ELSEVIER

0144-8617(95)00089-5

Carbohydrate Polymers 28 (1995) 367-373
Copyright © 1996 Elsevier Science Limited.
Printed in Great Britain. All rights reserved
0144-8617/95/$09.50+.00

A rheological study on the application of carbohydrate–protein incompatibility to the development of low fat commercial spreads

Ioannis S. Chronakis & Stefan Kasapis*

Department of Food Research and Technology, Cranfield University, Silsoe College, Silsoe, Bedford MK45 4DT, UK

(Received 15 October 1994; revised version received 3 January 1995; accepted 4 January 1995)

The small and large deformation properties of commercial low fat spreads and traditional full fat products have been investigated in order to develop a background understanding of the changes in viscoelastic properties and the structural organisation occurring as a result of addition of biopolymers to the aqueous phase of low fat dispersions. Parameters have been derived from compression analysis, dynamic oscillation (frequency, strain and temperature sweeps) and creep compliance testing.

It seems that the direct replacement of fat with a biopolymer-structured aqueous phase does not imitate the plastic rheology of butter and margarine. Thus, the ratio of plastic to maximum stress (σ_p/σ_m) of butter and margarine is substantially higher (0.96 – 1.0) than the ratio of inflectional to maximum stress (σ_i/σ_m) of commercial low fat spreads with a strong, gel-like character (up to 0.83). Additionally, some commercial embodiments with reduced amounts of structural components have stress–strain profiles resembling those of viscous solutions instead of a plastic product.

Dynamic oscillatory measurements have characterised the mechanical properties of water-continuous low fat spreads. Dispersions reproduced the mechanical profile of three-dimensional biopolymer gels with a high elastic component (tan $\delta \approx 0.04$) and a substantial linear response to increasing amplitude of oscillation (up to 10% deformation). Products comprising hydrolysed starch as one of the functional ingredients show long melting profiles upon heating, which contrast strongly with the 'melt in the mouth' properties of butter. In accordance with the above, butter requires lower initial strain to exhibit negligible recovery of shape after the removal of stress, than do commercial low fat spreads with a pronounced elastic element, during a creep compliance experiment. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Butter and margarine, the traditional oil continuous products for spreading, contain 80% fat. The large fat phase determines the sensory attributes of flavour release, thickness, sweetness, smoothness and 'melt in the mouth' behaviour. It also dictates the physical properties, rheological characteristics, chemical reactions and microbiological stability of traditional embodiments. All in all, butter and margarine satisfy the consumer's requirement for tasty bread spreads but they fail to meet today's nutritional recommendation for a reduced calorie and cholesterol diet. In addition, it is not convenient to spread butter straight from the refrigerator and keeping butter unrefrigerated is not an appealing option. Attempts have been made, therefore, to produce bread spreads of a high dietary value containing half, a quarter or even less than 5% of the fat of butter which, however, retain its desired appearance, flavour, texture and sensory characteristics (Mageean & Jones, 1989).

Obviously, production of low fat products with an increasingly larger aqueous phase requires the use of proteins and polysaccharides as thickeners or gelling agents. The ability of biopolymers to cross-link and at high enough concentrations to form a tangled, interconnected molecular network in water is widely known (Ross-Murphy, 1992). However, an aqueous phase structured by a single biopolymer behaves either as a viscoelastic liquid that cannot support its shape or as a solid-like material whose brittle or elastic character is unsuitable for spreading. Cain *et al.* (1989) claim that

---

*Author to whom correspondence should be addressed.

successful reduction in fat content (or, in the limit, complete elimination of fat) requires water-continuous systems with two phase-separated gelling agents, at least one of which must be an aggregate-forming gelling agent. It is then believed that the macromolecular heterogeneity contributes to a smooth spreading and a fatty mouthfeel in the product. Obviously, rheological measurements constitute a reliable measure of the ability of polymeric ingredients to compensate for the reduced contribution of fat to the texture and mouthfeel, and for providing an emulsion that breaks down easily in the commercial low fat spreads. This investigation addresses the question of how successfully the existing protein and polysaccharide based products imitate the viscoelastic and textural properties of butter and margarine.

