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Mechanical spectroscopy of karaya gum–alginate mixed dispersions

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The rheological properties of blends obtained by mixing alginate and karaya gum dispersions were described from oscillation, shear and creep experiments using a controlled stress rheometer. The mechanical spectra shown by such mixtures were strongly modified when compared with those of each of the blend components.

It was found that the viscoelastic behaviour of mixtures was strongly affected by the age of the karaya gum. Contrary to that which is observed with fresh karaya gum, maximum synergy was observed with a mixture containing 75% aged karaya gum. It is suggested that mutual incompatibility between the two polysaccharides could explain the formation of a mixed network.

INTRODUCTION

Polysaccharides are largely used as thickening and/or gelling agents for many applications in the food, cosmetics and building products industries. Polysaccharide gels are generally formed through physical associations and the establishment of networks involves regions of local order such as microcrystallites (amylose), entwinements or double helices (carrageenans) or cooperative interactions involving divalent cations (alginates and pectins) which provide the cross-links between the polysaccharide molecules. As the number of gelling agents is limited the study of interactions between polysaccharides to give novel rheological properties has attracted substituted attention (Oakenfull, 1987). There is much experimental evidence to show that synergistic interactions between two polysaccharides afford gels under conditions where neither polysaccharide forms gels independently as reported for the high methoxyl pectin/alginate systems (Toft, 1982) and the xanthan/locust bean gum (LBG) system (Cheetham & Mashimba, 1988). Interactions of agars, kappa-carrageenans and xanthan gums with galactomannans (guar and locust bean gum) have been extensively studied (Dea, 1989) in respect of their usefulness in the food industry. Many other polysaccharide blends show synergistic rheological properties, e.g. konjac mannan with xanthan or kappa-carrageenan (Day *et al.*, 1990). It must be recognised that the exact nature of synergistic interaction between different polysaccharides in solution is often only poorly understood and different models have been proposed for explaining the observed behaviour of systems such as xanthan/LBG and guar (Tako & Nakamura, 1985; Shatwell *et al.*, 1991) or kappa-carrageenan/LBG (Cairns *et al.*, 1987; Dea, 1987). For the special case of the xanthan/LBG system, two models have been proposed involving the formation of a network through specific junction zones or the formation of a phase-separated network (Dea *et al.*, 1977). Although it has been largely neglected in favour of the junction zone model, the concept of mutual incompatibility between the two reacting entities can afford an explanation for many systems and such mixed networks have been proposed for a number of protein/polysaccharide systems (Rocks, 1971; Kovacs, 1973; Brownsey & Morris, 1988; Tolstoguzov, 1990).

The aim of this work was to examine the associated characteristics and rheological properties of blends of sodium alginate, a linear polysaccharide of 1,4-β-D-mannuronic acid (M) and 1,4-α-L-guluronic acid (G), with karaya gum, a complex polysaccharide of rhamnose, galactose, galacturonic and glucuronic acid units (Aspinall *et al.*, 1987). In a preceding work (Le Cerf & Muller, 1993), the authors reported that karaya dispersions prepared from a fresh gum displayed gel properties contrary to what is observed with aged gum. It was

This paper is dedicated to the memory of Mrs Irinei Florica.

thus expected that mixtures of karaya gum with alginates could respond differently according to the age of the gum in the blended material and that new synergistic applications could be found.

EXPERIMENTAL

Measuring methods

Rheological experiments were performed using a controlled stress Carrimed CSL 100 rheometer with a cone and plate (2°; 4 cm radius cone) geometry. Oscillatory measurements were made over a frequency range 0·1–10 rad/s and a strain amplitude of 2·8% (10^{-3} rad) was used.

For creep experiments a stress of 20 dyn/cm^2 was applied and both the deformation and the recovery were followed as a function of time.

All the measurements were made at a temperature of 25°C.

The results are expressed in terms of G' the storage modulus, G'' the loss modulus, η^* the complex viscosity and J_0 the instantaneous creep compliance.

Materials and methods

Two samples of karaya gum (a dried exudate from *Sterculia urens*) supplied by Alland & Robert (France) were investigated. One sample is a fresh gum (FKG) whereas the other is an aged gum (AKG). The samples differ in their solution properties as previously reported (Le Cerf *et al.*, 1991). Nodules of both gums were ground to obtain a fine powder which was screened on 200 mesh before solubilisation.

