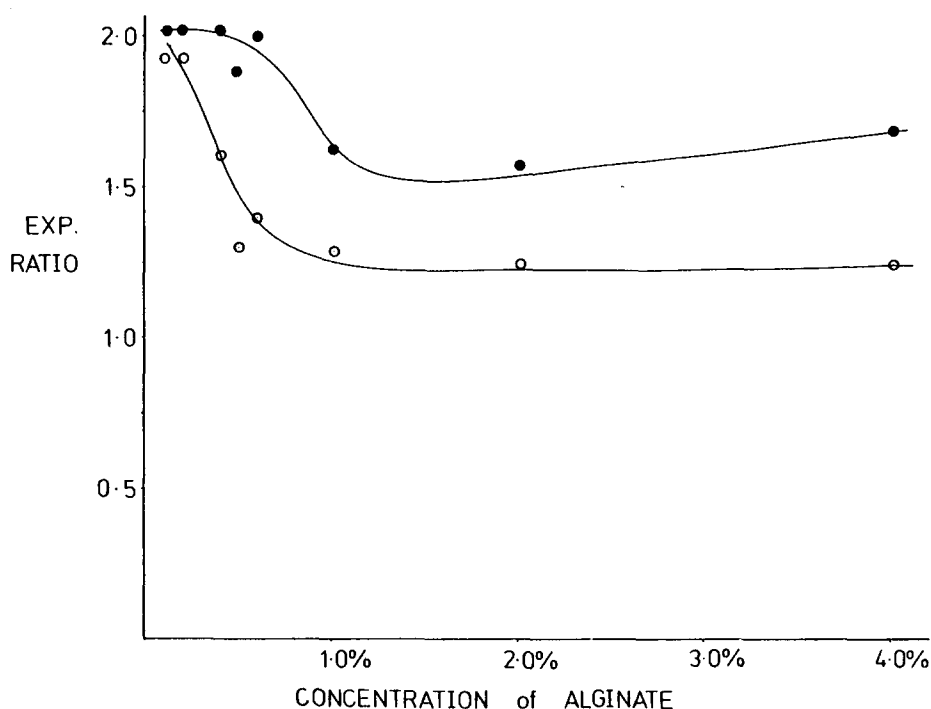


Fig. 6. Effect of concentration of included sodium alginate on expansion ratio. (Conditions as described in caption to Fig. 4.)

flight edge and the barrel at the die end had increased by a factor of 4. A comparison of the results obtained in the two cases is shown in Table 3. It is apparent that the effect of alginate addition on expansion ratio and product temperature is far less pronounced although the torque drop is of a similar magnitude for both situations.

4. DISCUSSION

The results reported in this paper confirm our original observation (Smith *et al.*, 1982) that the addition of alginate alters the extrusion behaviour of soya grits. This effect is observed at two widely separated points on the 'response surface' relating the measured variables (torque, extrudate temperature, pressure and expansion ratio) to the controlled variables (feed moisture content, extruder heater temperatures).