MATERIALS AND METHODS

A representative collection of bread spreads sold in the British market was purchased and left to equilibrate for a week at refrigerator temperature. 'Full fat' products included Anchor spreadable butter, Lurpak unsalted butter and Flora margarine. At the 40% level of fat (halvarines) the St Ivel Gold low fat spread was characterised. At approximately 25% fat in the product (quarterines), St Ivel Gold Lowest was selected as a typical example of a fat-continuous spread with the largest possible volume of aqueous phase. Finally, the viscoelastic, textural and melting profiles of typical water-continuous products, namely Promise (3% fat), Tesco Very Low Fat (5%) and Safeway Very Low Fat (3%) spreads were monitored as a measure of comparison with the physical properties of full fat and fat-continuous products.

Key parameters have been derived by monitoring the short range characteristics, the large deformation pattern of breakdown and the recovery properties of traditional and low fat products using compression testing, dynamic oscillation and creep compliance experiments. Conventionally, the spreading behaviour is characterised rheologically by compression testing using, in our case, a TA-XT2 Texture Analyser from Stable Microsystems. Cylindrical samples, measuring 26 mm in length and 26 mm in diameter, were compressed to 10% of their initial height (i.e. 90% compression) at 0.8 mm/s (~ 2"/min) between the flat parallel plates of the instrument (5°C). Small and large deformation measurements were made on a controlled stress Carri-Med CSL 500 rheometer using parallel plate geometry with 4 cm diameter and 1 mm gap. Samples were loaded on the rheometer at 5°C, and the development of modulus as a function of time was monitored. When conditions of apparent equilibrium were attained, i.e. the experimental moduli had not increased more than 0.5% in a 15 min measuring interval, samples were subjected to increasing frequency of oscillation at fixed amplitude (0.1%) or to increasing amplitude of oscillation at fixed frequency (10 rad/s). Selected products were also heated in order to monitor the temperature course of structure melting. Creep compliance experiments were carried out on the same rheometer at 5°C. Briefly, a constant shear stress was applied to a sample and the resultant strain was recorded as a function of time (60 min). The imposed stress was then withdrawn and the degree of recovery of the sample was recorded again as a function of time (30 min). The instantaneous elastic deformation, occurring within 1 s of the stress application, the retardation pattern and the relaxation properties of a spread are dictated by the amount of applied stress. All experiments were carried out in triplicate and mean results are reported.

RESULTS AND DISCUSSION

Figure 1 shows an idealised stress–strain curve under large deformation for a 'plastic' spread, in comparison with corresponding curves for a typical hydrocolloid gel and an extremely viscous solution. Initially, stress (σ) increases with increasing strain (ε), until the network breaks, behaviour similar to that of a gel. At higher strains, however, the response becomes more like that of a liquid, with the resistance remaining roughly constant. The breakdown and flow properties may be characterised by the stress and strain at the point of failure (σ_m and ε_m) and by the corresponding values (σ_p and ε_p) at the point of inflection in the 'plateau' region of the stress–strain curve, i.e. where resistance reaches its minimum value after failure, before increasing again as the gap between the moving and stationary plates closes.

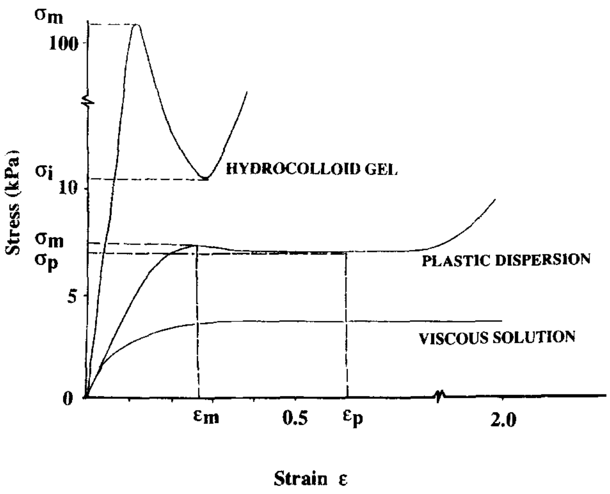

Fig. 1. Idealised graph of stress as a function of strain during compression testing of hydrocolloid gels, plastic dispersions and viscous solutions.

