ELSEVIER

0144-8617(95)00041-0

Carbohydrate Polymers 27 (1995) 123–127
Elsevier Science Limited.
Printed in Great Britain.
0144-8617/95/$09.50+.00

Synergistic interactions between yellow mustard polysaccharides and galactomannans

W. Cui,[a]* N.A.M. Eskin,[b] C.G. Biliaderis[c] & G. Mazza[d]

[a]*Department of Food Science; and* [b]*Department of Foods and Nutrition, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada*
[c]*Department of Food Science and Technology, School of Agriculture, Box 256, Aristotle University, Thessaloniki, Greece 54006*
[d]*Food Research Program, Agriculture and Agri-Food Canada Research Centre, Summerland, British Columbia V0H 1Z0, Canada*

(Received 29 December 1994; revised version received 14 March 1995; accepted 16 March 1995)

Small strain oscillatory rheological tests were carried out to study the synergistic interactions between yellow mustard mucilage and locust bean gum. Synergistic interactions were observed for blends of locust bean gum and yellow mustard mucilage ranging in ratios from 1:1 to 1:9 at total polymer concentrations of 0·5 and 2·0% (w/w), respectively. The rheological data indicated that the water-soluble fraction of yellow mustard mucilage was responsible for the observed synergistic behavior in the blends. The major component of the water-soluble yellow mustard mucilage consists of a 1,4-linked β-D-glucan backbone chain. This 1,4-linked β-D-glucan backbone chain is believed to adopt a rigid-ordered structure that may be responsible for the synergistic interaction with galactomannans.

INTRODUCTION

Galactomannans can interact synergistically with a number of polysaccharides, such as xanthan gum, agar and carrageenans, resulting in viscosity increases or gel formation (Dea & Rees, 1987; Dea, 1987; Morris, 1990, 1991). The ability of galactomannans to interact synergistically with other polymers is generally enhanced by decreasing their galactose content and the distribution pattern of galactose on the mannose backbone chain (Morris, 1990; Dea *et al.*, 1986*a*, 1986*b*). This kind of synergistic behavior between polysaccharides is commercially valuable because it leads to the development of new textures, for instance, biphasic gel structures (Morris, 1986; Morris, 1990).

Yellow mustard mucilage aqueous solutions/dispersions exhibit pronounced shear thinning flow behavior and 'weak-gel' structures resembling that of xanthan gum (Cui *et al.*, 1993). One of the major components responsible for the shear thinning flow behavior of yellow mustard polysaccharides was identified in the water-soluble fraction which had a 1,4-linked β-D-glucan backbone chain, similar to that of xanthan gum (Cui *et al.*, 1994, 1995). A pectic-like polysaccharide was also identified in the water-soluble fraction of yellow mustard mucilage which exhibited shear thinning flow behavior in solutions (Cui *et al.*, 1994). Yellow mustard mucilage was reported to interact synergistically with locust bean gum and guar gum (Weber *et al.*, 1974; Dea I.C.M., pers. commun. 1992). However, information on the synergistic behavior of yellow mustard mucilage–galactomannan systems is limited, thus preventing full comprehension of the mechanism involved. Traditionally, most synergistic interactions between polysaccharides have been attributed to co-operative intermolecular bindings to form 'junction zones' (Morris, 1990). In contrast to the co-operative binding mechanism, a mutual exclusion mechanism was recently proposed for some mixed systems in which the observed synergism, measured by an increase in viscosity or gel formation, was explained by complex mutual exclusion effects between the two polymers as a result of polymer incompatibility. This kind of mutual exclusion of each component from the 'polymer domain' of the other is thermodynamically favourable and will increase the effective concentration of both polymers in their own microdomains (Morris, 1990). This paper reports synergistic interactions between yellow mustard mucilage and galactomannans (LBG) using small strain oscillatory rheological measurements. Further investigations were carried out on the interactions between two subfractions of yellow mustard mucilage and locust bean gum in order to understand the origin of the synergistic effects observed for these mixed polysaccharide dispersions.

---

*Author to whom correspondence should be addressed.