Sodium alginate samples (Satialgine) were obtained from Sanofi Bio Industries (France). They have the same mannuronic to guluronic ratio (M/G = 1·20) but differ in their viscosity and weight-average molecular weight M_w (Table 1).

Karaya and alginate dispersions ($C = 10$ and 20 g/litre) were prepared by dispersing the required amount of each polysaccharide (powdered form) in deionised water containing 0·4 g/litre sodium azide as a bactericide then stirring at room temperature. All blends of polysaccharide dispersions were prepared by mixing the required volumes of each polysaccharide dispersion at room temperature and then stirring by hand. All mixed polysaccharide dispersions were allowed to stand at room temperature for 24 h. Rheological measurements were made 24 h and 8 days after the preparation of blends. No difference was observed.

Various blends of karaya gum and alginate having a total concentration of 10 and 20 g/litre were investigated. All the results are expressed as a function of the percentage of karaya gum in the blend.

Table 1. Intrinsic viscosity (in NaCl 0·1 M), weight molecular weight and ratio M/G of the two alginate samples LVA and HVA

Sample	$[\eta]_0$ (ml/g)	M_w (g/mol)	M/G
HVA	1 350	$5{\cdot}2 \times 10^5$	1·2
LVA	1 010	$3{\cdot}5 \times 10^5$	1·2

RESULTS AND DISCUSSION

Figure 1 illustrates the frequency dependence of the storage (G') and loss (G'') moduli for aqueous solutions ($C = 20$ g/litre) of high-viscosity alginate (HVA) (A),

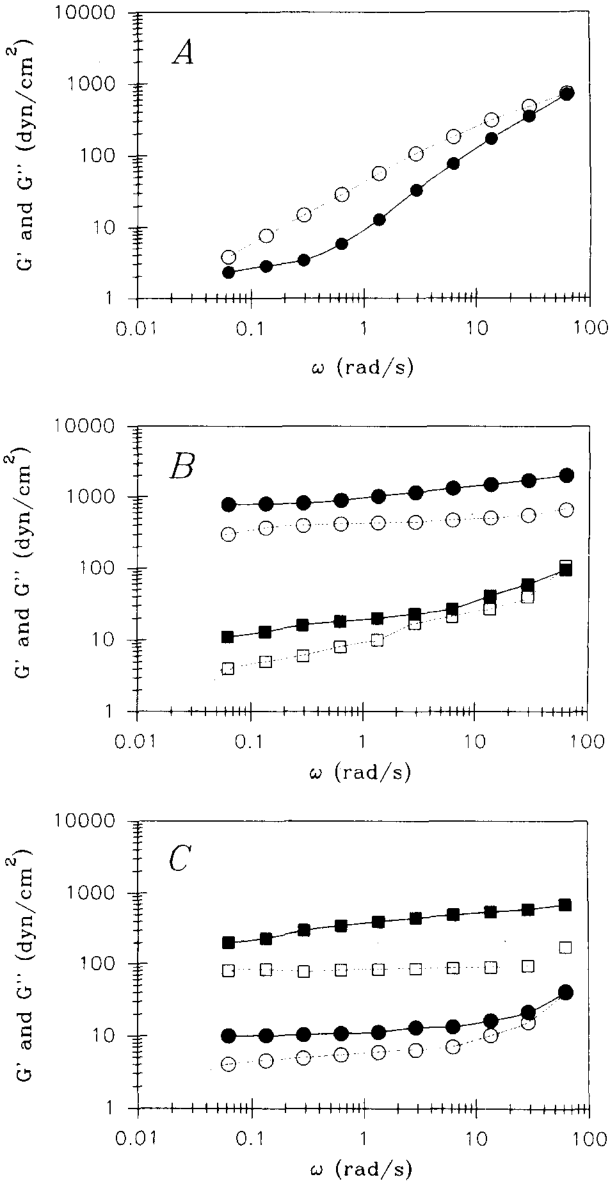

Fig. 1. Dependence of the storage modulus, G' (filled symbols) and of the loss modulus, G'' (open symbols) on frequency for dispersions (20 g/litre in pure water) of alginate (A); mixtures of 30% alginate and 70% aged (circle) and fresh (square) karaya gum (B); and aged (circle) and fresh (square) karaya gums (C).

aged and fresh karaya gums (C) and mixtures of 30% of HVA with 70% of aged and fresh karaya (B).