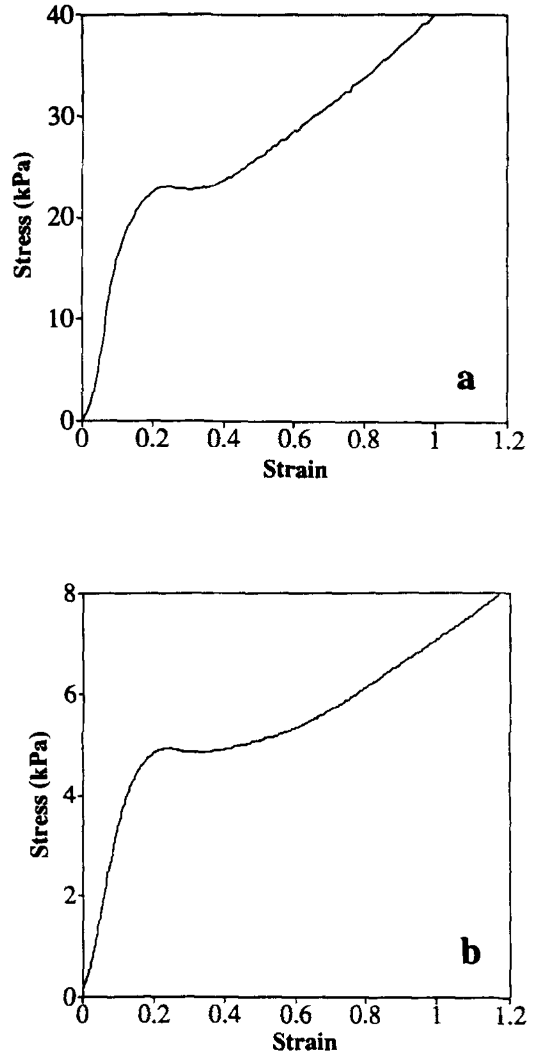

Fig. 2. Force–deformation profiles for: (a) Anchor spreadable butter; and (b) Flora margarine under compression analysis (5°C, 0.8 mm/s).

Figure 2 shows the force–deformation profiles of (a) Anchor spreadable butter; and (b) Flora margarine. To break the self-supporting network and follow the subsequent flow properties, compression continued until the height of the sample, L, was ~10% of the original height, L_o. At such large deformations, the simple definition of strain (ε) as ($L_o - L$) / L_o, is no longer valid because the fractional change in height relative to the absolute change increases rapidly as $L \to 0$. Instead, the 'true' strain is given by (Ross-Murphy, 1984):

$$\varepsilon = \ln(L_o/L)$$

Utilisation of the above equation in the plotting of Fig. 2 produces force–compression curves close to the textural profile of a plastic dispersion in Fig. 1. In both cases the plateau region of plastic flow is less pronounced than in the idealised representation but the ratio of plastic stress to maximum stress (approximately 0.98) and the strain at which the stress goes through a maximum (~0.25) for both products reveal an exemplary spreading behaviour. Obviously the lower ratio of triglyceride crystal to liquid oil in the network of Flora margarine causes an early flow (σ_m ~5 kPa) as compared with the yield strength of the crystalline network in Anchor butter (σ_m ~23 kPa).

St Ivel Gold Low Fat and Gold Lowest spreads typify attempts to produce butter-like products with fat content as low as possible. Although both spreads contain a fat-continuous matrix, production of a stable water-in-oil emulsion requires an aqueous phase of increased viscosity. Incorporation of milk proteins and modified starch in the formulation allowed the development of low fat products with a water content of up to 75% by weight of the composition (Gupta & Platt, 1989). However, production of a stable emulsion required at least 6% protein and as high as 4% starch by weight of the aqueous phase, which upon compression analysis showed a marked deviation from the long-range rheology of plastic dispersions. Figure 3 reproduces the relatively sharp force–deformation