MATERIALS AND METHODS

Materials and sample preparation

Yellow mustard mucilage (YMM) was extracted as described previously (Cui *et al.*, 1993). The crude mucilage was dialysed against distilled water for 3 × 24 h. The dialysed mucilage was subsequently fractionated into a water-soluble fraction (WS-YMM) and a water-insoluble fraction (WI-YMM) as described previously (Cui *et al.*, 1993). Locust bean gum (LBG) was purchased from Sigma Chemical Co. (USA) and used without further purification. Solutions and/or dispersions were prepared by heating the samples in water for 30 min at 90°C then adding sodium chloride or water to obtain the required concentration. The solutions/dispersions of WS-YMM and LBG were passed through a 5 μm filter, cooled and diluted as required (Zhan *et al.*, 1993; Doublier, 1994). The mixed dispersions or gels were prepared by combining the appropriate portion of solutions/dispersions of yellow mustard polysaccharides and LBG, heated at 85°C in a sealed tube for 30 min, and then slowly cooled to room temperature.

Rheological measurements

Small strain oscillatory rheological testing was carried out on a Bohlin VOR Rheometer (Bohlin Reologi, Sweden). A concentric cylinder geometry with height of 63·0 mm, radii of the inner and outer containers of 12·5 and 13·75 mm, respectively, was used to probe the rheological behavior of solutions/dispersions and mixed gels of crude mucilage and LBG. A plate-cone (5°) geometry was also employed for determination of the rheological behavior between blends of the two mucilage fractions and LBG which permitted the use of small samples (1·5 ml for cone-plate geometry compared to the 15 ml for concentric cylinder geometry). Light mineral oil was used to prevent loss of water by evaporation (Biliaderis & Zawistowski, 1990). The maximum strain input for all measurements was less than 2% which is within the linear viscoelastic range (Doublier, 1994).

RESULTS AND DISCUSSION

Typical mechanical spectra of galactomannans and YMM are shown in Fig. 1. The mechanical spectrum of LBG (Fig. 1A) is that of a typical viscoelastic solution where the storage modulus (G′) is lower than the loss modulus (G″) at lower frequencies with the reverse observed at higher frequencies. The mechanical spectrum of YMM is characteristic of a 'weak-gel' structure in which the storage modulus (G′) predominates over the loss modulus (G″) over the entire frequency range examined. The mechanical spectra of YMM and LBG blends in three ratios are presented in Fig. 2. The ratios of LBG and YMM were 9:1, 1:1 and 1:9 at a total polymer concentration of 0·5% (w/w). The responses (i.e. G′, G″ and dynamic viscosity) of the mixed blends were significantly different for these ratios. The blend of 9:1 ratio (90% LBG and 10% YMM, Fig. 2A) exhibited the behavior of a viscoelastic fluid where G′ was lower than G″ over most of the frequency range tested. In contrast, the 1:1 and 1:9 blends exhibited gel-like properties, particularly the 1:9 blend (10% LBG and 90% YMM, Fig. 2C) where G′ was much greater than G″ and the two moduli were almost independent of frequency. These findings suggested that, at a total polymer concentration of 0·5% (w/w), synergistic interactions occurred only for blends 1:1 and 1:9. In order to compare the rheological responses of the two polymers separately as well as their blends, data from the respective rheological parameters at a fixed frequency (1Hz) were plotted, as shown in Fig. 3. For the polymer blends, if only an additive effect occurred, the viscosity and G′ of the mixtures should fall between the values of LBG and YMM since the polymer concentration remained unchanged (0·5% w/w). The dynamic viscosity of the 9:1 blend (90% of LBG and 10% of YMM) was lower than pure LBG but slightly higher than that of YMM. In contrast, the dynamic viscosities of the other two blends (1:1 and 1:9) were significantly enhanced (Fig. 3A). It is particularly noteworthy that