The alginate mechanical spectrum is typical of a viscous solution with the loss modulus greater than the storage modulus over the entire range of frequency. Both parameters are found to be frequency dependent. Fresh and aged karaya gums both show gel-like properties as evidenced by the fact that elastic moduli exceed the loss moduli. This is particularly true for the fresh gum which behaves as a stronger gel as indicated by the higher storage modulus. Large differences in the mechanical spectra of the blends are observed according to the age of the karaya gum (Le Cerf & Muller, 1993). A decrease in both moduli is observed as a consequence of mixing the fresh gum with alginate; the storage modulus of the blend at 1 rad/s is about ten times lower than that of the fresh gum alone. In contrast the mechanical spectrum of alginate/aged karaya shows that this mixed polysaccharide system behaves as a gel with a storage modulus at 1 rad/s more than 100 times that of alginate and/or aged karaya alone.

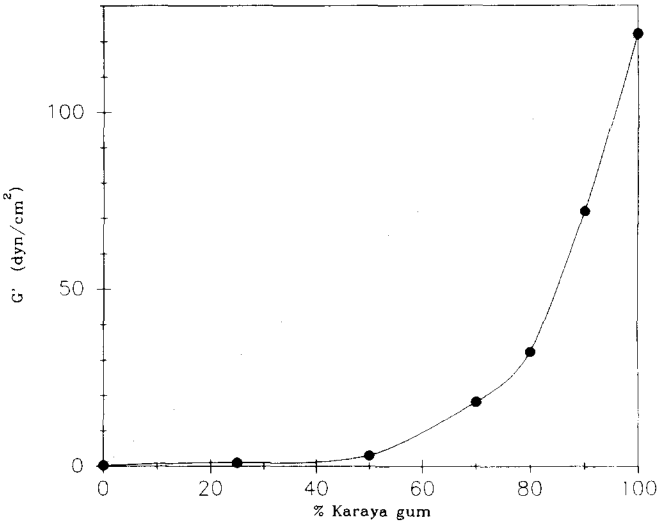

Fig. 2. Storage modulus (at $\omega = 0{\cdot}628\ s^{-1}$) of fresh karaya gum/high viscosity alginate blends ($C = 10$ g/litre in pure water) as a function of the percentage of karaya gum in the blend. The broken line refers to the expected variation of G' if additivity holds.