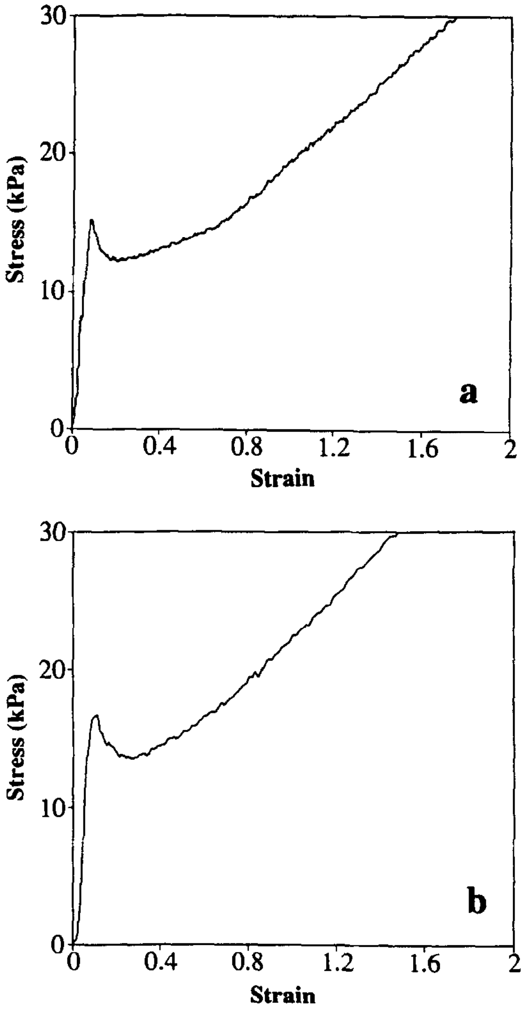

Fig. 3. Force–deformation profiles for: (a) St Ivel Gold Low Fat; and (b) St Ivel Gold Lowest spreads under compression analysis (conditions as in Fig. 2).

relationship of (a) St Ivel Gold Low Fat; and (b) St Ivel Gold Lowest spreads with pronounced stress maxima. The pattern of fracture does not exhibit a horizontal region of plastic flow but rather an inflection point (σ_i) where the stress reaches a minimum value at a strain larger than the maximum strain (see also Fig. 1). The low ratio of inflectional stress to maximum stress (σ_i/σ_m) is approximately 0.82, and the early breaking point (ε_m is $\sim$0.09 units of true strain) clearly expose the gel-like characteristics of both products.

The ever growing public concern about the increasing risk of heart disease as a result of a high fat intake in the Western world diet (Grainger, 1994) has prompted food manufacturers to make bread spreads containing an aqueous phase up to a level of 97% in the product. At such small amounts of fat in the system phase inversion occurs and the aqueous phase becomes the supporting matrix. In this case the problem is how to accommodate the elastic or brittle nature of a biopolymer network in a structure capable of maintaining its shape under gravity but also easily breakable under moderate stress, so allowing the material to flow. In high fat systems, this behaviour, of course, arises from weak interactions between fat crystals. The approaches taken in the improvement of fat substitutes have included the application of phase-separated biopolymer mixtures, such as gelatin and maltodextrin (Kasapis *et al.*, 1993), which create a non-aggregated continuous phase penetrated by small agglomerates of the second component in the form of an inert filler. The patent literature contains various proposals for making water-continuous spreads but the commercial products fall short of expectations from a rheological perspective, at least. As shown in Fig. 4a, the presence of gelatin at amounts higher than the minimum critical gelling concentration, the parameter described by Clark and Ross-Murphy (1985), adversely affects the spreading properties of Promise (Cain *et al.*, 1989) which like the fat-continuous counterparts (Fig. 3) repeats the pattern of a gel-like fracture as the strain increases with no horizontal or near-horizontal region in the curve ($\sigma_i/\sigma_m = 0.83$ and $\varepsilon_m = 0.2$). Being aware, perhaps, of the conundrum, the manufacturers of Tesco and Safeway Very Low Fat spreads replaced the gelatin-based technology with Simplesse, a fat substitute based on a formulation of egg white and skimmed milk or whey protein. They attempted to achieve the required plastic rheology by employing a special processing operation (i.e. particulation process) where the denatured protein mixture was subjected to high shear conditions and was turned into a dry form of spherical particles with a size distribution comparable to that of fat crystals. This combination of thermal and mechanical treatments, however, has converted the homogeneous protein network (when prepared quiescently) into a colloidal ensemble of roughly spherical particles with reduced functionality. Subsequently, for the amount of Simplesse used in the Tesco and Safeway spreads, so as to enable marketing of a financially viable product, a rather sticky preparation reminiscent of a very viscous solution has been obtained. Thus, the smooth stress–strain profiles of Figs 4b and c show no apparent signs of yield points on the curve during the compression cycle.