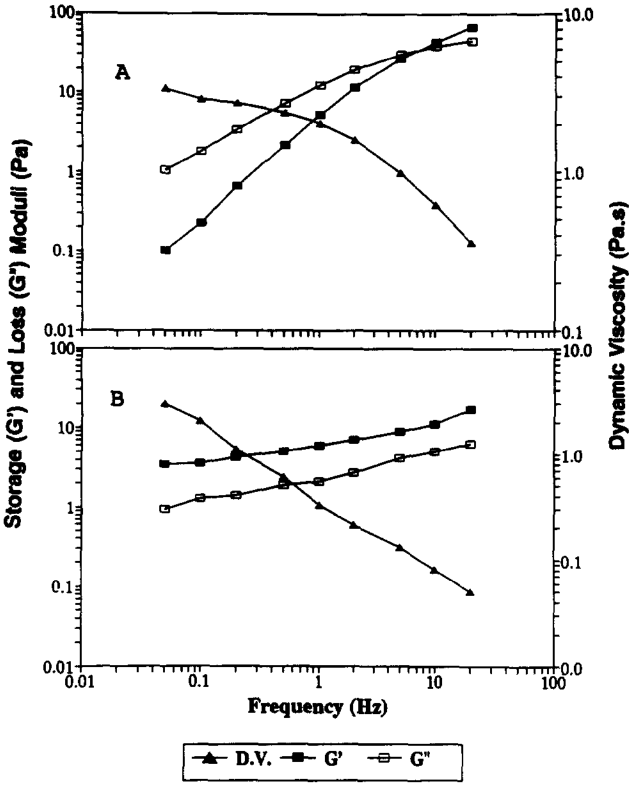

Fig. 1. Mechanical spectra of locust bean gum (A) and yellow mustard mucilage (B) at 25°C, 1·25% (w/w) in water.

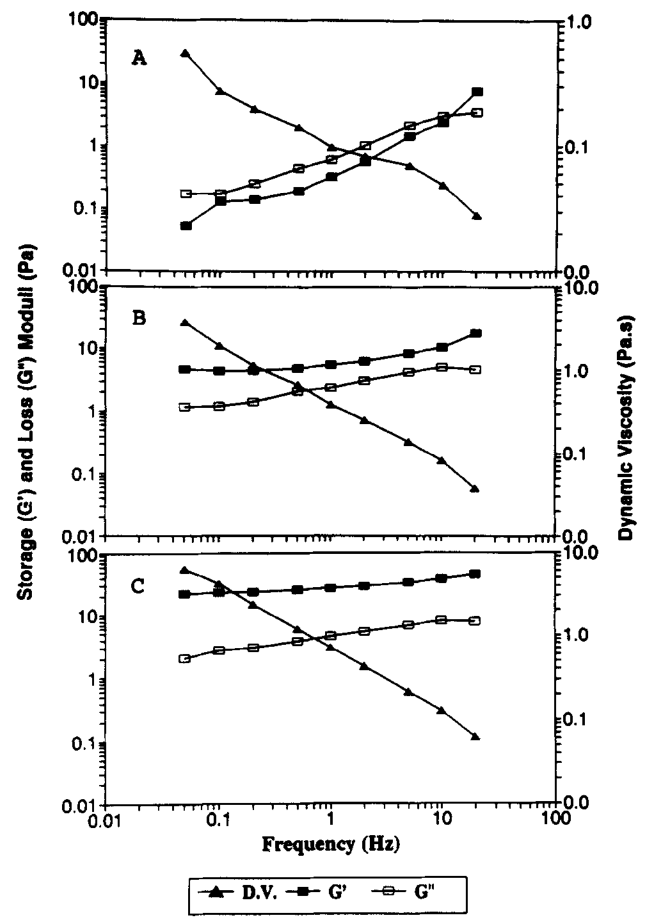

Fig. 2. Mechanical spectra of locust bean gum and yellow mustard mucilage blends (A: 9:1; B: 1:1 and C: 1:9) at 25°C, 0·5% (w/w) polymer concentrations.