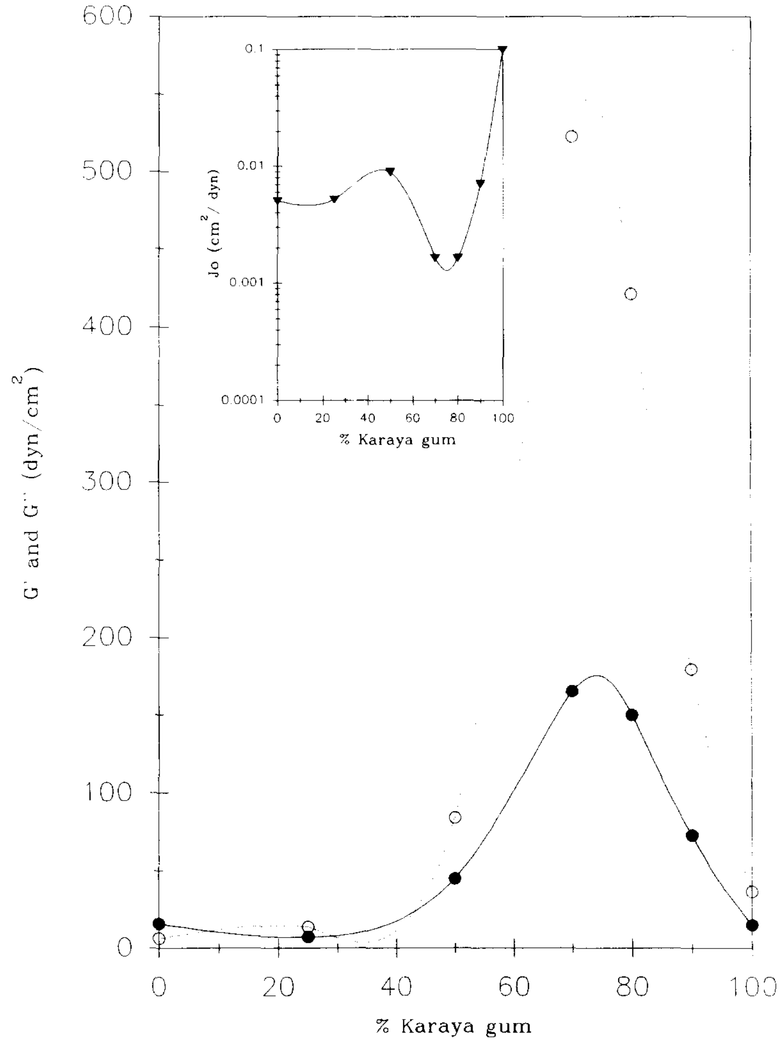

Fig. 3. Dependence of storage modulus (○), loss modulus (●) and instantaneous creep compliance (▲) on the percentage of gum for blends of aged karaya gum and high viscosity alginate (20 g/litre in pure water). Storage and loss moduli were measured at 0·628 rad/s and J_0 at an applied stress of 20 dyn/cm^2.

The effect of the ratio of fresh karaya gum (FKG) to HVA on the storage modulus (at 0·628 rad/s) at a concentration of 10 g/litre in pure water is reported in Fig. 2. Clearly a loss of the gel-like properties of the fresh gum results from its mixing with alginate as evidenced by the continuous decrease in G' with increasing HVA/FKG ratio. As the alginate in the mixture is the non-gelling component, the reported data should reflect the concentration dependence of G' for karaya alone. As shown in Fig. 2, a certain minimum concentration should exist below which karaya does not gel; above this concentration G' increases with a high power of concentration.

Figure 3 shows the variation of the dynamic rheological parameters of LVA/aged karaya gum (AKG) mixtures as a function of the percentage of karaya gum in the blend. An increase of both moduli is initiated when the proportion of karaya gum in the blend is near 50% and maximum synergy occurs with mixtures containing 75% of karaya gum. At the maximum synergy, the elastic modulus ($G' = 550$ dyn/cm^2) is about ten times that of the gum alone. Comparison of data reported in Figs 1(b) and 3 shows that the larger the intrinsic viscosity (or the molecular weight) of alginate blended with aged KG, the higher the storage modulus and therefore the stronger the resulting gel. At the maximum synergy the loss modulus also increased although by less than its elastic counterpart. Thus tan δ, which measures the elasticity of the system, reaches a minimum value at the maximum synergy. The variation of the creep compliance J_0 also reported in Fig. 3 shows a minimum at the same LVA/AKG ratio in agreement with the variation of G'.

A deviation from the Cox–Merz rule (Cox & Merz, 1958) with the complex viscosity η^* obtained from the oscillation measurements exceeding the shear viscosity η is observed when the percentage of aged KG in the blend is above 50%, and at the maximum synergy the complex viscosity is four times larger than the shear viscosity (as illustrated in Fig. 4). Such behaviour is typical of a gel.

The viscoelastic properties of the blend at the maximum synergy are only slightly modified after ageing for six months in the cold (4°C). This emphasises the stability of the gel which otherwise retains its characteristics upon heating; the gel strength is only slightly diminished at 80°C.

The gel has been found to be shear-sensitive but a time-dependent restructuration of the sheared gel is clearly observed after shearing ceased. This is illustrated in Fig. 5 which shows that the storage modulus, which was decreased from 540 dyn/cm^2 to 150 dyn/cm^2 upon shearing (1400 s^{-1} for 5 min), recovers its initial value after allowing the sample to rest. Complete restoration of the initial unsheared structure is achieved after 5 h, indicating that structure reformation needs a longer time than structure disruption.

Addition of salt to the mixture results in loss of the gel properties as evidenced by the fact that both moduli G' and G'' are decreased in the presence of 1 M NaCl and become more dependent on oscillation frequency (Fig. 6). In such salt conditions the mechanical spectrum of the blend shows a storage modulus of the same order of magnitude than aged karaya alone (see Fig. 1(c)). This decrease in the blend modulus could be explained by a more dispersed network in the presence of salt.