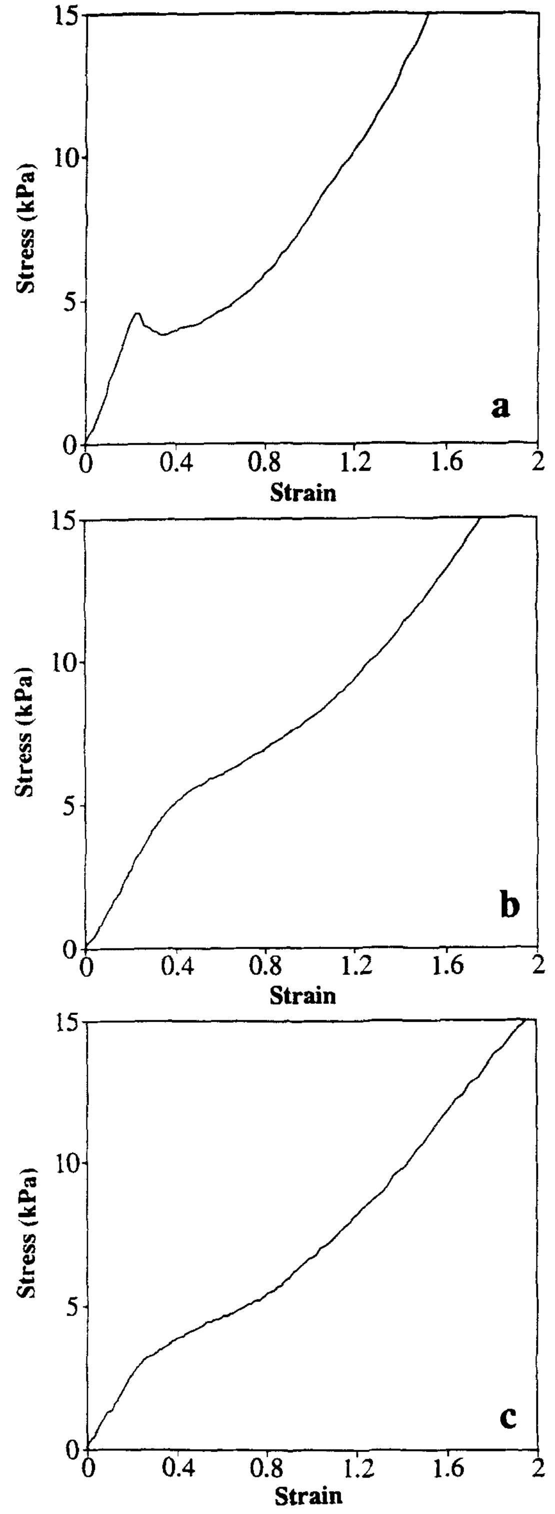

Fig. 4. Stress–strain curves for: (a) Promise; (b) Tesco; and (c) Safeway Very Low Fat spreads under compression analysis (conditions as in Fig. 2).

Besides compression analysis, the pattern of failure as a function of increasing amplitude of oscillation and the time-dependent breakdown of recovery properties can be used to characterise differences in the viscoelasticity of bread spreads. Figure 5 compares the long-range properties of Anchor spreadable butter with the mechanical disruption of the Promise network at 5°C. In the case of a crystalline lattice from animal fat, the strain profile argues for an early onset of shear thinning (above 0.1% applied strain) followed by a rapidly diminishing elastic component (G') which ceases to be the dominant response at approximately 40% strain. By contrast, the Promise graph shows that a linear response is maintained at almost two orders of magnitude higher (about 10%) than the beginning of breaking in butter. At 40% strain the storage modulus is below its initial value for the intact structure but the overall cohesion of the network is maintained ($G' > G''$). The linearity, the shear thinning and the catastrophic disruption (occurring at levels of deformation well in excess of one unit of strain) of the Promise network are comparable to the mechanical deformation characteristics of a single gelatin gel (Papageorgiou *et al.*, 1994).

The undue elasticity of Promise, as a result of the stable intermolecular bonds of the gelatin component, also becomes apparent on creep compliance analysis. Using this technique, one can characterise the viscoelastic properties of a spread on the basis of a minimum instantaneous deformation required for the product to exhibit substantially no recovery of shape. Generally, the lower the initial strain required for the spread to exhibit negligible recovery of shape after the removal of stress (relaxation), the less gel-like and more plastic the spread is. On the other hand, the higher the initial strain required, the more gel-like and less plastic the spread is. Figure 6a shows a graph of percentage strain against time for Lurpak unsalted butter in a creep