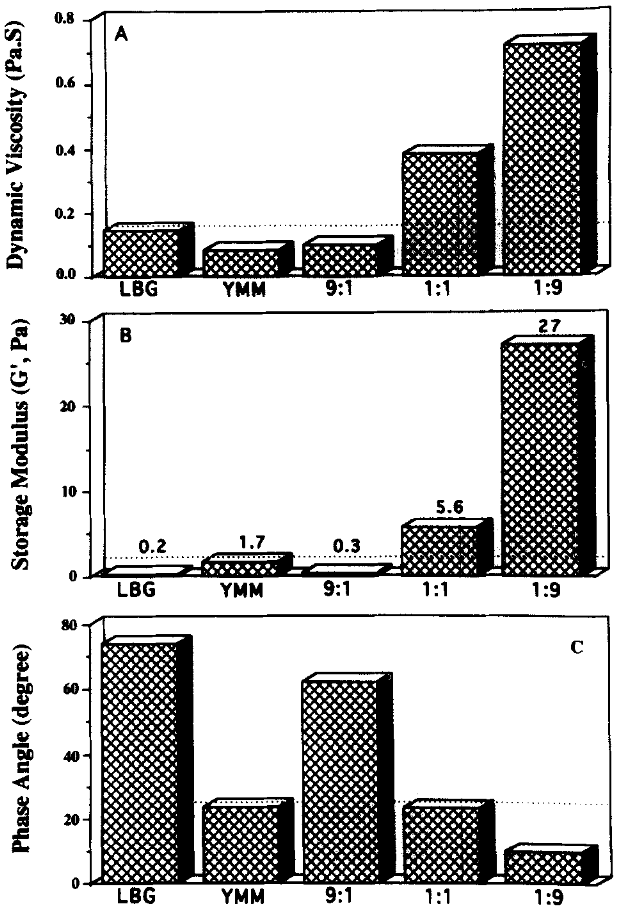

Fig. 3. Comparison of rheological parameters (1 Hz) of locust bean gum (LBG)-yellow mustard mucilage (YMM) blends and polymers in isolation (25°C, 0·5% w/w polymer concentration in water).

the mixture of 10% LBG and 90% YMM had the highest value of dynamic viscosity among all blends examined at 0·5% (w/w) total polymer concentration.

Changes in storage modulus G′ for the different blends are shown in Fig. 3B. The G′ of the 9:1 blend was 0·3 Pa which is in between the G′ values of LBG and YMM (0·2 and 1·7 Pa, respectively) at the same concentration. The G′ of blend 1:1 was 3 times (5·6 Pa) higher than that of YMM while the G′ of blend 1:9 (10% LBG and 90% YMM) was 15 times (27 Pa) higher. This trend is in agreement with the changes in dynamic viscosity among the blends presented in Fig. 3A, thus showing that the strongest interaction occurred in the 1:9 blend (LBG:YMM).

The phase angle is another parameter used to evaluate the viscoelastic properties of polymer dispersions. An ideal liquid system will have a phase angle of 90°; in contrast, an ideal solid system will have a phase angle of 0°. Phase angles of real systems are in between these two extreme values. A phase angle larger than 45° would suggest the system has a more liquid-like character. In contrast, a phase angle smaller than 45° would indicate a system with a more solid-like character. The LBG was a typical viscoelastic fluid since its 0·5% solution/dispersion had a phase angle value over 70° at 1 Hz. The phase angle value (23°) of YMM under the same experimental conditions was much smaller than 45° suggesting that the system was more solid-like in character, typical of a 'weak-gel' system. In the blends of the two polymers, the phase angle of blend 9:1 was comparable with that of LBG. The phase angle of blend 1:1 was similar to that of YMM indicating this blend was a 'weak-gel' system. The phase angle value for the 1:9 blend was smaller than that of YMM, indicating that this system had stronger gel-like properties than the other two blends. The observed improvement in the gelling behavior of YMM dispersions, by addition of small amounts of LBG, suggests that synergistic interactions occurred between LBG and YMM at low polymer concentration (0·5%, w/w) which may reflect co-operative associations of long stretches of the two polymers into mixed 'junction zones' (Morris, 1990). Heating was necessary to achieve maximum interaction (data not shown), which suggests that the associative synergistic interactions between LBG and YMM at low polymer concentration required melting the ordered structures in YMM. The proposed 'mixed junction' model for YMM and LBG at 0·5% (w/w) is analogous to that of mixtures of xanthan and LBG (Morris, 1990).