CONCLUSION

The data reported above clearly show that aged karaya gum and sodium alginate interact to give synergistic increases in viscosity and in gel strength whereas a negative non-linear effect is found upon mixing the fresh gum with alginate. At the moment it is difficult to propose a model to explain the experimental observations and further work is needed in order to clarify the mechanism of the observed synergistic effects, although formation of networks through specific junction zones can probably be excluded.

As karaya gum and alginate are acidic polysaccharides, both polyions have like charges. Therefore it could be expected that association would be facilitated by decreasing interchain repulsions, i.e. by increasing the ionic strength. Obviously this is not the case as it has been observed that the degree of synergism between aged karaya and alginate decreased in the presence of salt. Due to the predominance of electrostatic repulsive forces which prevail under the experimental conditions (neutral pH, absence of salt) where

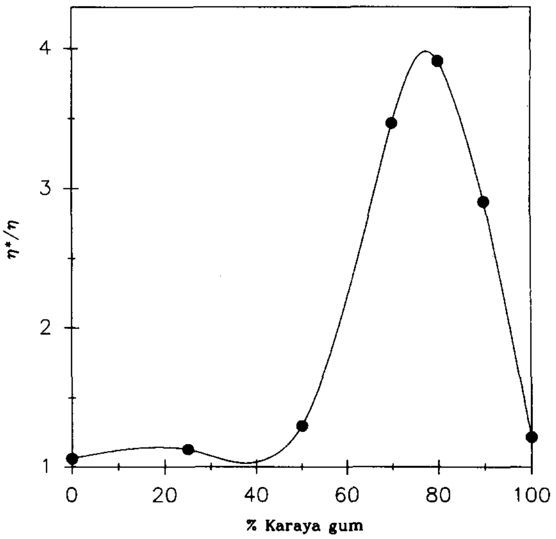

Fig. 4. Variation of the ratio η^*/η as a function of the percentage of karaya gum for blends of aged karaya gum and high viscosity alginate at 20 g/litre in pure water. The complex (η^*) and shear (η) viscosities were measured at $\omega = 0{\cdot}628$ rad/s and $\gamma = 0{\cdot}628$ s^{-1}.

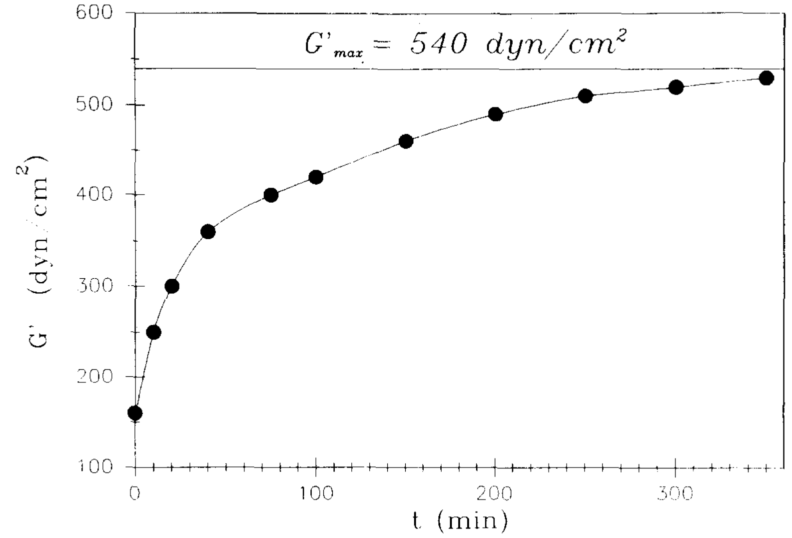

Fig. 5. Restoration of the storage modulus (G') of the 30/70 HV alginate/aged karaya gum blend ($C = 20$ g/litre in pure water) on removal of the shearing forces (5 min at $\gamma = 1400$ s^{-1}).