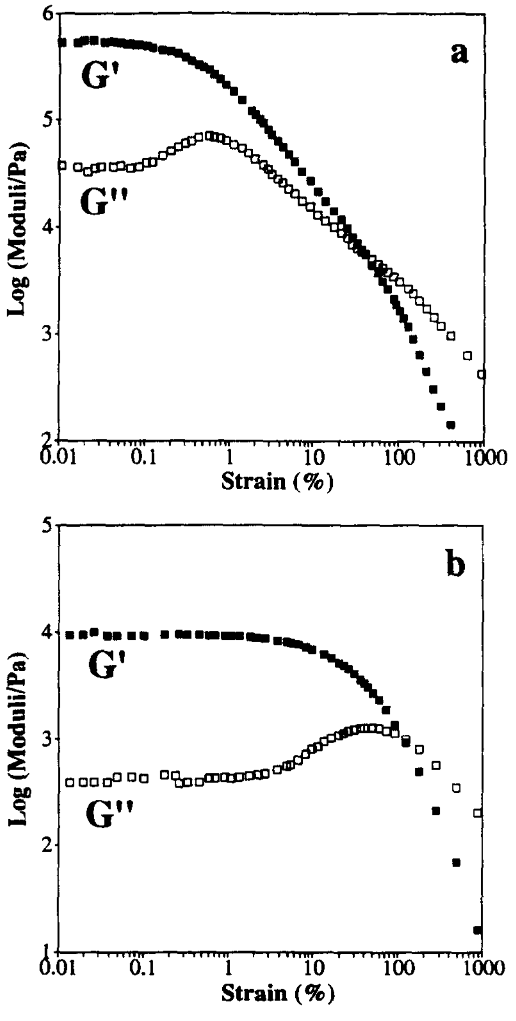

Fig. 5. Strain sweeps for: (a) Anchor spreadable butter; and (b) Promise spread (5°C, 10 rad/s).

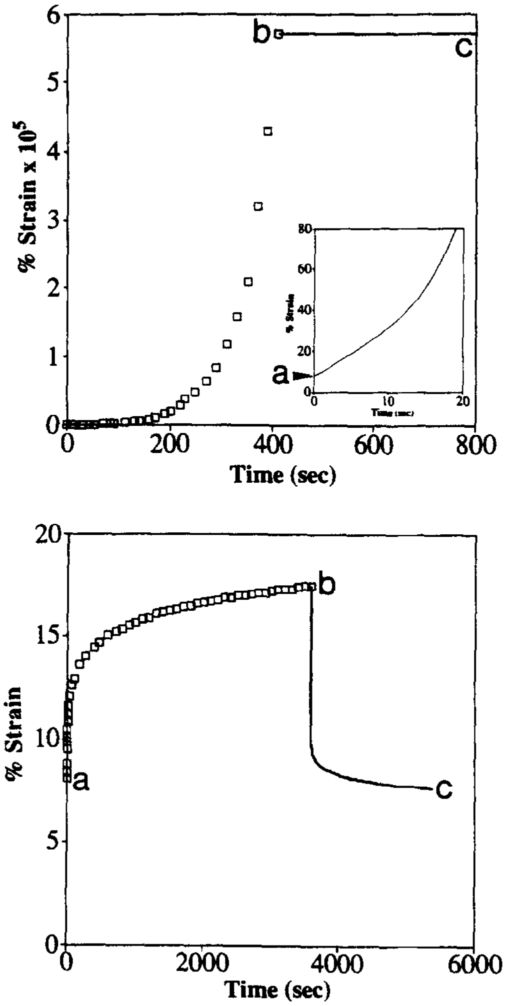

Fig. 6. Creep compliance experiments for: Lurpak unsalted butter (top graph); and Promise spread (bottom graph). Percentage strain is plotted against time on application of a stress sufficient to give an 8% instantaneous deformation (segment 0*a* on the *y* axis), retarded flow for 60 min (*ab* part of the curve) and sample recovery for 30 min (*bc* part of the curve) at 5°C. Only the first 7 min of strain recovery are shown in the top graph to allow a clear presentation of the retardation curve of the experiment.