Interactions between LBG and YMM at 2·0% polymer concentration were also examined in 0·1 M NaCl solution, as shown in Fig. 4. The dynamic viscosities of all blends at this concentration level were higher than that of either of the polymers. The extent of the synergistic interactions increased as the ratio of LBG decreased (Fig. 4A). Similar trends were observed for G′ but the degree of increase was much higher for blends 1:1 and 1:9 compared with 9:1 (Fig. 4B). These observations are consistent with previous results with polymer at 0·5% (w/w) concentration in which the highest synergistic interactions between LBG and YMM occurred at a ratio of 1:9. The phase angles of the three blends at 2·0% (w/w) polymer concentration were in between those of LBG and YMM (Fig. 4C) indicating that interactions of the two polymers did not improve the gelling properties of YMM at this concentration. The observed rheological responses at higher polymer concentrations could be due to the mutual exclusion of the two polymers. Assuming this mechanism, the increase in dynamic viscosity and storage modulus could be explained by the mutual exclusion of each polymer component from the microdomains of the other. A mutual exclusion of the two polymers would result in increasing the effective concentration of both polymers (Morris, 1990).

YMM was fractionated into a water-soluble fraction (WS-YMM) and a water-insoluble fraction (WI-YMM) as described previously (Cui *et al.*, 1993). Interactions between the two fractions and LBG were examined as shown in Fig. 5. The blend 9:1 was not included in these tests since it did not show significant synergistic interactions in previous experiments (Figs 2–4). As shown in Fig. 5A, the dynamic viscosities of LBG–WI-YMM blends fell in between those of the two polymers as did the corresponding phase angles (Fig. 5C). The storage modulus G′ of 1:9 blend revealed a synergistic response, as it was higher than that observed for WI-YMM or LBG (Fig. 5B).

In the blends of LBG and WS-YMM, significant synergistic interactions were found as shown in Fig. 5.

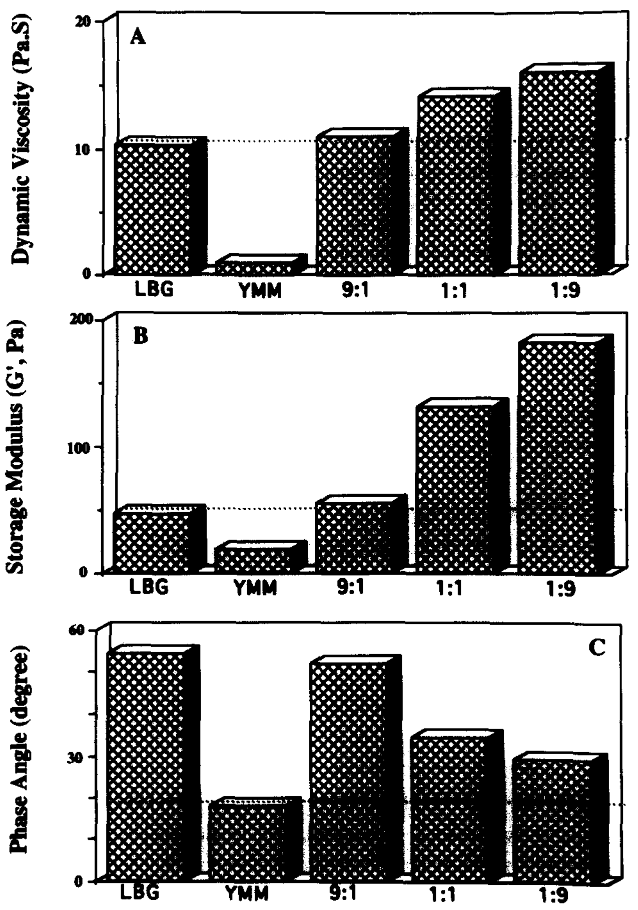

Fig. 4. Comparison of rheological parameters (1 Hz) of locust bean gum (LBG)–yellow mustard mucilage (YMM) blends and polymers in isolation (25°C, 2·0% w/w polymer concentration in 0·1 M NaCl solution).