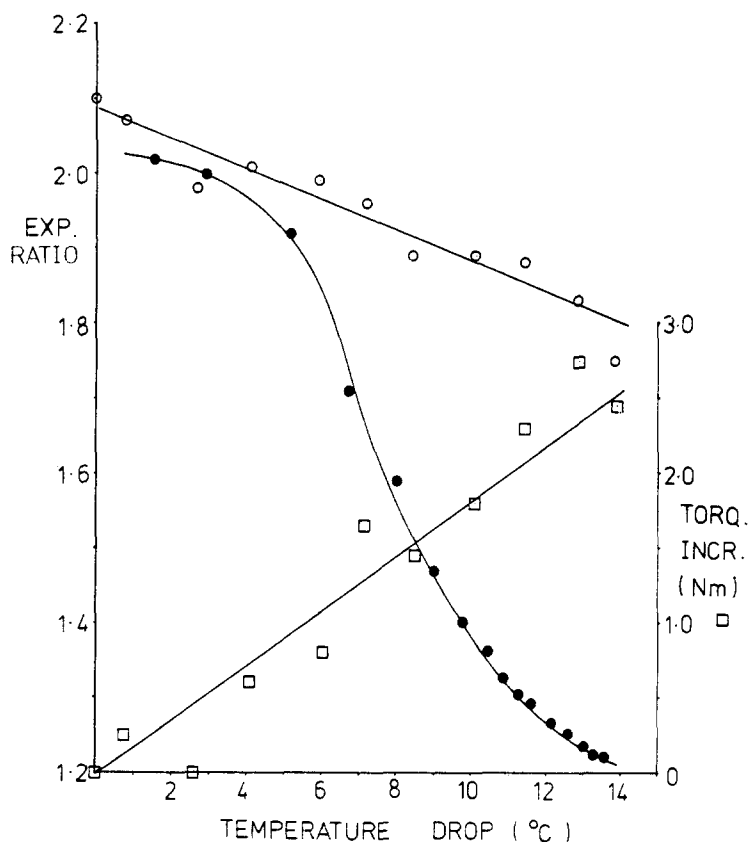


Fig. 7. Effect of product temperature at the end of the screw on expansion ratio. The abscissa shows the decrease in product temperature compared with the standard conditions of no added polysaccharide and the extruder temperatures and moisture content described in caption to Fig. 4. (●, ○) Expansion ratio. (—●—) Decrease in temperature caused by the addition of varying concentrations of alginate sample A. (—○—) Decrease in product temperature due to a decrease in the temperature of the jacket around the metering section of the extruder. (—□—) Increase in torque on reduction in product temperature caused by changing the extruder jacket temperature.

There are three new observations which we consider significant:

- (i) The effect depends on the alginate chemical composition being greatest for alginates with a high content of mannuronate residues.

- (ii) Low molecular weight alginates show the lubricating effect to a lesser extent than high molecular weight alginates.
- (iii) There is evidence that some cellulose ethers show a similar effect to alginates.

A direct comparison with the results of Boison *et al.* (1983) is not possible since their investigation was concerned mainly with the effect of hydrocolloid addition on the texture of the extruded product whereas this work deals primarily with extruder operating parameters. The observation that addition of alginate lowers the expansion ratio is consistent with the increase in bulk density reported by Boison *et al.* (1983).

Models of the flow behaviour and energy balance in an extruder (Harper, 1981) show that a drop in torque, product temperature and pressure at an approximately constant output is due to a decrease in the viscosity of the dough or melt. At any point within the dough the rate of energy dissipation is given by $\eta_{app} \dot{\gamma}^2$ where η_{app} is the appropriate apparent viscosity and $\dot{\gamma}$ the shear rate. Clearly a decrease in viscosity will result in less heat being generated internally and therefore a lower product temperature at the end of the screw. Since a large part of the mechanical energy used to drive the extruder is dissipated as heat then a decrease in viscosity will also result in a decrease in the power required to drive the extruder or torque at a constant screw speed.

The shear rate will be highest in the gap between the tip of the flights and the extruder barrel. It follows that a large amount of the total heat resulting from viscous dissipation will be generated in this region. Shear rate at this point will be given approximately by V/δ where V is the velocity of the tip of the flight and δ is the clearance between the flights and the barrel. For a Newtonian material the heat generated in this region will be inversely proportional to δ^2 . In practice the dough will be shear thinning so the dependence on δ will be somewhat less severe. It follows that the contribution to the product temperature at the end of the screw from heat generated internally will be less in a worn extruder and therefore the effect of an additive that reduces viscosity will be smaller. This is shown by the data in Table 3. Another factor may be that at the higher temperature and moisture contents used to obtain an expanded product the dough viscosity is lower and therefore

internally generated heat will be lower irrespective of the state of wear of the extruder.

A quantitative interpretation of the change in extruder parameters on alginate addition should be possible if information about the dependence of dough viscosity on shear rate and temperature were available. Work to obtain these data is currently in progress.

The molecular origin for the effect of alginate and the cellulose ethers on the viscosity of the soya dough is difficult to explain. The conventional view of the protein extrusion process is that the texture of the product and the viscosity changes during heating will be determined by protein denaturation followed by subsequent aggregation. In relatively dilute protein solutions it has been shown that the presence of a charged polysaccharide will effect both these processes (Imeson *et al.*, 1977). Where the protein has a nett negative charge an anionic polysaccharide will destabilise the protein molecule lowering the denaturation temperature and will inhibit aggregation. If the polysaccharide has a nett positive charge then an insoluble complex will be formed. An interpretation of these results in terms of the idea that the polysaccharide inhibits protein/protein interactions fails to explain why the effect is dependent on polysaccharide structure and so is observed with alginate and not with say sodium carboxymethyl cellulose, and assumes that concepts developed for systems where there is an excess of water are relevant to the very low water contents pertaining to the extrusion process.

It may be significant that both alginate and the cellulose ethers are capable of forming gels that can exist at high temperatures and therefore have the ability to associate via heat stable linkages. Thus it is possible that within the extruder both a polysaccharide and a protein network are formed. If the polysaccharide network became the continuous phase in which islands of associated protein were imbedded then the rheological properties of the system would be significantly changed from that of soya by itself. At this stage such interpretations must be highly speculative and a molecular understanding of these effects will only be possible when other techniques are applied to the system. One of the more interesting questions remaining to be answered is whether the influence of hydrocolloids on extrusion behaviour reported here is confined to the soya system or whether similar effects are also observed when other proteins or even starches are extruded.

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