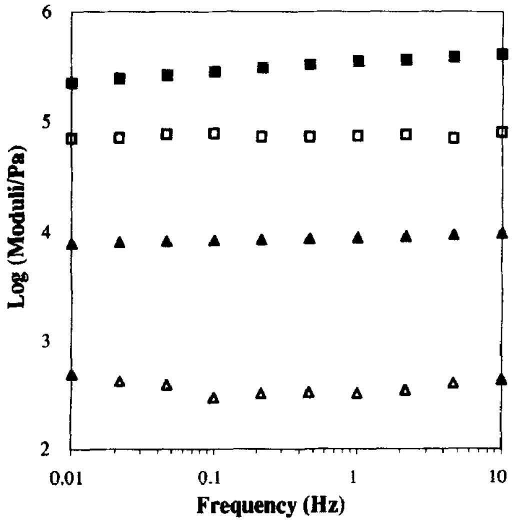

Fig. 7. Frequency dependence of shear moduli for Anchor spreadable butter (G'(■), G'' (□)) and Promise low fat spread (G' (▲), G'' (△)) at a temperature of 5°C and 0.1% strain.

compliance experiment on application of a constant stress and after removal of the stress. The spread responds instantaneously to the applied stress, producing an initial deformation of 8% which increases rapidly during the time of application of the constant stress, thus converting its solid-like structure into a flowing viscoelastic liquid that recovers less than 0.5% of its original shape during the 30 min relaxation time. An entirely different response is obtained in Fig. 6b where the mechanical spectrum is well defined in terms of three mechanisms, namely, instantaneous elastic, retarded-viscous flow, and elastic recovery (relaxation curve) which correspond, respectively, to the initial stretching of permanent (within the experimental constraints) assemblies, the gradual disintegration of the temporary associations and the partial recovery of the original shape upon removal of the imposed stress. For the same instantaneous initial deformation (8%) and a fixed stress application for 60 min, the Promise sample maintains most of its structural integrity and recovers 57% of the final deformation at the end of a 30 min relaxation period.

Non-destructive rheological measurements can also be used to characterise traditional and low fat spreads. For example, mechanical spectra from dynamic oscillation are able to differentiate between viscoelastic materials according to their phase angle values (tanδ = G'/G''). Figure 7 reproduces the frequency (ω) dependence of storage and loss moduli for Anchor spreadable butter and Promise at 5°C. Within the timescale of the measurements (0.01–10 Hz), the solid-like response predominates over viscous flow with little frequency dependence for both samples. The plastic behaviour of butter, however, is demonstrated by the high tanδ value (approximately 0.21 at 1.6 Hz, ~10 rad/s), which signifies a substantial viscous element (liquid oil) in its structure. In contrast, the traces of G' and G'' of Promise reflect the mechanical spectrum of an elastic gel with the value of energy lost to the energy stored per cycle of deformation being five times smaller (tanδ ~0.04) than the loss tangent of Anchor spreadable butter.