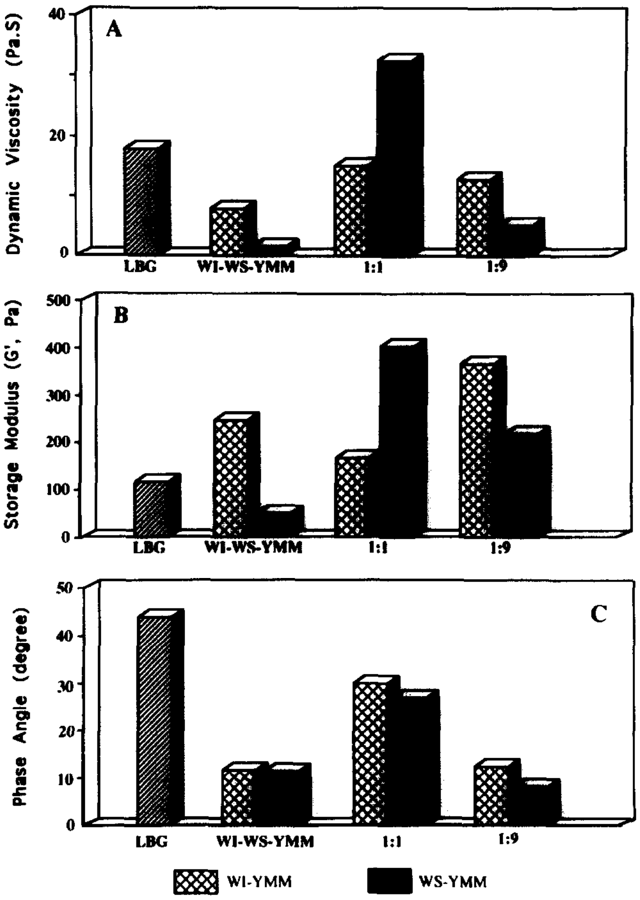

Fig. 5. Comparison of rheological parameters (1 Hz) of locust bean gum (LBG) and yellow mustard mucilage (water-insoluble, WI-YMM and water-soluble, WS-YMM, respectively) blends and polymers in isolation (25°C, 2·0% w/w polymer concentration in water).

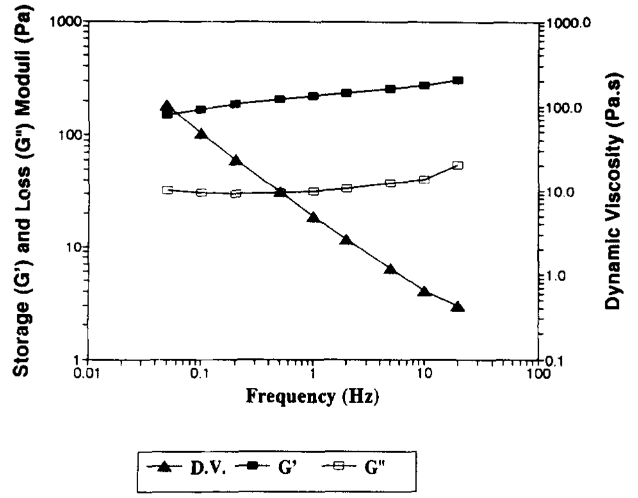

Fig. 6. Mechanical spectrum of locust bean gum and water-soluble yellow mustard mucilage 1:9 ratio at 25°C, 2·0% (w/w) in water.

Both dynamic viscosity and G′ of the blend 1:1 were much higher than those of the 1:9 blend suggesting a shift in the optimum ratio for synergistic interaction from 1:9 for LBG–YMM to 1:1 for LBG–WS-YMM systems, respectively (Fig. 5A and B). However, the phase angle value of the 1:1 blend was in between the two pure systems while the phase angle of the 1:9 blend had a much smaller value compared to that of WS-YMM (Fig. 5C). This finding suggests that the 1:9 blend exhibits the best gel-like behavior. The mechanical spectrum of the LBG:WS-YMM system at ratio 1:9 is presented in Fig. 6. This reflects a typical gel-like structure where G′ was much greater than G″ over the entire frequency range examined with the two moduli being almost independent of frequency (Zhan *et al.*, 1993). This study confirms the WS-YMM fraction as the major component responsible for the synergistic interactions between YMM and LBG.

