Carbohydrate Polymers 42 (2000) 97–98

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Reply to Letter to the Editor

In a previous issue of the journal Oakenfull and Tanner (1999) argue that their method for obtaining shear moduli from a penetration experiment is valid when used appropriately. At first sight this appears to conflict with the results we reported (Gregson, Hill, Mitchell & Smewing, 1999) which showed that for alginate and carrageenan gels the results obtained using penetration depend on the radius of the plunger employed. In this case the value calculated for the modulus cannot be a fundamental rheological parameter.

Oakenfull and Tanner (1999) suggest that the reason for the observed radius dependence in this work was that we did not allow a rest period after penetration before recording the force. While not wishing to completely discount this without some experimental work we think this unlikely to be the reason for the differences. Gels are viscoelastic materials and therefore because of stress relaxation the modulus obtained by penetration (or compression) will generally increase with increasing penetration rate (though a rate dependence is not observed for gelatin (Kamel & de Man, 1977)) and decrease with the holding time after penetration has ceased. Our results were obtained by taking data points off the force response from a continuous penetration experiment. Whereas the absence of a holding time could explain consistently higher moduli, it is unlikely to explain a dependence of the result on geometry. In our case results were calculated for the same penetration depth and penetration rate so the time period over which the stress was applied will be independent of probe radius. If the material shows linear behaviour stress relaxation effects should be independent of geometry.

The analysis used to relate the force on the plunger to the shear modulus used by Oakenfull, Parker and Tanner (1989) assumes linear elastic behaviour, and no slip at the plunger surface or the walls of the container. We consider it more probable that the reason for the probe radius dependence observed in our experiments was that the boundary and probably linearity conditions did not hold.

A possible reason for this is that different gels were used. The moduli of the κ-carrageenan gels we studied were an order of magnitude higher than that reported by Oakenfull and Tanner (1999) for the penetration data. We demonstrated that under our conditions the Oakenfull approach works with gelatin gels. It was recently reported (Ndoni, Marr & Neilson, 1999) that, at least in some cases, the Oakenfull method also give valid results when applied to ι-carrageenan and pectin gels when these were penetrated using a Texture Analyser. We would argue that strong κ-carrageenan gels prepared with high levels of K^+ and the high guluronate alginate have a greater tendency to show syneresis and slip than the more elastic gelatin, ι-carrageenan and pectin family. In addition the linear region will extend to larger strains for the latter. There has been clear demonstrations of slip effects for κ-carrageenan gels when measurements were made at low strains in oscillation (Richardson & Goycoolea, 1994) and the extent of the linear region for strong κ-carrageenan gels prepared with 0.1 M KCl has been reported to extend only up to strains of 0.004 whereas for weaker gels prepared with 0.01 KCl the linear region extended to strains of 0.04 (Hermansson, 1989). In extreme cases when measurements were made on alginate gels in penetration we observed detachment from the container walls.

The relative importance of a breakdown of the assumed boundary conditions and non-linearity is difficult to assess. We did report results obtained at different penetration depths and showed only relatively modest strain hardening effects. This might suggest that there is an interaction between the two factors with slip at the container walls acting to reduce the calculated modulus and strain hardening increasing it, which does not seem unreasonable.

The method is valid *if used appropriately* but it is of interest to define the window where it gives the correct results. We consider that the assumptions of linearity and the boundary conditions are more likely to breakdown as the penetration force and penetration depth increase and the gel has a more brittle, less elastic character. This is consistent with Oakenfull and Tanner's (1999) comment that the method is appropriate for weak gels. In this context a *weak* gel can be considered as a gel where the network chains joining junction zones are long and therefore flexible. Within this definition a high concentration, high modulus gelatin gel would also be considered weak. Such gels are more amenable to fundamental testing as they show a greater linear region, no syneresis and they are therefore are less prone to slip, and also have less time effects.

In our paper we did make it clear that the method failed for κ-carrageenan and alginate gels "at forces used with the Texture Analyser" and suggested non-linearity and slip as possible reasons for this. Our work suggests that this approach should not be used uncritically and in particular that it should be verified that results are independent of plunger radius.

This reply has been discussed with David Oakenfull and Roger Tanner who made the point that for viscoelastic materials and for when measurements are made in the

0144-8617/00/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0144-8617(99)00186-1

non-linear region further analysis would be required to define the exact meaning of the test. They also feel that wall slip effects would be trivial when the plunger radius is small compared with the container radius, so it may be that if slip is important it is the conditions at the plunger surface which is of significance rather than the container walls.

We all agree that it is encouraging to see that there has been recent interest in this early work which attempted to provide a fundamental understanding of one of the most common ways of evaluating the mechanical properties of gels.

References

Gregson, C. M., Hill, S. E., Mitchell, J. R., & Smewing, J. (1999). Measurement of the rheology of polysaccharide gels. *Carbohydrate Polymers*, *38*, 255–259.

Hermansson, A.-M. (1989). Evidence for transient state of κ-carrageenan with potassium ions. *Carbohydrate Polymers, 10* (3), 163–181.

Kamel, B. S., & de Man, J. M. (1977). Some factors effecting gelation, gel texture evaluation by penetration testing. *Journal of Texture Studies*, *8*, 327–337.

Ndoni, S., Marr, B. U., & Neilsen, H. (1999). Comparison of texture analyser and rheometer measurements on carrageenan and pectin gels. Paper presented at Tenth International Conference on Gums and Stabilisers in the Food Industry, in press.

Oakenfull, D. G., & Tanner, R. I. (1999). Comment on the measurement of the rheology of polysaccharide gels by penetration. *Carbohydrate Polymers*.

Oakenfull, D. G., Parker, N. S., & Tanner, R. I. (1989). Method for determining absolute shear modulus of gels from compression tests. *Journal of Texture Studies*, *19*, 407–417.

Richardson, R. K., & Goycoolea, F. M. (1994). Rheological measurements of κ-carrageenan during gelation. *Carbohydrate Polymers*, *24*, 223–225.

J.R. Mitchell
Division of Food Sciences, School of Biological Sciences,
The University of Nottingham, Sutton Bonington Campus,
Loughborough LE12 5RD, UK