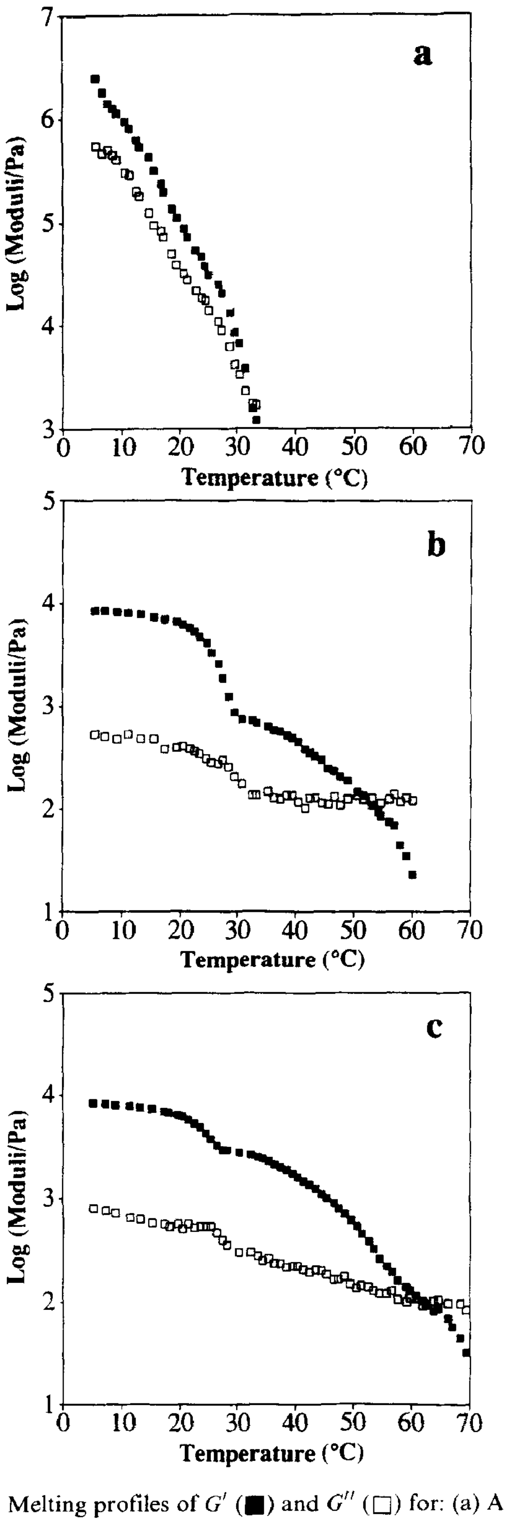

Fig. 8. Melting profiles of G' (■) and G'' (□) for: (a) Anchor spreadable butter; (b) Promise; and (c) Tesco Very Low Fat spreads (0.1% strain, 1 deg/min scan rate).

Perhaps the best rheological measurement for predicting the perceived meltability of spreads is the temperature course of structural melting in dynamic oscillation. Comparative examples of Fig. 8 for Anchor spreadable butter, Promise and Tesco Very Low Fat spreads clearly illustrate differences in the heating profiles of the samples. Thus, the application of a temperature ramp to butter results in a drastic decline of G' with the network melting out completely at 33°C (G' and G'' exhibit identical values). The early melting of fat crystals is then believed to contribute to a better flavour release in the mouth at 37°C (Borwankar *et al.*, 1992). This illustrative evidence is entirely different from the behaviour patterns of Promise and Tesco spreads where a slower, two-step melting profile is obtained during heating from 5 to 80°C. Both the gelatin–maltodextrin (Promise) and the whey protein–maltodextrin (Tesco) systems have been shown to form phase-separated gels with a phase inversion point above which the maltodextrin continuous matrix is penetrated by gelatin or whey protein discontinuous inclusions. Heating of the mixed gels at compositions beyond the inversion point results in a reduction of moduli (completion of the first wave of melting at approximately 30°C) but the gels remain intact until the higher temperature of 70°C (Kasapis *et al.*, 1993; Chronakis *et al.*, in press). This picture, of course, is identical to the temperature course in Figs 8b and c where initial heating disrupts the gelatin or Simplesse protein network but complete mechanical collapse does not occur until the higher temperatures associated with the melting transition of the maltodextrin component. Obviously, the slow melting profile of maltodextrin is not compatible with the 'melt in the mouth' property of butter and eventually it will compromise the mouthfeel, meltdown and flavour release of a low fat spread. In conclusion, there seems to be a need in the market for a new ingredient or a suitable combination of ingredients which will provide both the smooth texture and the creamy breakdown of butter, in the manner documented from the yield parameters of compression analysis and the small deformation melting profiles.

REFERENCES

Borwankar, R.P., Frye, L.A., Blaurock, A.E. & Sasevich, F.J. (1992). *J. Food Eng.* **16**, 55–74.

Cain, F.W., Clark, A.H., Dunphy, P.J., Jones, M.G., Norton, I.T. & Ross-Murphy, S.B. (1989). European Patent, 0,298,561.

Chronakis, I.S., Kasapis, S. & Richardson, R.K. (1996). *Carbohydr. Polym.*, in press.

Clark, A.H. & Ross-Murphy, S.B. (1985). *Br. Polym. J.*, **17**, 164–168.

Grainger, S. (1994). *The European Food and Drink Review*, Spring, 55–59.

Gupta, B.B. & Platt, B.L. (1989). UK Patent, 2,215,343.

Kasapis, S., Morris, E.R., Norton, I.T. & Brown, R.T. (1993). *Carbohydr. Polym.*, **21**, 261–268.

Mageean, P. & Jones, S. (1989). *Food Sci. Technol. Today*, **3**, 162–164.

Papageorgiou, M., Kasapis, S. & Richardson, R. (1994). *Food Hydrocoll.*, **8**, 97–112.

Ross-Murphy, S.B. (1984). In *Biophysical Methods in Food Research*, ed. H.W.-S. Chan. Critical Reports on Applied Chemistry, SCI, London, pp. 138–199.

Ross-Murphy, S.B. (1992). In *Viscoelasticity of Biomaterials*, eds W. Glasser and H. Hatakeyama. ACS Symp. Ser. 489, ACS, Washington DC, pp. 204–216.