CONCLUSIONS

Rheologically significant interactions were observed in mixed aqueous blends of LBG and YMM in the ratios 1:1 and 1:9. The water-soluble fraction of YMM, composed of 1,4-linked β-D-glucans and a pectic-like polysaccharide, is the major component responsible for the synergistic interactions between LBG and YMM; polysaccharides containing 1,4-linked β-D-glucose backbone chain in WS-YMM could be the species involved. At lower polymer concentrations, the function of the 1,4-linked β-D-glucose backbone chain is to provide rigid structures for intermolecular associations with the respective mannan chain segments of LBG. A mutual exclusion mechanism was proposed for the rheological behavior observed at higher polymer concentrations. In conclusion, the addition of small amounts of LBG to YMM results in a significant increase in viscosity and the development of gel-like structures in these mixed polymer dispersions which may be of commercial importance.

ACKNOWLEDGEMENTS

This work was supported by grants from Western Grains Research Foundation (Canada) and the Natural Science and Engineering Research Council (NSERC) of Canada. The authors thank Ms Liqian Yao for her computer assistance during the preparation of the figures presented.

REFERENCES

Biliaderis, C.G. & Zawistowski, J. (1990). *Cereal. Chem.*, **67**, 240.

Cui, W., Eskin, N.A.M. & Biliaderis, C.G. (1993). *Food Chem.*, **46**, 169.

Cui, W., Eskin, N.A.M. & Biliaderis, C.G. (1994). *J. Agricult. Food Chem.*, **42**, 657.

Cui, W., Eskin, N.A.M. & Biliaderis, C.G. (1995). *Carbohydr. Polym.*, **27**, 177–122.

Dea, I.C.M. (1987). In *Industrial Polysaccharides, Genetic Engineering, Structure/Property Relations and Applications*, ed. M. Yalpani. Elsevier, Amsterdam, p. 209.

Dea, I.C.M., Clark, A.H. & McCleary, B.V. (1986*a*). *Carbohydr. Res.*, **147**, 275.

Dea, I.C.M., Clark, A.H. & McCleary, B.V. (1986*b*). *Food Hydrocoll.*, **1**, 129.

Dea, I.C.M. & Rees, D.A. (1987). *Carbohydr. Polym.*, **7**, 183.

Doublier, J.L. (1994). In *Gums and Stabilizers for the Food Industry*, **7**, eds G.O. Philips, P.A. Williams & D.J. Wedlock. IRL Press, Oxford, UK, p. 257.

Fernandes, P.B., Goncalves, M.P. & Doublier, J.L. (1993). In *Gums and Stabilizers for the Food Industry*, **6**, eds G.O. Philips, P.A. Williams & D.J. Wedlock. IRL Press, Oxford, U.K., p. 181.

Morris, E.R. (1990). In *Food Gels*, ed. P. Harris. Elsevier Applied Science, London, UK, Chapter 8, p. 291.

Morris, V.J. (1986). In *Gums and Stabilizers for the Food Industry*, **3**, eds G.O. Philips, P.A. Williams & D.J. Wedlock. IRL Press, Oxford, UK, p. 97.

Morris, V.J. (1991). In *Gums and Stabilizers for the Food Industry*, **6**, eds G.O. Philips, P.A. Williams & D.J. Wedlock. IRL Press, Oxford, UK, p. 161.

Weber, F.E., Tailie, S.A. & Stauffer, K.R. (1974). *J. Food Sci.*, **39**, 292.

Williams, P.A., Day, D.H., Langdon, M.J. Philips, G.O. & Nishinari, K. (1991). *Food Hydrocoll.*, **4**, 489.

Zhan, D.F., Ridout, M.J., Brownsey, G.J. & Morris, V.J. (1993). *Carbohydr. Polym.*, **21**, 5.