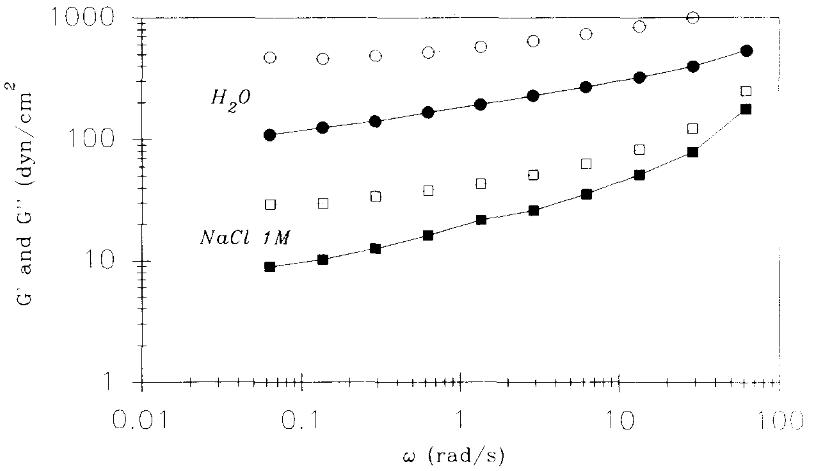

Fig. 6. Dependence of the storage modulus (G') (open symbols) and loss modulus (G'') (filled points) on frequency for the 30/70 HV alginate/aged karaya gum blend ($C = 20$ g/litre) in pure water (circle) and 1 M NaCl (square) respectively.

synergistic interaction is observed, probably a model based on mutual incompatibility between the two polysaccharide entities could be favoured for the formation of a mixed network. Such mixed networks have been reported for protein/polysaccharide blends (Rocks, 1971; Kovacs, 1973; Brownsey & Morris, 1988; Tolstoguzov, 1990). Thermodynamic incompatibility of the two components of the mixture with exclusion of one from the domain of the other should produce phase domains rich in each component, thus increasing the effective concentration of the individual species.

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REFERENCES

Aspinall, G.O., Khondo, L. & Williams, B.A. (1987). *Can. J. Chem.*, **65**, 2069.

Brownsey, G.J. & Morris, V.J. (1988). In *Food Structure. Its Creation and Evolution*, eds J.M.V. Blanshard & J.R. Mitchell. Butterworths, London, p. 7.

Cairns, P., Miles, M.J., Morris, V.J. & Brownsey, G.J. (1987). *Carbohydr. Res.*, **160**, 411.

Cheetham, M.W.H. & Mashimba, E.N.M. (1988). *Carbohydr. Polym.*, **9**, 195.

Cox, W.P. & Merz, E.H. (1958). *J. Polym. Sci.*, **28**, 619.

Day, D.H., Langdow, M.J., Phillips, G.O. & Williams, A.A. (1990). In *Gums and Stabilisers for the Food Industry*, Vol. 5, eds G.O. Phillips, D.J. Wedlock & P.A. Williams, p. 571.

Dea, I.C.M. (1987). In *Industrial Polysaccharides. The Impact of Biotechnology and Advance Methodologies*, eds S.S. Stivala, V. Crescenzi & I.C.M. Dea. Gordon and Breach Science Publishers, New York, p. 367.

Dea, I.C.M. (1989). *Pure Appl. Chem.*, **61**(7), 115.

Dea, I.C.M., Morris, E.R., Rees, D.A., Welsh, E.J., Barnes, H.A. & Price, J. (1977). *Carbohydr. Res.*, **57,** 249.

Kovacs, P. (1973). *Food Technol.*, **27,** 26.

Le Cerf, D. & Muller, G. (1993). *Polymer Networks and Blends*, **3** (4), 207.

Le Cerf, D., Irinei, F. & Muller, G. (1991). *Food Hydrocoll.*, **5**(1/2), 155.

Oakenfull, D. (1987). *Crit. Rev. Food Sci. Nutr.*, **26,** 25.

Rocks, J.K. (1971). *Food Technol.*, **25,** 476.

Shatwell, K.P., Sutherland, I.W., Ross-Murphy, S.B. & Dea, I.C.M. (1991). *Carbohydr. Polym.*, **14,** 115.

Tako, M. & Nakamura, S. (1985). *Carbohydr. Res.*, **138,** 207.

Toft, K. (1982). *Prog. Food Nutr. Sci.*, **6,** 89.

Tolstoguzov, V.B. (1990). In *Gums and Stabilisers for the Food Industry*, eds G.O. Phillips, D.J. Wedlock & P.A. Williams. Oxford University Press, p. 157.